UNIVERSITY OF COIMBRA
FACULTY OF SCIENCES AND TECHNOLOGY
Department of Earth Sciences

EVALUATION OF THE POTENTIAL IN CRITICAL METALS IN THE FINE TAILINGS DAMS OF THE PANASQUEIRA MINE (BARROCA GRANDE, PORTUGAL)

- TUNGSTEN AND OTHER CRMs CASES -

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MASTER IN GEOSCIENCES – Specialisation in Geological Resources

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Scientific Advisors:
Doctor Alcides Pereira, Faculty of Sciences and Technology, University of Coimbra
Doctor Elsa Gomes, Faculty of Sciences and Technology, University of Coimbra

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RESUMO

No âmbito da Estratégia Europa 2020, a Comissão Europeia identificou dois constrangimentos que têm condicionado a competitividade e o crescimento da economia europeia: a elevada dependência de importação de produtos acabados e a insegurança no fornecimento de matérias-primas. Relativamente a este último, a Comissão Europeia promoveu a “Iniciativa Matérias-Primas”, estimulando a eficiência no uso de recursos e a circularidade, com destaque para a valorização dos resíduos de extração mineira. Estes resíduos devem, portanto, passar a ser reconhecidos como uma potencial fonte de recursos, nomeadamente de matérias-primas críticas, essenciais para a produção de equipamentos de alta tecnologia, cruciais para a competitividade da indústria europeia. A utilização de resíduos de extração mineira como fonte de matéria-prima pode reduzir a exploração de recursos naturais usados com o mesmo objetivo, introduzindo-se assim o conceito de economia circular.

Tendo em consideração a relevância deste tópico para a sociedade de hoje, o objetivo principal desta dissertação consistiu em averiguar o potencial em metais críticos dos resíduos de extração mineira depositados nas células de lamas da mina da Panasqueira, localizadas em Portugal, no concelho da Covilhã, no lugar de Barroca Grande. Do ponto de vista metodológico, o trabalho centrou-se na: (i) recolha de amostras superficiais e em profundidade; (ii) caracterização granulométrica das amostras (LDPS); (iii) caracterização químico-mineralógica das amostras (XRD e SEM); e (iv) caracterização elementar das amostras (XRF).

Este trabalho permitiu determinar a concentração de metais críticos relevantes no contexto da economia nacional e europeia. Os resultados obtidos sugerem que em ambas as células de lamas, com granulometria a variar de silte médio a areia média, as concentrações anómalas de metais críticos, nomeadamente dos semi-metais germânio (Ge) e antimónio (Sb), e do metal e terra rara leve cério (Ce), são significativas. Em alguns casos, estas concentrações são 24 vezes superiores à abundância natural destes elementos na crosta continental superior.

Palavras-chave: Mina da Panasqueira; resíduos de extração mineira; células de lamas; metais críticos; economia circular.

ABSTRACT

As part of the Europe 2020 strategy, the European Commission identified two constraints that have affected the competitiveness and growth of the European economy: its high dependency on the importation of finished products, and the insecurity of the supply of raw materials. With regards to the latter, the European Commission developed the "Raw Materials Initiative", which promotes an efficient use of resources, as well as encouraging recycling, with particular emphasis on mining waste. This waste must therefore be recognised as a potential source of resources, in particular critical raw materials, which are essential for the production of high-tech equipment, crucial for the competitiveness of the European industry. This use of mining waste as a source of raw materials may also reduce the exploitation of natural resources, which are used for the same purpose, thus introducing the concept of a circular economy.

Taking into consideration the relevance of this issue in today’s society, the main goal of this dissertation was to evaluate the potential in critical metals of the mining waste deposited in the fine tailings dams of the Panasqueira mine, located in Portugal, in the municipality of Covilhã, at the Barroca Grande site. From a methodological point of view, the work focused on: (i) surface and borehole sampling; (ii) particle size characterisation of the samples (LDPS); (iii) chemical-mineralogical characterisation of the samples (XRD and SEM); and (iv) elemental characterisation of the samples (XRF).

This work allowed us to determine the concentration of critical metals, which are relevant in the context of the national and European economy.The results obtained suggest that in both of the fine tailings dams, which granulometrically range from medium silt to medium sand, and the anomalous concentrations of critical metals, more specifically the semi-metals germanium (Ge) and antimony (Sb), and the metal and light rare earth element cerium (Ce), are significant. In some cases these concentrations are 24 times higher than the natural abundance of these elements in the upper continental crust.

Keywords: Panasqueira mine; mining waste; fine tailings dams; critical metals; circular economy.

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LIST OF ACRONYMS

3D	Third dimension
4D	Fourth dimension
AIF3	Aluminium fluoride
AMT	Ammonium Metatungstate
APT	Ammonium Paratungstate
BTW	Sojitz Beralt Tin & Wolfram (Portugal), S.A.
CD	Compact Disc
CIS	Commonwealth of Independent States
COM	Communication from the European Commission
CRM	Critical Raw Material
CV	Coefficient of Variation
CWS	Crushing, Washing and Screening
DGEG	Directorate General for Energy and Geology of Portugal
DG-ENTR	Directorate General for Enterprise and Industry
DG-GROW	Directorate General for Internal Market, Industry, Entrepreneurship and SMEs
DRC	Democratic Republic of Congo
DVD	Digital Video Disc
EC	European Commission
EDS	Energy Dispersive Spectrometry
EESC	European Economic and Social Committee
EIP	European innovation Partnership
EIP-RM	European Innovation Partnership on Raw Materials
EIT	European Institute of Innovation and Technology
EIT-RM	European Institute of Innovation and Technology – Raw Materials
ENRG-RM	National Strategy for Geological Resources – Mineral Resources
EoL	End-of-Life
EPI	Environmental Performance Index
ERA-MIN2	ERA-NET Cofund on Raw Materials
ERA-NET	European Research Area network
ERECON	European Rare Earths Competency Network
ETP SMR	European Technology Platform on Sustainable Mineral Resources
EU	European Union
EU-28	Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, and United Kingdom
EU-36	EU-28 + EU associates: Iceland, Norway and Switzerland + EU candidates: Albania, Macedonia, Montenegro, Serbia, and Turkey (as of 1st January 2017)

FTD	Fine Tailings Dam
GDP	Gross Domestic Product
GFC	Global Financial Crisis
GGE	Greenhouse Gas Emissions
GIS	Geographic Information System
GTP	Global Tungsten & Powders Corp.
H2020	Horizon 2020
HF	Hydrofluoric acid
HLSG	High Level Steering Group
HMS	Heavy Media Separation
HREE	Heavy Rare Earth Element
HSLA	Hard Strength Low Alloys
HSS	High-Speed Steel
IC	Integrated Circuits
IR	Infrared
IT	Information Technology
ITO	Indium Tin Oxide
IUPAC	International Union of Pure and Applied Chemistry
KIC	Knowledge and Innovation Community
KPI	Key Performance Indicator
LDPS	Laser Diffraction Particle Size
LED	Light-Emitting Diode
LED&MAT-IPN	Laboratory for Wear, Testing & Materials of Pedro Nunes Institute
LG-UC	Laboratory of Geotechnics of the Department of Earth Sciences, Faculty of Sciences and Technology, University of Coimbra
LGXR-UC	Laboratory of Geochemistry and X-Ray of the Department of Earth Sciences, Faculty of Sciences and Technology, University of Coimbra
LNEG	National Laboratory on Energy and Geology of Portugal
LOD	Limit of Detection
LOT-UC	Laboratory of Ore Treatment of the Department of Earth Sciences, Faculty of Sciences and Technology, University of Coimbra
LREE	Light Rare Earth Element
LSPMS-UC	Laboratory of Sample Preparation and Mineral Separation of the Department of Earth Sciences, Faculty of Sciences and Technology, University of Coimbra
LS-UC	Laboratory of Sedimentology of the Department of Earth Sciences, Faculty of Sciences and Technology, University of Coimbra
MRI	Magnetic Resonance Imaging
NGO	Non-Governmental Organisation
NiMH	Nickel–Metal Hydride
OECD	Organisation for Economic Co-operation and Development

PC	Personal Computer
PCA	Principal Component Analysis
PET	Polyethylene terephthalate
PGM	Platinum Group Metal
ProSUM	Prospecting Secondary raw materials in the Urban mine and Mining wastes
PVC	Polyvinyl Chloride
R&I	Research and Innovation
REE	Rare Earth Element
REMINE	Reuse of Mining Waste into Innovative Geopolymeric-based Structural Panels, Precast, Ready Mixes and Insitu Applications
RMI	Raw Materials Initiative
ROM	Run-of-Mine
ROW	Rest of the World
RSC	Royal Society of Chemistry
SD	Standard Deviation
SEM	Scanning Electron Microscopy
SGC	Schist-Greywacke Complex
SIORMINP	Information System for Portuguese Occurrences and Mineral Resources
SIP	Strategic Implementation Plan
SME	Small and Medium-sized Enterprise
SUN	Stiftungsfonds für Umweltökonomie und Nachhaltigkeit
SWD	Staff Working Document from the European Commission
TBO	Tungsten Blue Oxide
TIG	Tungsten Inert Gas
UF6	Uranium hexafluoride
UK	United Kingdom
UNICE	Union of Industrial and Employers' Confederations of Europe
USA	United States of America
USD	United Sates Dollar
USGS	United States Geological Survey
WDS	Wavelength Dispersive Spectrometry
WEEE	Waste of Electrical and Electronic Equipment
WFS	Web Feature Service
WGI	Word Governance Indicator
WHA	Tungsten Heavy metal Alloy
WP	Working Package
WWI	World War I
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

LIST OF ABBREVIATIONS, CHEMICAL SYMBOLS AND FORMULAS, AND UNITS

Ab	Albite
Aeg	Aegirine
Anh	Anhydrite
Ap	Apatite
Arg	Aragonite
Bn	Bentonite
Bo	Borate
Bt	Barites
Bx	Bauxite
Cal	Calcite
CC	Coaking Coal
Chr	Chromite
Cy	Clays
Dt	Diatomite
Fl	Fluorspar
Fo	Forsterite
Fp	Feldspar
Gr	Graphite
Gy	Gypsum
Hem	Hematite
Hl	Halite
Ilm	Ilmenite
Lct	Leucite
Lrn	Larnite
Ls	Limestone
Mag	Magnetite
Ms	Muscovite
Mt	Magnesite
Pe	Perlite
PR	Phosphate Rock
Prh	Prehnite
Py	Pyrite
Qtz	Quartz
Sd	Siderite
Sl	Silica
SM	Silicon Metal
Sme	Smectite

Str	Strontianite
Tc	Talc
Usp	Ulvöspinel
Zeo	Zeolite
Ag	Silver
Al	Aluminium
Au	Gold
B	Boron
Be	Beryllium
Ce	Cerium
Co	Cobalt
Cr	Chromium
Cu	Copper
Dy	Dysprosium
Er	Erbium
Eu	Europium
Fe	Iron
Ga	Gallium
Gd	Gadolinium
Ge	Germanium
Ho	Holmium
In	Indium
La	Lanthanum
Li	Lithium
Lu	Lutetium
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
Nb	Niobium
Nd	Neodymium
Ni	Nickel
Pm	Promethium
Pr	Praseodymium
Re	Rhenium
Sb	Antimony
Sc	Scandium
Sm	Samarium
Sn	Tin
Ta	Tantalum
Tb	Terbium

Te	Tellurium
Ti	Titanium
Tm	Thulium
V	Vanadium
W	Tungsten
Y	Yttrium
Yb	Ytterbium
Zn	Zinc
$(NH_4)_{10}(W_{12}O_{41}) \cdot 5H_2O$	Ammonium paratungstate
$(NH_4)_6(H_2W_{12}O_{40}) \cdot nH_2O$	Ammonium metatungstate
CaF_2	Fluorspar
$CaWO_4$	Calcium tungstate
$CuFeS_2$	Chalcopyrite
FeAsS	Arsenopyrite
FeS_2	Pyrite
FeW	Ferrotungsten
$FeWO_4$	Ferrous tungstate (ferberite)
$KAl_2O_{10}(OH,F)_2$	Muscovite
$MgCO_3$	Magnesite
$MnWO_4$	Manganous tungstate (hübnerite)
MoW	Molybdenum-tungsten
NbW	Niobium-tungsten
$PbWO_4$	Lead tungstate (stolzite)
SiO_2	Quartz
TaW	Tantalum-tungsten
W_2C	Tungsten Semi-Carbide
WC	Tungsten Carbide
WCu	Tungsten-copper
WNi	Nickel-tungsten
$WO_{2.29}$	Tungsten blue oxide
WO_3	Tungsten trioxide
WRe	Tungsten-rhenium
WS_2	Tungsten disulphide (tungstenite)
€	Euro (European Monetary Unit)
µA	microampere
µm	micrometre
Bt	Billion tonnes
cm	centimetre
kg	kilogram
km	kilometre

kV	kilovolt
m	metre
m^2	square metre
m^3	cubic metre
mA	miliampere
mRL	metre reduced level
mt	metric tonne
Mt	Million tonnes
mtu	metric tonne unit
nA	nanoampere
ppm	parts per million
t	tonne
tt	thousand tonnes

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CHAPTER 1.

INTRODUCTION

CHAPTER 1. INTRODUCTION

1.1. RATIONALE

Raw materials are essential to the EU’s economy, which is still highly dependent on their importation. This means that ensuring their secure supply is essential for the competitiveness of EU industries, particularly for the development of the “Industry 4.0” and “green technology” in Europe. These raw materials, especially the twenty defined as “critical” in 2014 by the EU, are becoming increasingly in-demand from the emerging technologies that require large amounts of these CRMs.

Since 2006, the EU has been promoting several initiatives, which belong to an integrated strategy to overcome the different challenges related to the safe and sustainable access to non-energy and non-agricultural raw materials, as they are becoming further centralised by China, which, together with the global financial crisis, has endangered the entire industry of the European Union. These initiatives are promoted with the goal of understanding the EU’s dependency on critical raw materials, and promoting policies for the scientific and technological development of the extractive industry.

Considering the aforementioned supply risk and high dependency on the importation of these critical raw materials, in particular critical metals, by the EU, the mining waste can be seen as part of the solution for these European concerns. This waste should be considered as an opportunity to create and promote recycling, as well as the economic recovery of these critical metals from the mine tailings, such as fine tailings dams or ponds, in a sustainable way. In fact, when raw materials are wasted, society is undervaluing the intrinsic potential value of mining waste, which can be converted into a raw material source, referring to the concept of circular economy.

Furthermore, according to Martins & Viegas (2011), the lack of efficiency in the processing of ores, due to technological constraints, the limitations of analytical means, the lack of knowledge and interest in certain elements, not valued at the time, and the cut-off rates practiced over time, led to the accumulation of tonnes of mining waste that urgently needed to be located, mapped and characterised from a mineralogical, geochemical and granulometric point of view, and have its volume and tonnage calculated and valued economically.

Based on the above-mentioned framework, we proposed that in this dissertation we will physically and chemically characterise and evaluate the potential in critical metals of the two fine tailings dams of the Panasqueira Mine (Portugal) in the Barroca Grande tailings disposal area.

The physical characterisation involved two techniques: one regarding the grain-size of the samples (the Laser Diffraction Particle Size (LDPS) technique); and the other regarding the mineralogy of the samples (the X-Ray Diffraction (XRD) technique). The chemical characterisation involved two techniques: one regarding the chemical/mineralogical composition of the samples (the Scanning Electron Microscopy (SEM-EDS/WDS) technique); and the other exclusively for the chemical composition of the samples (the X-Ray Fluorescence (XRF) technique), which used two different types of equipment: the portable spectrometer, used as a first test to guide us to the elements we wanted to trace (the critical metals and semi-metals, and associated base metals); and the benchtop spectrometer, which gave us more precise and specific results of the critical and base metals, as well as the associated base metals.

1.2. MAIN AND SPECIFIC GOALS

The main goals of this dissertation were:

1- To systemise EU and Portuguese policies on critical raw materials;
2- To characterise the physical and chemical properties of the tailings samples collected in the two fine tailings dams;
3- To evaluate the potential in critical metals content from each of the fine tailings dams.

The specific goals of this dissertation were:

1- To determine the grain-size of the tailings samples;
2- To determine the mineralogical composition of the tailings samples;
3- To determine the elemental composition of the tailings samples;
4- To compare the elemental composition with the mineralogical composition of the tailings samples;
5- To compare the elemental composition of the fine tailings dams with other studies;
6- To verify whether or not the concentration of these critical metals was anomalous compared to their upper continental crust abundance.

1.3. STATE OF THE ART

Due to the increase in demand for the use of “new” and “green” technology products, there is a global concern regarding the supply of the raw materials used in the construction of these technological devices. China is miles ahead in this race for global resources, and therefore does not have any direct competitors, hence its accumulating stockpiles of these raw materials, including tungsten, which, for the EU, is a critical raw material.

Due to the concerns regarding the security of the supply of these resources, particularly from China, there is a clear revival in the development of new mines and, most importantly, there are several technical and/or scientific works, at European and international level, which propose the valorisation of mining waste, such as by tailings recovery.

In North America, the North American Tungsten Corporation Ltd. is recovering its own tailings facilities, in the Cantung tungsten mine in Canada, for all underground and surface production from 1971 until February 2007. Mill feed graded considerably higher than current feed, during this period of operation, leading to large amounts of WO_3 being discarded as tailings, despite good plant recoveries at the time (North American Tungsten Corporation, 2013).

In South America, in December 2011, Largo Resources Ltd. announced its very first commercial shipment of tungsten concentrates from its Currais Novos project in Brazil, which is reprocessing and recovering tungsten from two tailings, known as the Barra Verde and Boca de Laje tailings piles. They were deposited during the processing of ore from the Barra Verde and Boca de Laje tungsten mines, which have operated sporadically since the early forties (Largo Resources, 2010 and 2011).

In Australia, another international example of this type of recovery is in the Mount Carbine tungsten mine. It was here that the company, Carbine Tungsten Ltd., after an earlier feasibility study to recover tailings and mineralised wastes in 2010, resumed production of tungsten concentrate from tailings material at the Mount Carbine deposit in 2012, produced by historical mining between the seventies and eighties. These tailings could be treated in order to produce a recovery mixed concentrate with a grade of 52% of WO_3. The company also signed an off-take agreement with Mitsubishi Corporation, from Japan, to supply all concentrates produced from the retreatment plant at a price based on the monthly London Metal Bulletin price (Carbine Tungsten, 2013).

In Europe, there are also various examples of these recycling practices of CRMs that have taken place over the past few decades. One of them occurs in La Parrilla mine (Spain), where, between 1980 and 1982, the mining wastes (tailings) were evaluated, which confirmed 2835ppm of WO_3. More recently, in 2010, W Resources Plc calculated the volume of heaps at 1,200,000m^3. Currently in this mine, the process is being successfully carried out, which allows the company to market the concentrates that it produces (Matos, 2016).

Another European example of a possible waste recovery is at the Panasqueira Mine (Portugal), where heaps of metallic mineral residues, from the extraction of tungsten, accumulate, and do not have any use (Herrera *et al.*, 2013). There has been a development of new process routes for the recovery of ultrafine wolframite, in order to allow the efficient reprocessing of the tailings from the Panasqueira Mine. Much of the wolframite found in the tailings has a size of less than 25μm and is associated with a complex mixture of other metallic minerals, including zinc (Zn), copper (Cu) and other sulphides, tourmaline, siderite, and other strongly ferromagnetic material (Clemente *et al.*, 1993). This waste not only constitutes an eyesore in the surrounding landscape, but also occupies space in the so-called “Couto Mineiro” of Panasqueira, consequently requiring the construction of new spaces (heaps) for the depositing of such waste. For these reasons, Almonty Industries Inc. announced initiatives to enhance tailings recovery at the Panasqueira mine. In order to achieve that, it announced a partnership with Crominet Mining Processing SA (PTY) Ltd. to increase its overall recovery rates. Coarser grained tailings from the so-called Heavy Media Separation (HMS) unit, containing, on average, 0.03% WO_3, were sent to the Crominet facilities, where an X-Ray Transmission (XRT) sorting test showed a potential recovery of up to 93.6% of W content. Under the agreement, Crominet will install and operate an XRT ore sorter and respective equipment at Panasqueira by the end of the current year, with sufficient capacity to treat the entirety of the coarser grained tailings generated by the HMS unit (Almonty Industries, 2017).

The state of the art review, regarding valorisation of mining waste, is also visible in several ongoing European projects, under the Horizon2020 programme, for example, the ProSUM project (Prospecting Secondary raw materials in the Urban mine and Mining waste), the REMINE project (Reuse of mining waste into innovative geopolymeric-based structural panels, precast, ready mixes and *in situ* applications), and the BIOCriticalMetals project (Recognition of microbial functional communities and assessment of the mineralising potential (bioleaching) for high-tech critical metals).

It is important to note that, in the area of knowledge of geological resources, a number of measures have already been implemented, such as the ProMine (Nano-particle products from new mineral resources in Europe) and EuroGeoSource (EU information and policy support system for sustainable supply of Europe with energy and mineral resources) projects, aiming to create a Europe-wide GIS database to locate and determine the value of existing mineral resources.

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CHAPTER 2.

EUROPEAN UNION AND PORTUGUESE POLICIES ON RAW MATERIALS

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The European industry, as well as the OECD industry, has been increasing its dependency on mineral resources, in particular, the metallic and industrial minerals. This situation could create a substantial politic risk for the EU economy because Europe is becoming more and more dependent on its external suppliers, as shown in Chart 1, where we can see that the imports (4.2%) on raw materials are almost double the exports (2.4%).

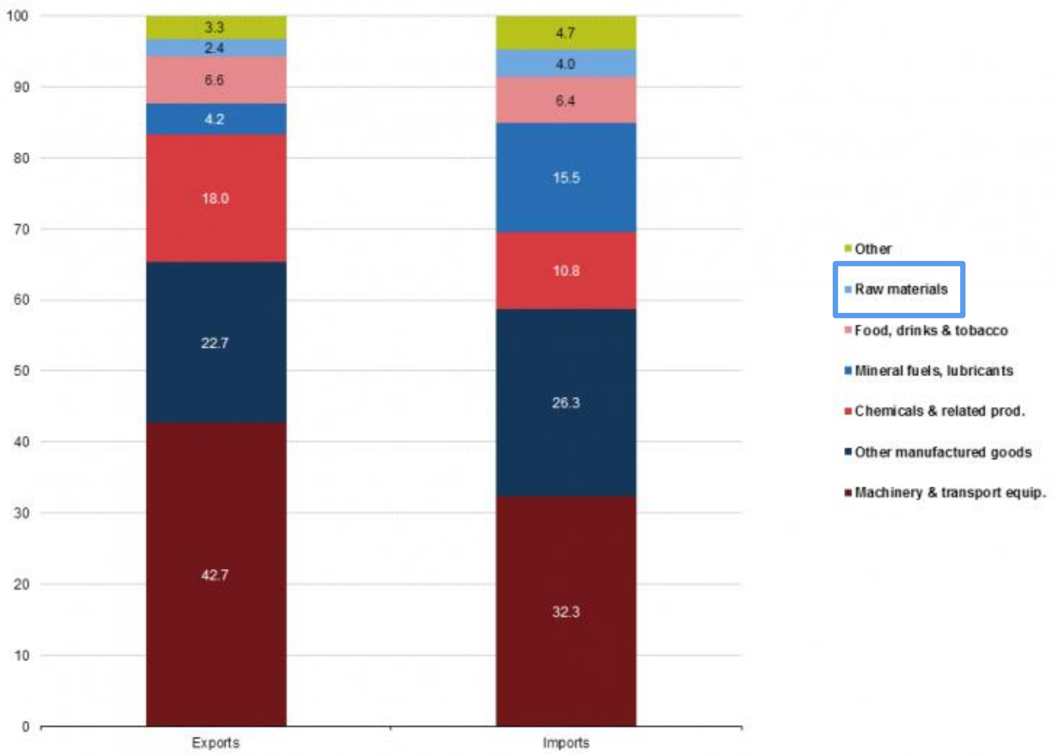

Chart 1 - Main exports and imports of the EU-28 in 2015 (Eurostat, n.d.).

In fact, there has recently been a significant increase in the price of minerals in the global market, especially of the metallic minerals. Developed countries, such as China, Brazil and India, traditionally only producers of mineral resources, have now also become consumers. Some of these developed countries, particularly China, have even adopted restrictive policies for the exportation of raw materials.

Industrial sectors that depend on access to raw materials, such as construction, chemical, automotive, aerospace, machinery, equipment, and renewable energy devices, have a combined added value in excess of €1,000 billion and provide employment for close to 30 million people in the EU. The EU addressed these challenges in the EU Raw Materials policy and strategy called "**Raw Materials Initiative**". (EC, n.d.a)

2.1. RAW MATERIALS INITIATIVE

This EU initiative is an integrated strategy to respond to the different obstacles related to the safe and sustainable access to non-energy and non-agricultural raw materials, as they are becoming more and more centralised, especially by China, which, accentuated by the recent global financial crisis, has endangered the entire EU industrial sector.

These concerns, referenced above, provoke a reaction from the UNICE (now known as BusinessEurope), a lobby group representing enterprises of all sizes in the EU and six non-EU countries, which delivered a position paper called "**Towards an EU strategy to secure access to industrial raw materials**" to the DG-ENTR (now called the DG-GROW) on the 8th September **2006**. On 21st March **2006,** before this position paper was delivered, the European extractive industry launched the European Technology Platform on Sustainable Mineral Resources (ETP SMR), with the goal of modernising and restructuring the European extraction and processing sector for the energetic and non-energetic minerals.

The ETP SMR vision is to modernise and reshape the European minerals industries, the fundamental pillar of the European economy, and more specifically to: reshape the traditional industry into a knowledge-driven industry; foster new and better jobs (SME level); supply and secure the mineral resources needed by the EU economy, while minimising the related environmental footprint (decoupling); strengthen world leadership and competitiveness in minerals sector technology; and add value for customers and society (ETP SMR, 2017).

During **2007**, other institutions expressed concern about the state of the extractive sector in Europe, and about the weakness of the safe supply to the European industry, consumer of these resources, which included the Vice-President of DG-ENTR (now the DG-GROW) at the time, Günter Verheugen, who declared, on the 5th June **2007**, that "European industries need predictability in the flow of raw materials and stable prices to remain competitive. We are committed to improve the conditions of access to raw materials, be it within Europe or by creating a level playing field in accessing such materials from abroad." (EC, 2007).

In addition, before Verheugen's statement, on the 21st May **2007**, the European Council, in the 2801st council meeting, with the theme of "Competitiveness (Internal Market, Industry and Research)", requested that the European Commission 'develop a coherent political approach with regard to raw materials supplies for industry, including all relevant areas of policy (foreign affairs, trade, environmental, development and research and innovation policy) and to identify appropriate measures for cost-effective, reliable and environmentally friendly access to, and exploitation of, natural resources, secondary raw materials and recyclable waste, especially concerning third-country markets'.

On the 4th November **2008**, the European Commission (EC) issued a communication on raw materials, "**The raw materials initiative — meeting our critical needs for growth and jobs in Europe**" (EC, 2008), which introduced a paradigm shift that has had a positive impact on the extractive sector, and has boosted all the developments that have been followed in this area.

The Raw Materials Initiative (RMI) is based on three pillars, subdivided into different actions:

- **1st Pillar: Ensuring fair and sustainable supply from global markets**
    - EU trade strategy for raw materials;
    - Raw materials diplomacy;
    - Assistance to developing countries.
- **2nd Pillar: Fostering sustainable supply of raw materials within the EU**
    - Exchange of good practice between EU member states;
    - Enhancing EU knowledge base;
    - Promoting research and skills.
- **3rd Pillar: Boosting resource efficiency and promoting recycling**
    - Better implementation and smarter EU waste legislation promoting resource-efficiency and recycling;
    - Strengthen the enforcement of the EU Waste Shipment Regulation.

In conclusion, these three pillars of the proposed strategy aim to ensure a state of equality in access to resources in third-world countries, better framework conditions for extracting raw materials within the EU, and a reduced consumption of primary raw materials by increasing resource efficiency and promoting recycling.

In April **2009**, in sequence with the RMI, the DG-ENTR (now the DG-GROW) promoted the creation of two Ad-hoc Working Groups, which are subgroups of the Raw Materials Supply Group[1], with the following tasks:

- "Exchanging best practices on land use planning, permitting and geological knowledge sharing";
- "**Defining critical raw materials**".

The conclusions of the work produced by these two working groups were integrated into two reports published in June **2010**.

The first Ad-hoc Working Group had the mandate 'to research and identify examples of best practice covering minerals policy, application and authorisation processes, land use planning, and codes and technical guidance, in order to disseminate these for consideration by interested parties in member states and to make recommendations'. It published the report called "**Improving framework conditions for extracting minerals for the EU**" (EC, 2010a).

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[1] This expert group includes representatives from EU countries, European Economic Area countries, EU candidate countries, and organisations representing stakeholders - industry, research and civil society.

The second Ad-hoc Working Group had the mandate to identify a list of critical raw materials (CRMs) at EU level based on a quantitative methodology[2] using three different criteria:

- **Economic importance** (importance of a raw material per economic sector, as well as the importance of the sector in the EU economy, particularly in emerging technologies, such as renewable energy, energy efficiency, the electronics and aerospace industries);
- **Supply risk** (including components such as, political and economic stability, level of production concentration, potential for substitution, and recycling rate);
- **Environmental country risk** ('the risks that might be taken by countries with weak environmental performance in order to protect the environment and, in doing so, endanger the supply of raw materials to the EU') – which the working group included in the Supply Risk criteria when they built Chart 2.

In the report called "**Critical raw materials for the EU**" (EC, 2010b), it analysed 41 'candidate' minerals and metals[3] were analysed. From those 41 'candidate' minerals, only 14, including 8 metals (**beryllium**, **cobalt**, **gallium**, **indium**, **magnesium**, **niobium**, **tantalum** and **tungsten**), 2 groups of metals (the Platinum-Group Metals – **PGMs**[4] and the Rare Earth Elements - **REEs**[5]), 2 semi-metals[6] (**antimony** and **germanium**) and 2 non-metals (**fluorspar** and **graphite**), were classified as critical, as shown in Chart 2 in the higher-right sub-cluster.

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[2] This methodology is discussed in "Annex I: Methodology for the quantitative assessment" from the "Critical raw materials for the EU" (EC, 2010b).

[3] Aluminium, antimony, barites, bauxite, bentonite, beryllium, borates, chromium, clays (and kaolin), cobalt, copper, diatomite, feldspar, fluorspar, gallium, germanium, graphite, gypsum, indium, iron ore, limestone (high grade), lithium, magnesite, magnesium, manganese, molybdenum, nickel, niobium, perlite, PGMs, REEs, rhenium, silica sand, silver, talc, tantalum, tellurium, titanium, tungsten, vanadium and zinc (in alphabetical order).

[4] According to the IUPAC and the EC (2010b), this critical raw material group includes platinum, palladium, iridium, rhodium, ruthenium and osmium.

[5] According to the IUPAC and the EC (2010b), the REEs are a series of 17 transition metals: yttrium (Y), scandium (Sc), and the so-called lanthanides (lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu).

[6] Also known as metalloids.

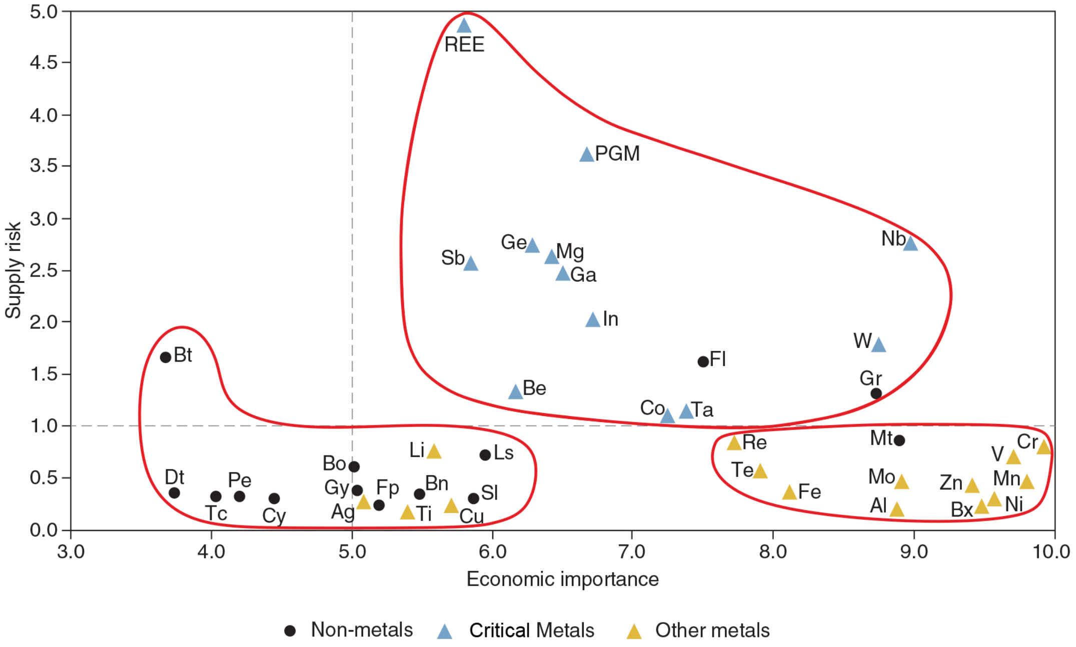

Chart 2 - Supply risk vs. economic importance of the 41 'candidate' materials (modified from EC, 2010b).

In this report (EC, 2010), the 'raw material is labelled "critical" when the supply risk shortage and its impacts on the economy are higher compared to most of the other raw materials' (see Chart 2). The CRMs 'high supply risk is mainly due to the fact that a high share of the worldwide production comes from China (antimony, fluorspar, gallium, germanium, graphite, indium, magnesium, rare earths, and tungsten), Russia (PGM), the Democratic Republic of Congo (cobalt and tantalum) and Brazil (niobium and tantalum). This production concentration, in many cases, is compounded by low substitutability and low recycling rates'.

On the 2nd February **2011**, the EC presented the communication "**Tackling the challenges in commodity markets and on raw materials**" (EC, 2011b) with the goal of continuing the preparation for the Europe 2020 strategies, which 'ensure smart, sustainable and inclusive growth and is closely linked to the flagship initiative for a resource efficient Europe.' This communication, which formally adopted the list of CRMs, also approaches the State of the Art of the RMI, and had the intention of exploring 'with the extractive, recycling and user industries, the potential for targeted actions, notably with regard to recycling'. The EC 'is also ready to examine, with member states and industry, the added value and feasibility of a possible stockpiling programme of raw materials.' For that purpose, the EC concluded that it will:

- Monitor the issues of critical raw materials in order to identify priority actions, and will examine this with members states and stakeholders;
- Regularly update the list of critical raw materials, at least every 3 years.

On the 24th June **2013**, the EC produced a communication called "**On the implementation of the Raw Materials Initiative**" (EC, 2013) that provided an overview of the ongoing initiatives (RMI), while highlighting the joint interest for the EU and third-world countries, rich in raw materials, to work as a partnership. EU member states were requested to develop national strategies in support of the raw materials industry and of fostering access to resources.

On the 16th December **2013**, Oakdene Hollins, Research & Consulting and the Fraunhofer, ISI, for the DG-ENTR (now the DG-GROW) prepared a new "**Study on Critical Raw Materials at EU Level, Final Report**" (Chapman *et al.*, 2013). This updated assessment was summarised in the 2014 "**Report on critical raw materials for the EU**", elaborated by the Ad-hoc Working Group on defining raw materials (EC, 2014a).

Also in **2013**, the European Rare Earths Competency Network (ERECON[7]) was established, which 'is a network of excellence comprising more than 80 European rare earths experts from industry, academia, and the policy world. It provides the appropriate organisational structures and meeting opportunities for a cross-disciplinary exchange to examine key challenges and develop recommendations for fostering a sustainable and secure rare earth supply for Europe.' This network is formed by three Working Groups, which were focused on:

- Opportunities and road blocks for primary supply of rare earths in Europe;
- European rare earths resource efficiency and recycling;
- European end-user industries and rare earths supply trends and challenges.

On the 26th May **2014**, the EC presented the communication "**On the review of the list of critical raw materials for the EU and the implementation of the Raw Materials Initiative**" (EC, 2014c). This communication was based on the aforementioned new report by the Ad-hoc Working Group on defining critical raw materials (EC, 2014a) that revised the list of 2010 CRMs for the EU.

This review, according to the EC, 2014c, was done with three main objectives:

a) ***Widening the scope of raw materials analysed*;**

'In the 2013 study, 54 non-energy, non-food materials were analysed (41 were analysed in 2010), using the same methodology as the previous study. This extended scope included seven new abiotic[8] materials and three biotic[9] materials (rubber, pulpwood and sawn softwood).'

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[7] Initiative developed by the European Commission's Directorate-General for Enterprise and Industry on the request of the European Parliament.

[8] Abiotic raw materials are non-renewable raw materials.

[9] Biotic raw materials are renewable, naturally occurring substances of animal and vegetable origin.

b) *Refining the analysis and using additional data*;

'In comparison to the 2010 study, greater detail is provided on the rare earth elements by splitting them into 'heavy' and 'light' categories, both included as separate entries in the new list. New European data has been integrated into the study and a 'value chain assessment' is included for all critical raw materials.'

c) *Preserving comparability with the 2010 study*.

'To enable comparability with the 2010 report, the methodology was not fundamentally changed. New information and insights, on downstream supply chains for example, have therefore been used to improve the qualitative analysis, not the quantitative methodology. The new report contains recommendations for changing the methodology for the next report.'

From the 54 'candidate' materials, 20 were classified as "critical", including 13 of the 14 CRMs identified in the previous study, with only tantalum, due to its lower supply risk, being removed from the EU critical raw materials list. Six new materials[10] were added to the new list, and the REEs were divided into heavy and light (note that there are different interpretations concerning REEs sub-groups) - Table 1.

Table 1 - Classification of REEs according to different authors (adapted from Zepf, 2013).

Authors	**Rare Earth Elements**			
	Scandium	**LREEs**	**MREEs**	**HREEs**
Binder USGS	-	**La** to **Gd**	-	**Tb** to **Lu**
Röhr	-	**Ce** to **Gd**	-	**Tb** to **Lu**
Cesbron ROMPP Online	-	**La** to **Eu**	-	**Y**, **Gd** to **Lu**
Pohl[11]	-	**La** to **Sm**	-	**Gd** to **Lu**
Kingsnorth[12]	-	**La** to **Nd**	**Sm** to **Gd**	**Y**, **Tb** to **Lu**
Stosch	-	**La** to **Nd**	**Pm** to **Dy**	**Y**, **Ho** to **Lu**
Chen	-	**La** to **Eu**	**Gd** to **Ho**	**Sc**, **Y**, **Er** to **Lu**
EU CRMs (EC, 2014a)[13]	**Sc**	**La** to **Sm**	-	**Y**, **Eu** to **Lu**

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[10] The 6 new materials include: borates, chromium, coking coal, magnesite, phosphate rock and silicon metal.

[11] According to this author the element europium (Eu) is not included in this classification.

[12] According to this author the element promethium (Pm) is not included in this classification.

[13] According to this author the element promethium (Pm) is not included in this classification and scandium is considered as a separate group from LREEs, MREEs and HREEs.

According to the Report on Critical Raw Materials for the EU (EC, 2014a), as cited in Table 1, this group of 17 metals were divided into three main sub-groups: Scandium (Sc), Heavy Rare Earth Elements (HREEs) and Light Rare Earth Elements (LREEs).

SCANDIUM

Scandium can be found in most REEs deposits, and is sometimes classified as a LREE. However, because it is formed from a sub-group itself, it cannot be classified as an LREE or HREE (CRM Alliance, n.d.). In the Report on Critical Raw Materials for the EU (2014), it has been treated as entirely separate as a result of its production and applications, which are not heavily linked to the other REEs.

LREEs[14]

In spite of the fact promethium (Pm) belongs to this sub-group of metals (only found in nature in trace quantities), it was not regarded as a critical raw material in the Report on Critical Raw Materials for the EU (2014).

HREEs[15]

In spite of the fact that yttrium is lighter than the light rare earth elements, it is included in the heavy rare earth elements sub-group due to its chemical and physical associations with heavy rare earths in natural deposits. On account of the fact that its ionic radius is nearly the same as dysprosium or holmium, and the chemical behaviour of yttrium is very similar to holmium, they can be grouped together into the HREEs (Zepf, 2013).

Overall, we have 8 metals (**beryllium, chromium, cobalt, gallium, indium, magnesium, niobium and tungsten**), 3 group of metals (**PGMs, HREEs and LREEs**), 2 metalloids[16] (**antimony and germanium**) and 7 non-metals (**borates, coking coal, fluorspar, magnesite, natural graphite, phosphate rock** and **silicon metal**) – Table 2.

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[14] According to the EU Critical Raw Materials studies, the sub-group LREEs is formed by the elements lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd) and samarium (Sm).

[15] According to the EU Critical Raw Materials studies, the sub-group HREEs is formed by the elements yttrium (Y), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu).

[16] Metalloids, or semi-metals, have properties that are somewhat of a cross between metals and non-metals. They tend to be economically important because of their unique conductive properties, which make them valuable in the semi-conductor and computer chip industry.

Table 2 - List of the 20 CRMs at EU level and its own applied and emerging technologies - in alphabetical order (adapted from EC, 2014a and BIO by Deloitte, 2015).

Critical Raw Material	Applied and emergent technologies	
	Semi-finished products	**Finished products**
Antimony (Sb)	Sb oxide, Pb-Sb alloys, Sb chemicals, flame-retardant plastics and rubber.	Electrical and electronic equipment, cables and wires, textiles, PET containers, lead acid batteries, articles made with Sb alloys, glass and ceramics.
Beryllium (Be)	Be ceramic, Be alloys, Be metal.	Telecommunications and electronics, auto electronics, aerospace/defence, industrial components.
Borates (Bo)	-	Glass, frits and ceramics, fertilisers, construction materials, detergents.
Chromium (Cr)	Stainless steel and alloy steel.	Products made of stainless steel and alloy steel, refractory bricks and mortars, casting moulds, products made of chromium chemicals
Cobalt (Co)	-	Batteries and products containing batteries, pigments, superalloys for aeronautic applications, hard metals, catalysts.
Coking Coal (CC)	Coke for electrodes production.	Coke used in blast furnaces and in other applications, electrodes.
Fluorspar (Fl)	Fluorocarbons and fluoropolymers, fluoroaromatics, UF6 in nuclear energy production, HF in oil alkylation and metal pickling/etching, AIF3 in aluminium making.	Products containing fluorocarbons and fluoropolymers and fluoroaromatics, inorganic fluorine compounds.
Gallium (Ga)	Wafers of gallium arsenide and gallium nitride, gallium compounds.	IC applications (smartphones), sensor applications (radars), photovoltaic applications, optoelectronic applications (LEDs), permanent magnets.
Germanium (Ge)	-	Optical fibres, IR optics, satellite solar cells, IT applications, PET catalysts.
Indium (In)	ITO, indium chemicals and alloys, semiconductors.	Batteries, architectural and automotive glass, electrical and electronic equipment, photovoltaic panels, LEDs.
Magnesite (Mt)	-	Magnesia-based refractory goods, animal feed and fertilizers.
Magnesium (Mg)	-	Aluminium packaging, vehicles, aluminium construction elements, magnesium powders for steel-desulphurisation.
Natural Graphite (Gr)	-	Refractories, Li-Ion cells, primary batteries, friction materials, lubricants.

Niobium (Nb)	HSLA, stainless steel, superalloys, lithium niobate, superconductors.	Automotive, pipelines, construction, aero engines, gas turbines, electrical equipment, MRI.
PGMs[17]	-	Automotive and industrial catalysts, electronic applications.
Phosphate Rock (PR)	-	Phosphatic fertilisers, feed and food additives, detergents.
HREEs[18]	Permanent magnets, oxygen sensors.	Applications using permanent magnets, coloured glass, vehicles with oxygen sensors, fluorescent lamps.
LREEs[19]	Permanent magnets, auto catalysts and alloys.	Applications using permanent magnets and alloys, single cells and applications using batteries NiMH, vehicles with auto catalysts.
Silicon Metal (SM)	Silicones and silanes in primary forms, Si containing aluminium alloys, silicon in wafers.	Chemical products containing silicones and silanes, products made of aluminium alloys in the automotive and construction industries, electronic and photovoltaic applications.
Tungsten (W)	Tungsten oxides, metal and cemented carbides, tungsten alloy, chemical compounds and containing steel.	Lighting and electronic industry, aeronautics and energy uses, mill and cutting tools, mining and construction tools, catalysts and chemical uses, HSS applications, heat resisting steel applications.

After the EC classified the twenty 2014 CRMs, they produced Chart 3, where we were able to see the critical assessment of each CRM, based on the following two parameters, calculated using the same method[20] as the previous one (Chapman *et al.*, 2013):

- **Economic importance**

a) **Distribution of end uses:** the key issue lies in the different geographical regions to which end use data applies. In the majority of cases, there are no significant differences between these geographical regions, but this is not a rule;

b) **Value added of the megasectors**[21]**:** the proportion of each material associated with industrial megasectors, such as construction, combined with its gross value added to EU GDP. This total is scaled according to total EU GDP in order to calculate the overall economic importance of a material.

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[17] Considering rhodium (Rh), palladium (Pd) and platinum (Pt).

[18] Considering yttrium (Y), europium (Eu), dysprosium (Dy), erbium (Er) and terbium (Tm).

[19] Only considering neodymium (Nd).

[20] This methodology is described in “Annex B – Description of EU Criticality Methodology” from the “Study on Critical Raw Materials at EU Level, Final Report,” (Chapman *et al.*, 2013).

[21] The “megasectors” used in the calculation of the economic importance include: aeronautics, trains, ships; beverages; chemicals; construction material; electrical equipment; electronics & ICT; food; mechanical equipment; metals; mining of metal ores; other final consumer goods; paper; plastic, glass, rubber; pharmaceuticals; refining and road transport (Chapman *et al.,* 2013).

- **Supply risk (APPENDIX I)**

a) **Production data:** is widely available and is of a good quality for metals, natural rubber and some industrial minerals. In this report, a combination of data, ranging from 2010 for World Mining Data, up to 2012, for Raw Materials Data, was used;

b) **World Governance Indicator:** '(…) is used to measure the supply risks of raw materials. This indicator takes into account accountability, political stability and absence of violence, government effectiveness, regulatory quality, and rule of law.'

c) **Recycling rates:** '(…) measures the proportion of metal and metal products that are produced from end-of-life scrap and other metal-bearing low grade residues in end-of-life scrap worldwide (data is available but of varying quality).'

d) **Substitutability index[22]:** this 'issue is relevant especially for the materials close to the threshold of the supply risk (borates, phosphate rock, PGMs, cobalt, coking coal, chromium, vanadium, bauxite, tin, tantalum and lithium).' This substitutability is a 'measure of the difficulty in substituting the material, scored and weighted across all applications.'

e) **Environmental performance index:** although this indicator is available for all countries that were assessed, the Ad-hoc Working Group on Defining Critical Raw Materials states that "not all the parameters of the complex EPI are relevant for the assessment of critical raw materials" because in certain cases it doesn't show the reality of the mining sector of certain countries (EC, 2014a).

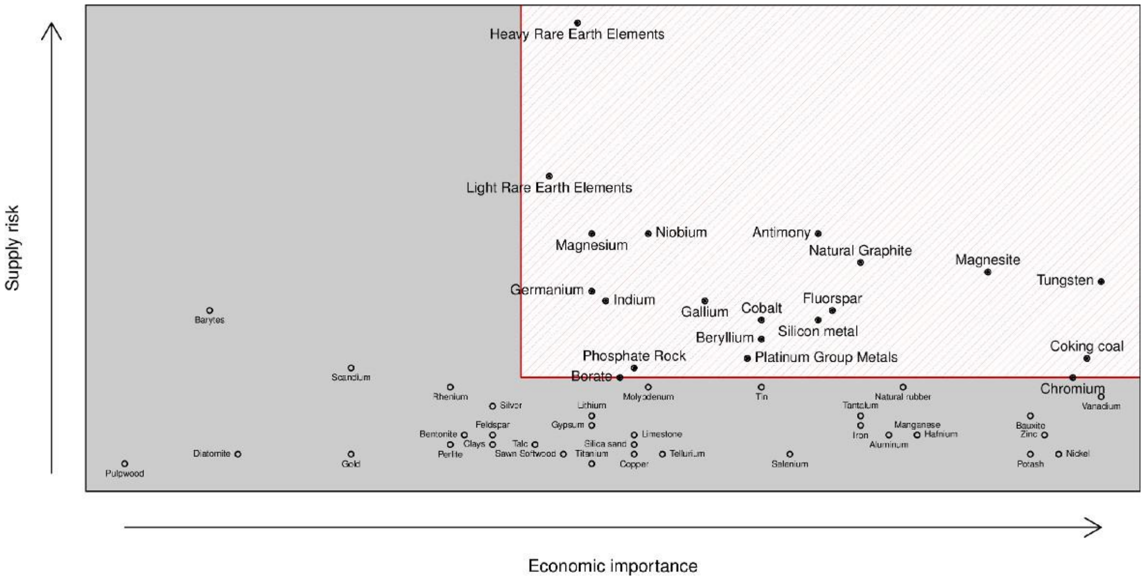

Chart 3 - Supply risk vs. economic importance of the 54 materials (EC, 2014a).

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[22] According to the Chapman *et al.* (2013) study, the values are between 0 and 1.0, which means that the raw material is easily and completely substitutable at no additional cost; 0.3 means that it's substitutable at low cost; 0.7 means it's substitutable at high cost and/or loss of performance; and 1 means it isn't substitutable.

It is also important to be aware that, according to the EC, 2014a, 'all raw materials, even when not critical, are important for the European economy and therefore not being critical does not imply that a given raw material and its availability to the European economy should be neglected.' For that reason, 'the availability of the new data may affect the list in the future and therefore the policy actions should not be limited to critical raw materials exclusively.'

Statistically speaking, 90% of the global primary supply of the 54 'candidate' materials analysed in this study, especially base, speciality and precious metals, as well as rubber, come from extra-EU sources (especially China, which is the major supplier of these materials). The 'EU primary supply across all the candidate materials is estimated at around 9%', mainly from France, Germany and Italy (EC, 2014a).

For each of the 20 EU CRMs, the dominant producers are shown in Figure 1, with China once again being the most influential in terms of global supply. Nevertheless, other countries also play an important role in supplying specific raw materials, for example, the USA for beryllium and Brazil for niobium. It is also clear to see that the supply of PGMs, borates, and chromium is more diverse, but still relatively concentrated.

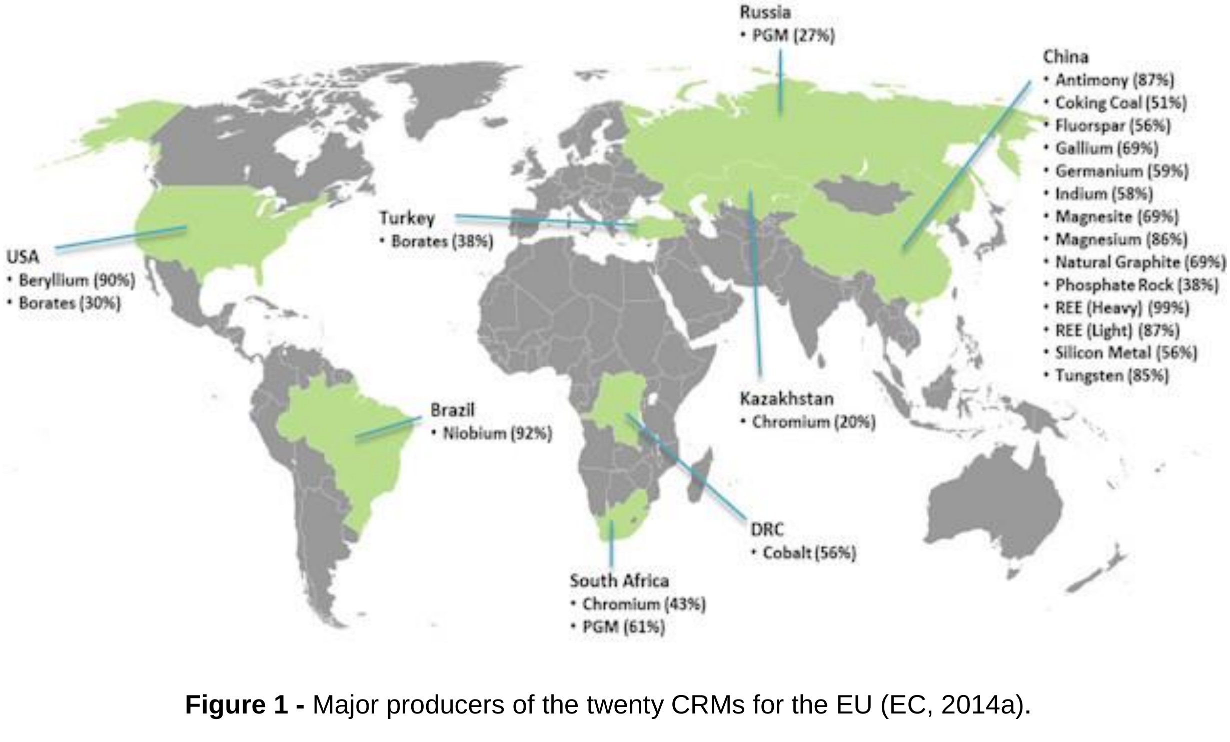

Figure 1 - Major producers of the twenty CRMs for the EU (EC, 2014a).

As we already know, the EU economy's development greatly depends, in large measure, on those twenty CRMs. This EC 2014 report on CRMs, and its predictions for the year of 2020, based on the 'forecast average annual demand growth up to 2020 for critical raw materials (% per year)' from the Roskill Information Services Ltd., summarises the annual demand forecast for each of the 20 CRMs.

In Chart 4, the CRMs are divided into four different rates of demand growth forecast: **very strong** (>8%, such as Nb, Ga and HREEs); **strong** (4.5% - 8%, such as Co, LREEs, In, Mg, CC, and W); **moderate** (3% - 4.5%, such as Cr, Ge, PGMs, Bo, and Gr); and **modest** (<3%, such as Mt, SM, Sb, Fl, PR, and Be) - % per year.

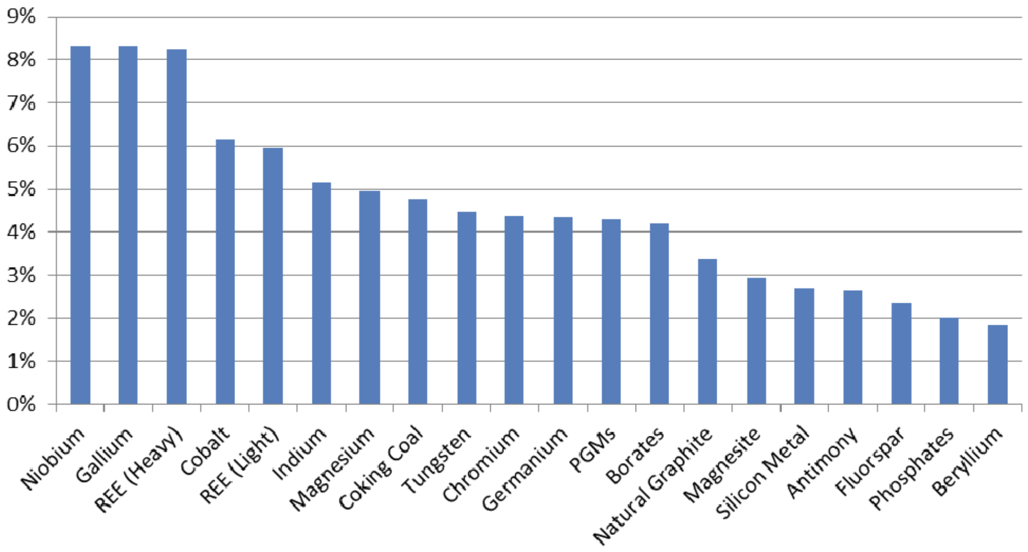

Chart 4 - Annual demand growth forecast to 2020 for all the twenty CRMs (EC, 2014a).

This EC 2014 report also analysed the forecast market balance for the 20 CRMs for 2020, which is resumed in Table 3.

Table 3 - Forecast market balance for the twenty CRMs for 2020 (EC, 2014a).

Risk of deficit	Balanced market	Surplus
Antimony	Beryllium	Borates
Coking Coal	Chromium	Magnesium Metal
Gallium	Cobalt	Natural Graphite
Indium	Fluorspar	Niobium
PGMs	Germanium	LREEs
HREEs	Magnesite	Phosphate Rock
	Tungsten	
	Silicon Metal	

The EC 2014 report from the Ad-hoc Working Group on Defining Critical Raw Materials also alleges that ‘the purpose of the list is to contribute to the implementation of the EU industrial policy and to ensure that European industrial competitiveness is strengthened through actions in other policy areas. This should increase the overall competitiveness of the EU economy, in line with the Commission’s aspiration of raising industry’s contribution to GDP to as much as 20% by 2020. It should also help to incentivise the European production of critical raw materials and facilitate the launching of new mining activities. The list is also being used to help prioritise needs and actions. For example, it serves as a supporting element when negotiating trade agreements, challenging trade distortion measures or promoting research and innovation. Information on its use by member states and industry is, however, very scarce.'

On the 11th July **2017**, the EC published its guidelines on the "**Assessment of the Methodology for establishing the EU list of critical raw materials – Background Report**" (JRC, 2017). This is an authoritarian document that contains the guidelines and the 'ready-to-apply' methodology for the EU criticality assessment as a revision of the EC methodology that was used to identify the list of critical raw materials (CRMs) for the EU in 2014.

2.2. INTERNATIONAL DIPLOMACY ON RAW MATERIALS

The international diplomacy on raw materials, which is also a significant concern for the RMI, has commenced with the organisation of several international events, with the intention of starting dialogues with non-EU countries, in order to work together with a higher mutual benefit.

The first event, organised in December 2013 by the DG-ENTR (now the DG-GROW), was called "**US-Japan-EU Trilateral Workshop on Critical Raw Materials**". This event has already taken place six times, and exists with the purpose of 'exchanging information on the upcoming review of the critical raw materials list, to inform on the progress and to possibly compare analyses and data on critical raw materials. The review of the EU list entered its final stage and therefore the opportunity was taken to comment and discuss the preliminary results' (EC, n.d.b).

Since 2014, and after the success of this first event, similar events were organised with Greenland, the African Union, Canada, Australia, Chile, South Africa, the USA, Argentina, Brazil, Colombia, Mexico, Peru, Uruguay, and China (EC, n.d.b).

2.3. RAW MATERIALS INITIATIVE DEVELOPMENT

The Europe 2020 strategy, which includes "**A resource-efficient Europe**" (EC, 2011a) as one of the seven flagships of this strategy, materialised in several initiatives, highlighting the European Innovation Partnership (EIP) and the constitution of a Knowledge and Innovation Community for Raw Materials (KIC Raw Materials), stimulated by the European Institute of Innovation & Technology (EIT).

2.3.1. THE EUROPEAN INNOVATION PARTNERSHIP ON RAW MATERIALS

The EIP is the major EU initiative implementing the RMI stakeholder platform, which brings together representatives from industry, public service, academia, EU countries, companies, researchers, and NGOs, to promote innovation in the raw materials sector, and development of the Strategic Implementation Plan (EIP RM, 2013a).

This partnership will create critical mass towards the single objective of ensuring sustainable access to raw materials by creating synergies between different policy instruments (technological, regulatory and standardisation), reinforcing co-ordination with member states, where their contribution is crucial, and ensuring the development of integrated value chains (EC, 2012c).

On the 29th February **2012**, the EC issued a communication called "**Making raw materials available for Europe's future well-being**" (EC, 2012a) where the Commission adopted the proposal for an Innovation Partnership on raw materials.

The overall intention of this partnership is to contribute to the Europe 2020[23] targets of the EU industrial and resource efficiency policy, by ensuring a safe and sustainable supply of raw materials to the European economy and society, and help raise industry's contribution to the EU's GDP to around 20% by 2020. It will also play an important role in meeting the objectives of the EC's flagship initiatives, known as Innovation Union[24] and Resource-Efficient Europe[25]. It will do this by ensuring the sustainable supply of raw materials to the European economy, whilst also increasing benefits for society as a whole (EIP RM, 2013a). The more specific objectives of this partnership are as follows (EC, 2012a):

- **Reduce import dependency and promote production and exports**
    - Improve supply conditions from European and other sources;
    - Diversify raw materials sourcing;
    - Improve resource efficiency, including recycling;
    - Find alternative raw materials.
- **Push Europe to the forefront in the raw materials sectors**
    - Make Europe a leader in the raw materials capabilities;
    - Mitigate negative environmental, social and health impacts.

With that being said, we know that the EIP plays a crucial role in the EU's raw materials policy framework as it (EIP RM, 2013a):

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[23] The Europe 2020 is the European Union's ten-year jobs and growth strategy. Five headline targets have been agreed for the EU to achieve by the end of 2020. These cover employment; research and development; climate change and energy sustainability; education; and fighting poverty and social exclusion.

[24] This initiative, launched in 2010, is one of seven initiatives under the Europe 2020 strategy for smart, sustainable and inclusive growth.

[25] The Resource-Efficient Europe initiative is also part of the Europe 2020 strategy for a smart, sustainable and inclusive growth.

- Reinforces the RMI by translating the strategic policy framework into concrete actions and by mobilising the stakeholder community to implement them;
- Has been instrumental in securing Research and Innovation (R&I) funding: from the Framework Programme 7 (the R&I funding tool for the period 2007-2013) to the Horizon 2020 (the R&I funding tool for 2014-2020) it was increased by €420 million for research on the challenges related to raw materials.

The governance structure of the EIP on raw materials, which follows the principles set out in the Innovation Union, divides the structure into four different levels of action: **decision making, orientation level, planning and monitoring** (Sherpa Group[26]), and **advice and implementation** (Operational Groups[27]). Different operational groups may be assembled to provide the necessary expertise according to the different subjects covered by the working packages. (EC, 2012c)

The aforementioned Working Packages (WP) are divided into three groups, according the EC, 2012c:

- **Technology-focused policy areas (WP1 and WP2);**
- **Non-technology-focused policy areas (WP3 and WP4);**
- **International cooperation – horizontal approach (WP 5).**

To accelerate this process, the EC proposed concrete targets (EIP targets) to be achieved, at the latest, by 2020 (EIP RM, 2013a). These targets are as follows: up to **10 innovative pilot actions** (e.g. demonstration plants) for exploration, extraction and processing, and collection and recycling; **substitutes** for at least three key applications of critical and scarce raw materials; **enhanced efficiency in material use and in prevention, re-use and recycling** of valuable raw materials from waste streams, with a specific focus on materials having a potentially negative impact on the environment; a **network of research, education and training centres** on Sustainable Mining and Materials Management (M^3); **European standardised statistical instruments** for the survey of resources and reserves, and a 3-D geological map; a **dynamic modelling system** linking trends in supply and demand with economically exploitable reserves and a full lifecycle analysis; and a **pro-active strategy of the EU in multi-lateral organisations and in bilateral relations**, such as with the USA, Japan, and Australia, in the different areas covered by the partnership.

These targets are non-energy, non-agricultural raw materials, which are vital inputs for the innovative technologies, and also offer environmentally-friendly, clean-technology applications. They are also paramount for the manufacture of the new and innovative

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[26] This group has the intention of planning the major actions and events, and to prepare the meetings and follow-up of the HLSG.

[27] The main task of these groups is to provide advice to the HLSG, to convert the Strategic Implementation Plan (SIP) into tasks and actions, and to organise and carry out the detailed planning of the actions of the SIP.

products required by our modern society, such as batteries for electric cars, photovoltaic systems and devices for wind turbines (EC, 2012a). Nowadays, about thirty million EU jobs are dependent on the availability of raw materials, as previously mentioned, which means that the EIP has a clear positive impact on the EU industrial competitiveness.

On the 25th September **2013,** the EIP's HLSG approved the Strategic Implementation Plan (SIP) (EIP RM, 2013b) for the EIP on raw materials. This action plan incorporates contributions from EU governments, industry, academia, and NGOs, consulted at meetings of the EIP's Operational Groups.

This SIP has several objectives, targets, and actions to be reached or implemented by 2020. It consists of two parts:

- <u>Part I</u> - EIP objectives, targets, and methodology; overall strategy;
- <u>Part II</u> - priority areas, action areas, and actions targeting sector-specific stakeholders and practitioners. This document shows us **95 Concrete Actions** (including Research and Development, addressing Policy Framework conditions, disseminating Best Practices, building a Knowledge Base, and fostering International Cooperation), structured into **7 Priority Areas** and **24 Action Areas**, all of those divided into three pillars, which were referenced previously, the technology policy pillar, the non-technology policy pillar, and the international cooperation pillar (EIP RM, 2013b).

On the 14th of July **2016,** the Raw Materials Scoreboard was published. This document is an initiative of the European Innovation Partnership (EIP) on Raw Materials, and its purpose is to provide quantitative data on the EIP's general objectives and on the raw materials policy context. This scoreboard consists of **24 indicators** grouped into **5 thematic clusters,** including **raw materials extraction**, **basic manufacturing**, **final products and distribution**, **consumption and use**, and **EoL** (RMS, 2016) represented in Figure 2.

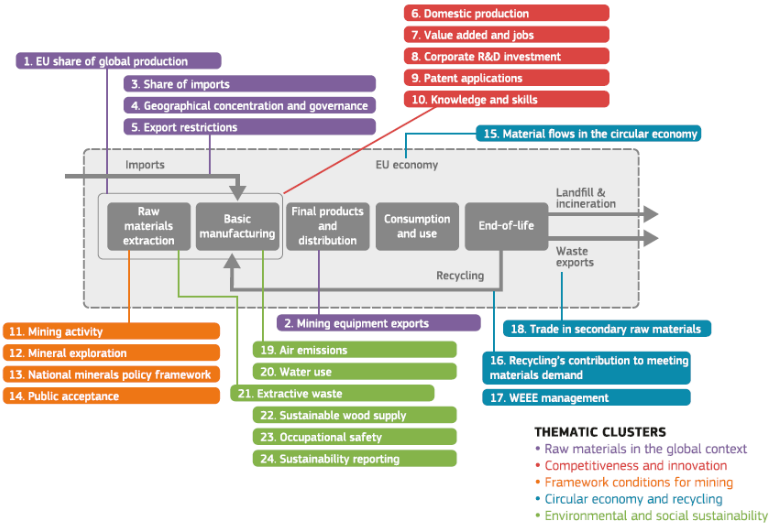

Figure 2 - Value chain of the raw materials, thematic clusters, and its indicators (RMS, 2016).

The Raw Materials Scoreboard presents appropriate and solid information, which may be used in policy-making in a range of areas. The scoreboard, for example, will be partly responsible for monitoring progress towards a circular economy, a vital issue on which the EC adopted a bold action plan. The scoreboard will be published every other year.

2.3.2. EUROPEAN INSTITUTE OF INNOVATION & TECHNOLOGY

On the 9th December 2014, the EIT Governing Board appointed EIT Raw Materials as an EIT Knowledge and Innovation Community (KIC). The subsequent information provides some understanding of the challenges the KIC will address in the area of raw materials (sustainable exploration, extraction, processing, recycling, and substitution) and the impact it will have.

EIT Raw Materials has the bold vision of transforming the challenge of raw materials dependency into a vital strength for Europe. Its aim is to increment the competitiveness, growth and attractiveness of the European raw materials sector through profound innovation and entrepreneurship. This KIC will combine a variety of disciplines, diversity, and complementarity along the three sides of the knowledge triangle (business, education, and research) and across the entire raw materials value chain.

The approach will pay particular attention to systemic thinking and de-siloing across the value chain. Innovative service contributions will be put into action in order to empower the EIT Raw Materials community and other stakeholders, including four customised tracks, concentrating on growth and job creation, by furthering start-ups, SMEs, radical innovation, and education.

By the end of 2019, EIT Raw Materials aspires to, among other things (EIT, n.d.):

- Develop 50-80 new or improved products, processes or services, and to have these marketed by 10-20 new start-ups;
- Develop 120-180 patents, and commercialise 5-15 of these;
- Have 300-600 graduates of EIT-labelled courses;
- Produce a significant number of impact KPIs by bettering the industrial competitiveness and the innovation ability of the EU. For example, EIT Raw Materials wants to create 500-1,500 new jobs within the EU.

2.4. CIRCULAR ECONOMY

2.4.1. CONCEPTS AND PRINCIPLES

The concept of circular economy is far from being new or innovative. In fact, its origin is possibly the analogy established in an article published in the mid-sixties of the last century, by the American evolutionary economist Kenneth Boulding, between planet earth and a resource-limited spaceship, where the survival of the crew depended entirely on the recycling and the incessant reuse of available resources (Boulding, 1966).

Boulding argued that, "the essential measure of success of the economy is not production and consumption at all, but the nature, extent, quality, and complexity of the total capital stock, including in this the state of the human bodies and minds included in the system." (Boulding, 1966).

In spite of that, during the seventies of last century, the notion of circular economy had already been developed by the "economy of the environment", integrating the conventional wisdom of this discipline. It gained prominence in the nineties, specifically in 1996, when John Tillman Lyle published the book “Regenerative Design for Sustainable Development” (Lyle, 1996), in which he began evolving ideas on regenerative design that could be applied to all systems, including, but not limited to, beyond agriculture, for which the concept of regeneration had already been formulated.

Circular economy presents itself as a conceptual framework with the ability to conform different sets of intellectual ideas, which share the aspiration of an (absolute) decoupling of "economic development from finite resource consumption" (EMF, 2015), including the functional service economy of Walter Stahel, the "cradle to cradle" design philosophy of McDonough and Braungart, biomimicry, as made clear by Janine Benyus, the industrial ecology of Lifset and Graedel, natural capitalism by Amory and Hunter Lovins and Paul Hawken, and the blue economy systems approach described by Gunter Pauli.

In more recent times, from 2010, the Ellen MacArthur Foundation has adopted circular economy as a conceptual framework of an economy that “is restorative and regenerative by design" (EMF, 2015).

As opposed to the current "linear economy" - characterised as a "take, make, dispose" model, circular economy is described by the Ellen MacArthur Foundation as an economy whose purpose is “to keep products, components, and materials at their highest utility and value at all times" (...) "a continuous positive development cycle that preserves and enhances natural capital, optimises resource yields, and minimises system risks by managing finite stocks and renewable flows." (EMF, 2015).

The circular economy is based on three principles (EMF, 2015) as shown in Figure 3:

- **PRINCIPLE 1:** Preserve and enhance natural capital by controlling finite stocks and balancing renewable resource flows (to regenerate[28], to virtualise[29], and to exchange[30]);

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[28] Shift to renewable energy and materials; Reclaim, retain, and restore the health of ecosystems; Return recovered biological resources to the biosphere.

[29] Dematerialise directly (e.g. books, CDs, DVDs); and dematerialise indirectly (e.g. online shopping).

[30] Replace old materials with advanced non-renewable materials; Apply new technologies (e.g. 3D printing); and Choose new product/service (e.g. multimodal transport).

- **PRINCIPLE 2:** Optimise resource yields by circulating products, components, and materials at the highest utility for the longest possible time, in both technical and biological cycles (to regenerate, to share[31], to optimise[32], and to loop[33]).

  The **technical cycle** involves the management of stocks of finite materials. Use replaces consumption, and technical materials are recovered and mostly restored in the technical cycle. The **biological cycle** encompasses the flows of renewable materials. Consumption only occurs in the biological cycle, and renewable (biological) nutrients are mostly regenerated in the biological cycle.
- **PRINCIPLE 3:** Foster system effectiveness by revealing and designing out negative externalities.

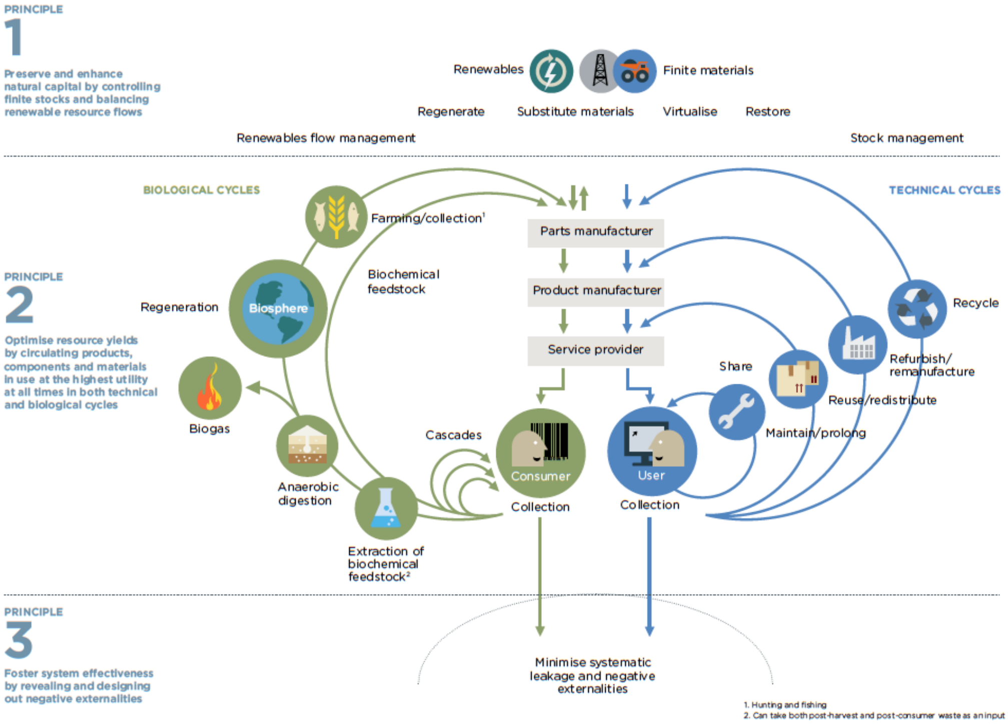

Figure 3 - Infographic of a circular economy (EMF, McKinsey & SUN, 2015).

2.4.2. EUROPEAN UNION POLICIES ON CIRCULAR ECONOMY

Every year in the European Union, approximately 15 tonnes of materials are used per person, while each European Union citizen produces, on average, more than 4.5 tonnes of waste every year, almost half of which is disposed of in landfill sites. Consequently, the linear economy, which depends entirely on resource extraction, is no longer a feasible option. (EC, n.d.c)

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[31] Share assets (e.g.: cars, rooms, appliances); Reuse/Use second-hand; Prolong life through maintenance, design for durability, upgradability, etc.

[32] Increase performance/efficiency of product; Remove waste in production and supply chain; and Leverage big data, automation, and remote sensing.

[33] Remanufacture products or components; Recycle materials; Digest anaerobically; and Extract biochemical from organic waste.

On the 17th December **2012**, the EC adopted the "**Manifesto for a Resource-Efficient Europe"** (EC, 2012d). This manifesto states that 'In a world with growing pressures on resources and the environment, the EU has no choice but to go for the transition to a resource-efficient and ultimately regenerative circular economy'. The EU Commissioner for Environment, Janez Potočnik, invited The Ellen MacArthur Foundation to work alongside the European Resource Efficiency Platform.

In a communication from July **2014**, the EC formally adopted the circular economy as a conceptual framework, together with a proposal for a directive on waste called "**Towards a circular economy: A zero waste programme for Europe"** (EC, 2014d). There was apprehension regarding this proposal due to the EU's high dependency on imported raw materials (Chart 5).

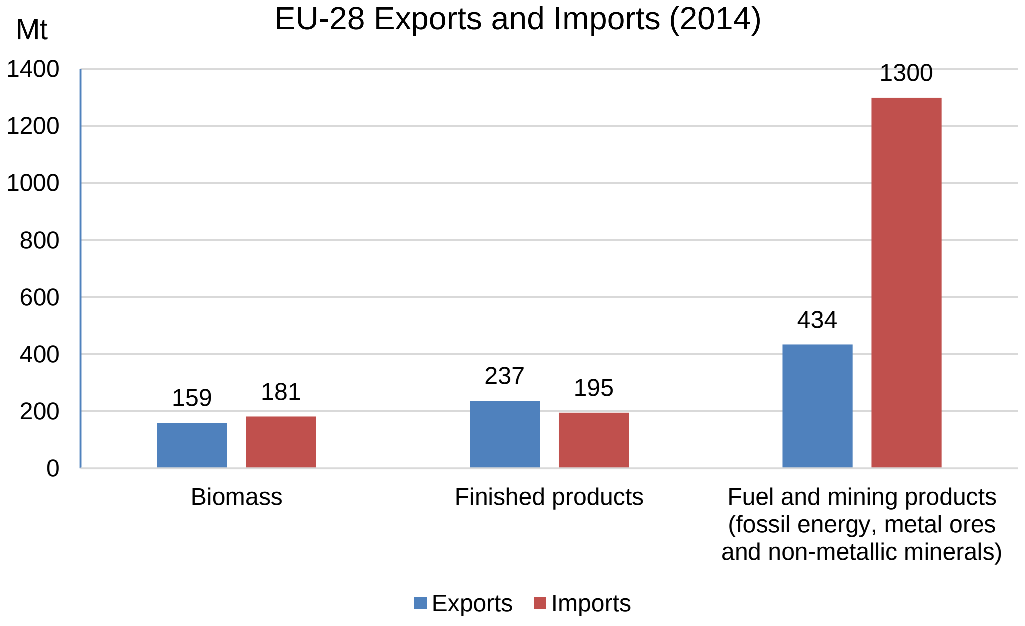

Chart 5 - EU-28 exports and imports of 2014 (Henry, 2016).

In June **2015**, the EMF, together with the McKinsey Centre for Business and Environment, and the Stiftungsfonds für Umweltökonomie und Nachhaltigkeit (SUN), published a report titled "**Growth within: a circular economy vision for a competitive Europe"** (EMF, McKinsey & SUN, 2015), which has influenced the EU's new action plan for circular economy and a legislative package, directed towards the entire business cycle and not just to the waste management.

As a matter of fact, on the 2nd December **2015**, the EC adopted an action plan for the circular economy called "**Closing the loop – An EU action plan for the Circular Economy"** (EC, 2015) which includes, adjacent to new legislative proposals on waste, indications on future action in other areas and their agenda for drafting and adoption.

In this action plan, the circular economy is conceived in the perspective of a virtuous articulation between "a sustainable, low-carbon, resource efficient, and competitive economy" and the "EU's top priorities", namely competitiveness, growth, employment, and social cohesion (EC, 2015).

Also in this action plan, 5 sectors are identified (plastics, food waste, **critical raw materials**, construction and demolition, and biomass and bio-based products) which face specific obstacles in the context of the circular economy because of the particularities of their products or value-chains and their environmental footprint or dependency on material from outside Europe (EC, 2015).

On the 26th January **2017**, the EC reported on the delivery and evolution of key initiatives of its 2015 Action Plan, publishing the "**Report on the implementation of the Circular Economy Action Plan"** (EC, 2017). The primary conclusion of this report is that it is imperative to maintain the momentum created by the adoption of the circular economy package and by action at all levels, in order to realise the circular economy with benefits for all Europeans.

The anticipated benefits until 2030 (BCSD Portugal, 2016) from the circular economy package include:

- Growth and job creation:
    - Up to >7% GDP;
    - Up to 600 billion in savings (8% of annual turnover for business in the EU);
    - An estimated 170,000 direct jobs in waste management sectors by 2035.
- Boosting competitiveness and ensuring security of supply;
- Building economic and environmental resilience;
- Encouraging innovation;
- Reduction of total annual GGE by 2 to 4%.

Therefore, a progression to a circular economy shifts the focus to reusing, repairing, refurbishing, and recycling existing materials and products. What used to be regarded as "waste" in the past, can be converted into a resource (EC, 2015).

2.4.3. CRITICAL RAW MATERIALS IN THE EUROPEAN UNION'S CIRCULAR ECONOMY

In the EU's Circular Economy Package, the metals (including CRMs) are a priority field and an ideal candidate for circular economy, as they are perpetually recyclable. Furthermore, secondary metals do not face downcycling or quality issues as they do not lose their intrinsic properties during the recycling process, and may be used and reused multiple times. Recycling provides an extremely efficient way of reintroducing valuable materials back into the economy, thereby dealing with the key strategic challenges, while lessening environmental impacts and energy intensity of materials supply (Hagelüken *et al.*, 2016).

According to Hagelüken (2014), the use of metals, especially technology metals in industrial and consumer products, has increased very quickly in recent decades. A large quantity of these metals is still bound in the "technosphere" or "anthroposphere". As a consequence, products, such as cars, electronics, batteries, and industrial catalysts, have developed into a potential "renewable" metal resource for the future – referred to as an "urban" or "above ground" mine – that must not be wasted ["**To some it's just a mountain of garbage, but for others it's a gold mine**", Nozomu Yamanaka (Yoshikawa, 2008)].

The COM (2015) 614 final identifies 5 priority areas facing specific challenges in the field of economics, namely plastics, food waste, critical raw materials, construction and demolition, and biomass. Regarding CRMs, the EU is concerned about the low recycling rate of WEEE containing CRMs, and the need to value waste from the extractive industry (extractive waste).

- **WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT IN THE EU**

Presently, waste electrical and electronic equipment (WEEE) is considered to be one of the most rapidly growing waste streams in the European Union, growing at 3-5% per year. If not treated effectively, WEEE contains distinct substances that pose considerable environmental and health hazards. On the other hand, the recycling of WEEE offers considerable opportunities with regard to making secondary raw materials available on the market.

According to EC (2015), the CRMs, often present in electronic devices, have a very low rate of recycling; meaning significant economic opportunities are wasted. In fact, the EU generated 9Mt in 2012 (with projected growth expected to reach over 12Mt by 2020). However, only around one third (3Mt) of this waste is officially reported as collected and made available for reuse and recycling (Huisman *et al.*, 2015).

On the 27th January **2003**, the first WEEE Directive (EC, 2002) was provided for the creation of collection schemes, whereby consumers may return their WEEE free of charge. These schemes intend to encourage and boost the recycling and/or re-use of WEEE.

On the 13th August **2012**, the second WEEE Directive was published (EC, 2012b), however it only came into effect on the 14th February 2014. This new directive was a revision of the first one, created with the purpose of increasing the quantity of WEEE that is appropriately collected and treated, reducing the volume that goes to disposal, and giving member states the sufficient and correct tools to combat illegal export of waste more effectively. It also sets a minimum collection target of 4kg per year, per inhabitant, of WEEE from households.

Mobile phones are a brilliant example of how we can recycle the WEEE, which, the majority of the time, contains CRMs in its compounds. These devices incorporate over 40 different chemical elements, including metals, such as Au, Ag, Cu, As, Ta, and Sn, and critical metals, such as Si, P, Sb, B, In, and Ga (Figure 4).

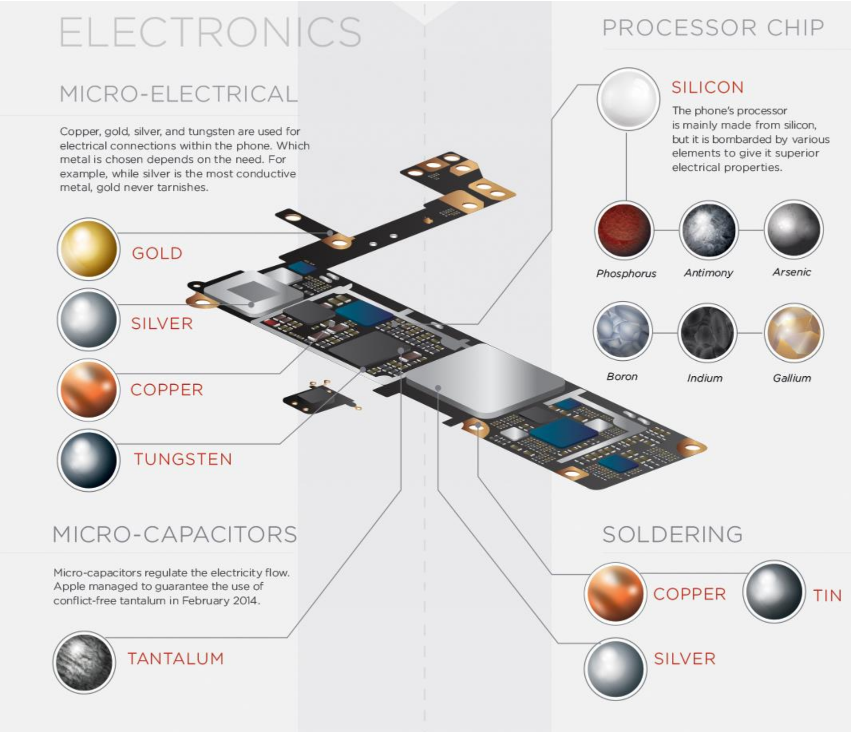

Figure 4 - Electronic components of the iPhone 6s (Visual Capitalist, 2016).

In fact, in one tonne of mobile phones (the same as 13,000 units without batteries) we can find 3.5kg of Ag, 340g of Au, 130g of Pd (CRM), and as much as 130kg of Cu. These metals have an estimated value of over €10,000/t, particularly as a consequence of these precious metals (Izatt & Hagelüken, 2016).

According to an article, written in a Portuguese national newspaper, (Rodrigues & Pereira, 2014) the estimated number of electronic devices shipped to the global market in 2017 will be approximately 2.25 billion (including PCs, laptops, tablets, and smartphones).

- **EXTRACTIVE WASTE IN THE EU**

The EU, concerned about the management of extractive waste (one of the largest waste streams in the EU), launched the Directive 2006/21/EC “**On the management of waste from extractive industries and amending Directive 2004/35/EC”** on the 15th of March **2006.** In this directive, the EC has urged the countries in the EU ‘to encourage the recovery of extractive waste by means of recycling, reusing, or reclaiming such waste, where this is environmentally sound in accordance with existing environmental standards at Community level and with the requirements of this Directive where relevant’ (EC, 2006).

In addition, it is crucial to emphasise that in January 2009, the EC published the reference document on best available techniques (BAT) for **“Management of Tailings and Waste-Rock in Mining Activities**” (EC, 2009).

In relation to the aforementioned information, the opinion of the European Economic and Social Committee (EESC) was published, in 2011, regarding "**The processing and exploitation, for economic and environmental purposes, of industrial and mining waste deposits in the European Union (own-initiative opinion)**" (CCMI, 2011), with guidelines committed to the recovery of existing mining waste in Europe.

Extractive waste is important from an environmental perspective (EIP, 2016) as it possesses the ability to contain a wide variety of materials, ranging from inert materials to heavy metals, which can be toxic to the environment. From an economic perspective (EIP, 2016), extractive waste can also be viewed as a potential source of valuable materials, as it contains many raw materials that are often not recovered in this day and age. This includes materials that are considered critical for the EU economy (CRMs).

In conclusion, recycling **WEEE** and **extractive waste** carries considerable benefits from an environmental perspective, as well as increasing the security of the supply of CRMs. These benefits include (Hagelüken, 2014):

a) Substituting primary raw materials;
b) Reducing environmental and CO_2 impact of the production of secondary raw materials (recycling) compared to primary raw materials (mining);
c) Alleviating the environmental impact of mining;
d) Extending the lifetime of, and preserving, primary geological resources;
e) Minimising the geopolitical dependency on imported critical raw materials;
f) Avoiding landfill and the incineration of metals;
g) Supporting ethical sourcing of raw materials (ensuring that no "conflict metals"[34] are used);
h) Diminishing metal price fluctuations by improving the demand-supply balance, and limiting speculation by broadening the supply base;
i) Valuing tailings and landfills waste by remining them (mining of abandoned surface and underground mines for reuse or recycling of their waste).

'The potential for recycling critical metal-containing waste can be thought of as an "urban mine", and can complement the primary source of metal supply from mining.' (Hagelüken, 2014). For this reason, increasing the recovery of critical raw materials is one of the main challenges that must be addressed in the transition to a more circular economy (EC, 2015).

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[34] The documentary *"Blood in the Mobile"* is an example of these conflict metals in DRC, where slave labour is used to finance conflicts between the military and rebels.

2.5. PORTUGUESE POLICIES ON THE RAW MATERIALS

2.5.1. NATIONAL LEGISLATION

The Portuguese national legislation, regarding prospecting, research, exploitation, and waste management of geological resources, referring to the raw materials from extractive industry, includes the following legislation:

- Decree-Law no. 90/90 from 16 March 1990 (Base Law): which establishes the general regime of revelation and exploitation of geological resources;
- Decree-Law no. 89/90 from 16 March 1990: which establishes the regulation of mineral deposits;
- Decree-Law no. 554/99 from 13 December 1999: which establishes the rules that concern the construction, operation and closure of tailings, resulting from the extractive activity;
- Decree-Law no. 198A/2001 from 6 July 2001: which establishes the legal regime of concession of the exercise of the environmental recovery activity of degraded mining areas[35].
- Decree-Law no. 183/2009 from 10 August 2009: which establishes the legal regime for the deposition of landfill waste, the technical characteristics, and the requirements to be observed in the design, licensing, construction, exploitation, closure, and post-closure of landfills;
- Ministers Council Resolution no. 78/2012 from 11 September 2012: which establishes the national strategy for geological resources – mineral resources (ENRG-RM). In the scope of action in this document, we highlight, in relation to the management of mineral residues, the action to support the pilot projects of mineral treatment, complementary to the main extraction, and the measure to take advantage of the integral life cycle and recycling of the mineral resources;
- Decree-Law no. 31/2013 from 22 February 2013: which establishes the legal regime governing the management of waste from mineral deposits and mineral masses. This legislation is the first amendment to the Decree-Law no. 10/2010, of February 4. This legislation also specifies in Article 10, number 2, line b, that the management waste plan must promote the valorisation of extractive waste by means of reuse or recovery of the waste;
- Law no. 54/2015, from 22 June 2015: which establishes the legal regime for the disclosure and exploitation of the geological resources existing in the national territory,

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[35] A study produced by EDM, SGPS, SA, at the end of 2001, called "Estudo Base para a Reabilitação de Áreas Mineiras Degradadas", identified 175 abandoned mines in Portugal (of which forty tin and tungsten mines were identified, the most relevant of which are Argozelo, Covas, Montesinho, and Terramonte mines).

including those located in the national maritime space. This law repeals the aforementioned Decree-Law no. 90/90 from 16 March 1990.

2.5.2. NATIONAL POLICIES ON RAW MATERIALS

Regarding legislation, Portugal does not have an objective strategy relating to critical raw materials. Although the aforementioned national strategy for geological resources - mineral resources (ENRG-RM) slightly approaches the EU strategy on critical raw materials, it does not clearly propose a national strategy on this subject. This national strategy only refers to the critical raw materials in its ENRG-RM 2020 Action Plan (Axis of Action B - Development of knowledge and valorisation of national potential) when it mentions the need to promote "synergies between public and private entities in the scope of critical raw materials”.

As a result, every approach to the topic of critical raw materials has been developed by the extractive industry and its associations, in partnership with the academic and scientific community, as well as with public and private entities dedicated to the extractive sector.

Based on this framework, it is important to mention the “Portugal Mineral Resources” partnership, which was established in April 2014 and involved more than 20 public and private institutions. Later on, in January 2017, this partnership was recognised as the “Cluster Portugal Mineral Resources”, which is represented in the High Level Group of the EIP RawMaterials (EIP-RM). This cluster, as its main goals, wishes: to produce knowledge and induce innovation; to promote value creation and internationalisation; to promote efficiency in the use of resources; to enable Cluster actors; and to strengthen synergies between sectors.

It also should be noted that the scientific and academic community has been creating its own research and development dynamics in critical raw materials for the Europe Union, through research projects funded by EU programmes, such as Horizon 2020 (H2020) or ERA-NET Cofund in Raw Materials (ERA-MIN 2), and consortiums, such as the aforementioned EIT RawMaterials (EIT-RM).

2.5.3. CRITICAL RAW MATERIALS IN PORTUGAL

Like the rest of Europe, Portugal saw its extractive sector weaken and was consequently faced with the same problems and needs as the remaining EU countries. As a result of the recent policies on raw materials, in a global context, with a particular focus on Europe, the extractive sector is experiencing promising times in Portugal, which can be seen in the sheer volume of requests for access to areas to be used for experimental exploitation, period and prospecting, and research, which has increased significantly since 2010.

In relation to the critical raw materials defined by the EU in 2014, Portugal has significant tungsten resources in the northern and central regions of the country. It is also worth noting the presence of the antimony resources in the Valongo-Gondomar belt, beryllium resources in Tabuaço and Sabugal, niobium resources in Serra d'Arga, and the indium and REEs resources in the south of the country.

After consulting the mining concessions of Portugal, available from DGEG's web service, with a WFS format, and accessibility through software QGIS version 2.18 Las Palmas, we were able to verify that, in Portugal, there are 5 mining concessions (for Be, Co, Nb, W, HREEs, and LREEs), 7 contracts in experimental exploitation periods (for Be, Co, Nb, W, and Sb), and 58 prospecting and research projects (for Be, Cr, Co, Ga, In, Mg, Nb, W, HREEs, LREEs, Sb, and Ge), which possess some of the twenty CRMs (metallic and metalloid minerals, and groups of metallic minerals) for the EU in Portugal (APPENDIX II). These raw materials may appear individually, or associated with other minerals in a mineralogical association.

Regarding industrial CRMs (borates, coking coal, fluorspar, magnesite, natural graphite, phosphate rock, and silicon metal), in Portugal, there are no mining concessions, neither experimental exploitation periods nor prospecting and research projects available in the SIORMINP (LNEG geoportal).

UNIVERSITY OF COIMBRA
FACULTY OF SCIENCES AND TECHNOLOGY
Department of Earth Sciences

CHAPTER 3.

METAL CHARACTERISATION – TUNGSTEN CASE

CHAPTER 3. METAL CHARACTERISATION – TUNGSTEN CASE

This chapter is based on information primarily from: Pitfield & Brown, 2011 and Brown & Pitfield, 2014.

3.1. PHYSICAL AND CHEMICAL PROPERTIES

Tungsten, also known as wolfram, was discovered in 1781, when Carl Wilhelm Scheele produced tungstic acid from scheelite. Several years later, in 1783, two brothers, Juan José and Fausto de Elhuyar, discovered that the same acid could be produced from the mineral wolframite, and, as a result, they were able to isolate the metal by reducing this acid with charcoal. Its name is derived from the Swedish “tung-sten”, meaning heavy stone (RSC, n.d.). The main physical and chemical properties of this metal are described in Table 4.

Table 4 - Selected properties of tungsten (RSC, n.d.).

PHYSICAL/CHEMICAL PROPERTIES	
Group	6
Period	6
Block	D
Chemical number	74
Atomic symbol	W
Melting point	3414^{o}C
Boiling point	5555^{o}C
Crystal system	Cubic
Natural state[36]	Solid
Element category	Metal
Density	19.3g/cm^{3}
Moh’s hardness	7.5 to 8

This dense non-ferrous transition metal is shiny, and a lustrous greyish-white to steel-grey, in appearance. In its pure state it is quite adaptable and ductile, however, the inclusion of tiny amounts of carbon and oxygen give the metal substantial hardness and brittleness, making it difficult to work with in its raw state (RSC, n.d.).

Tungsten possesses the highest melting point of all non-alloy metals and, among all elements, it comes second only to carbon. It also possesses the highest tensile strength at

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[36] In normal pressure and temperature conditions.

temperatures above 1650°C (Christie & Brathwaite, 1996) and the lowest coefficient of thermal expansion of any pure metal. Similar to gold, it is exceptional for its very high density. It also possesses high thermal and electrical conductivity.

3.2. DISTRIBUTION AND ABUNDANCE IN THE EARTH'S CRUST[37]

The abundance of tungsten in the continental crust is, on average, about 1.0ppm. The upper continental crust contains 1.9ppm, while the middle and lower continental crust contain 0.6ppm each (Rudnick & Gao, 2014). The average concentration in workable ores is normally between 0.1 and 1.0% tungsten trioxide (WO_3).

According to the BIO by Deloitte (2015) study, reserves of tungsten in the EU are measured at 79kt of tungsten content, located in Portugal, Spain, Austria, and the UK. On the other hand, global reserves are measured at around 3,077kt of tungsten content. Resources of tungsten are estimated at 500kt in the EU, whereas global resources are estimated to be at 7,000kt of tungsten. Tungsten extraction accounts for around 2,000t of tungsten content within the EU, which is only 3% of that of the global extraction. China accounts for 80% of the global extraction of tungsten content. Close to 45% of the EU-extracted tungsten is sold on the EU market, whereas around 700t is disposed of annually in mine tailings, as extraction waste. The majority of the tungsten ores to be processed in the EU (APT and ferrotungsten) are imported (2,600t of tungsten) and the processed materials (APT and ferrotungsten) are primarily sold on the EU market rather than exported outside of the confines of the EU.

3.3. MINERALOGY

Tungsten never occurs as a free metal in nature. The main tungsten minerals are the monotungstates[38], such as scheelite ($CaWO_4$) and wolframite ($FeWO_4$ and $MnWO_4$). The most common minor tungsten minerals are stolzite ($PbWO_4$) and tungstenite (WS_2) - Table 5.

Scheelite, also known as white ore, is the most abundant tungsten mineral and is present in roughly two thirds of all known tungsten deposits. A significant characteristic of scheelite is the blue-tainted white it glows when it fluoresces under short-wavelength UV radiation, which is particularly beneficial in exploration and mining (adapted from Pitfield & Brown, 2011).

Wolframite, also known as black ore, is the name adopted for the intermediate 20-80% range between the ferberite and hübnerite end-member compositions. The wolframite group normally possesses typically tabular morphology, as well as usually being black/dark grey (Figure 5) or reddish-brown in colour (adapted from Pitfield & Brown, 2011).

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[37] The stocks represented in this section are calculated considering mass of tungsten (W) and are representative of the year 2012.

[38] In inorganic chemistry, this is any salt containing a single tungstate anion.

Figure 5 - Wolframite from the Panasqueira mine, Portugal (author's private collection).

Tungstenite (WS_2) is the most common example of the sulphide group of tungsten minerals. It possesses the equal hexagonal layered structure as molybdenite (MoS_2), but the main difference is its higher specific gravity. Tungstenite is a dark lead-grey mineral that occurs in enormous form, in feathery or scaly aggregates (adapted from Pitfield & Brown, 2011).

Table 5 - Basic properties of the monotungstates - ordered by tungsten minerals group (adapted from Pitfield & Brown, 2011).

Group	Mineral	Formula	Tungsten content (WO_3%)	Appearance	Crystal system
Wolfram Group	**Ferberite**	$FeWO_4$	76.3	Black, sub-metallic to metallic	Monoclinic
	Wolframite	$(Fe,Mn)WO_4$	76.5	Dark grey to black, sub-metallic to metallic	Monoclinic
	Hübnerite	$MnWO_4$	76.6	Red-brown to black, sub-metallic to adamantine	Monoclinic
Scheelite Group	**Scheelite**	$CaWO_4$	80.6	Pale yellow to orange, green to dark brown, pinkish-tan, dark blue to black, white or colourless, vitreous or resinous	Tetragonal
Minor Group[39]	**Stolzite**	$PbWO_4$	50.9	Reddish-brown to yellow-green, sub-adamantine to resinous	Tetragonal
	Tungstenite	WS_2	74.14 (W%)	Dark lead-grey to black, metallic	Trigonal or Hexagonal

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[39] This minor tungsten minerals group only considered the most abundant tungsten minerals.

3.4. DEPOSIT TYPES

Metallic deposits are local concentrations of metal-bearing minerals that occur in nature. Metallic deposits are categorised into four different groups: ferrous, non-ferrous, precious, and speciality. The ferrous metals include V, Cr, Mn, Fe, Ni, Nb, and Mo, while the non-ferrous metals include Mg, Al, Ti, Co, Cu, Zn, Sn, and Pb. Precious metals are rare and include Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au, while specialty metals, also called “newcomers”, include Li, Be, B, Sc, Ga, Ge, As, Se, Sr, Y, Zr, Cd, In, Sb, Te, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Hg, Tl, and Bi (UNEP, 2011).

All primary tungsten deposits are associated with granitic intrusions or with medium to high-grade metamorphic rocks. It was during the Mesozoic period (251-65 million years ago) that the majority (more than 70%) of intrusion-related tungsten deposits formed (251-65 million years ago), however, other ages are known too. Tungsten deposits are normally situated within, or near to, orogenic belts resulting from subduction-related collisional plate tectonics (Pitfield & Brown, 2011).

Five types of tungsten ore deposits are of considerable significance, as indicated in Table 6.

Table 6 - Major producing tungsten deposit types (Brown & Pitfield, 2014).

Deposit type	Deposit size range (mt)	Typical grade (WO_3%)	Example
Vein/stockwork	<10^5 to 10^8	0.1 to 0.8	Panasqueira (Portugal), Pasto Bueno (Peru), Hemerdon (UK)
Skarn	<10^4 to 10^7	0.1 to 1.5	Mactung and Cantung (Canada), Xintianling and Yaogangxian (China)
Disseminated	<10^7 to 10^8	0.1 to 0.5	Akchatau (Kazakhstan), Krásno (Czech Republic)
Porphyry	<10^7 to 10^8	0.08 to 0.4	Xingluokeng and Yangchulin (China), Northern Dancer (Canada)
Stratabound	<10^6 to 10^7	0.2 to 1.0	Mittersill-Ferbertal (Austria), Damingshan (China)

Additional types of deposits include brine/evaporite, placer, pegmatite, breccia, pipe and hot spring deposits. The majority of the current production of tungsten is from vein/stockwork, skarn, porphyry, and stratabound deposits. Hydrothermal processes are vital in large numbers of these types of deposits and may bring about complex mineralisation styles and morphologies.

Tungsten deposits combined with granitoid rocks can be efficiently grouped into two extensive categories: deposits associated with I-type granite series that typify continental volcanic arcs above subduction zones; and deposits associated with alumina-rich S-type granites that are emplaced during the late stages of continental plate collision and A-type granites derived from mantle depths and emplaced in zones of largescale extension of the Earth’s crust (adapted from Pitfield & Brown, 2011).

3.4.1. MAJOR DEPOSIT CLASSES

According to Werner *et al.* (1998) and Pitfield & Brown (2011), there are 7 types of major tungsten deposits (A to G) and 4 more additional types, although they are of relatively minor economic interest (H to K):

A) VEIN AND STOCKWORK DEPOSITS

The classic tungsten vein bedrock deposits commonly consist of tungsten bearing quartz veins, which occur close to granitic intrusions with the bigger deposits containing hundreds of parallel to sub-parallel mineable veins. The principal tungsten-bearing mineral is wolframite, however other common minerals can also be recovered from these deposits, including Sn, Cu, Mo and Bi. According to Cox & Bagby (1986) the geochemical signature expected in tungsten veins deposits are W, Mo, Sn, Bi, As, Cu, Pb, Zn, Be, and F.

Vein and stockwork deposits are characterised by a single and multiple systems of simple or complex fissure filing or replacement veins of quartz up to several metres in width (Pitfield & Brown, 2011). Large vein deposits can incorporate several individual veins, while stockworks deposits consist of swarms of parallel, or near parallel, veins with interconnecting veinlets (Werner *et al.*, 1998). They are genetically related to fracture development coeval with granite emplacement and crystallisation (Pitfield & Brown, 2011).

The vein mineralogy ranges from simple, almost completely composed of quartz and wolframite, to complex, for example, Pasto Bueno in Peru, and Panasqueira in Portugal, where more than fifty vein-forming minerals have been identified.

Accompanying, economically-significant metals include tin, copper, molybdenum, bismuth and gold. In addition, complex uranium, thorium, REEs and phosphate minerals can be present (Brown & Pitfield, 2014).

Vein-type tungsten deposits usually possess multi-stage mineral parageneses that demonstrate a silicate-tungstate, oxide-sulphide (and tungstate)-carbonate sequence. Customarily, when compared to sulphide or carbonate minerals, tungsten minerals form earlier, at higher temperatures and deeper levels in the crust, as well as closer to the igneous source. Scheelite usually forms in lower-temperature environments, in veins emplaced in rocks rich in calcium, such as limestone, mafic and intermediate igneous rocks, and their metamorphic equivalents (Pitfield & Brown, 2011).

Examples of these deposits are present across the globe, including **Panasqueira (Portugal)**, San Fix (Spain), Xihuashan (China), Bolsa Negra (Bolivia), Erzgebrige (Czech Republic) Pasto Bueno (Peru), and Hemerdon (England).

B) SKARN DEPOSITS

This type of bedrock deposit is a tabular or lenticular scheelite-dominated orebody in calc-silicate rocks, formed by the replacement of carbonate rocks, and less commonly, carbonaceous rocks in contact with S- and I-type granitoid intrusions. These deposits are normally found within extensive thermal aureoles and local greisens, possibly associated with porphyry W+/-Mo and stockwork Sn deposits.

Some examples of this type of deposit are Tyrnyauz and Vostok-2 (Siberia), Uludag (Turkey), Mactung and Cantung (Canada), Sang Dong (South Korea), King Island (Tasmania, Australia), and Los Santos (Spain).

C) DISSEMINATED/GREISEN DEPOSITS

These low-grade greisen bedrock deposits are formed by pervasive metasomatic (endoskarn) alteration in the cupolas of granitic stocks.

They are locally incorporated with greisen-bordered tungsten-bearing veins and stockworks.

Examples of these deposits include Shizhuyuan, Xihuashan and Dangping (China), and Akchatau, Kara-Oba and Lultin (Commonwealth of Independent States).

D) PORPHYRY DEPOSITS

These bedrock deposits are medium to large, low-grade stockwork of quartz veinlets and disseminations in subvolcanic felsic intrusive rocks +/- country rocks. They can have concentrically zoned metals and alteration, and are characterised by pervasive greisenisation.

Some examples include Xingluokeng, Fujan and Yangchulin, Jiangxi (China), Northern Dancer (Canada), and Climax (USA).

E) STRATABOUND DEPOSITS

These bedrock deposits are identified by concordant lenses of stratiform scheelite in submarine volcano-sedimentary sequences. They have a volcanogenic exhalative origin. Their features can include eruption breccias and metamorphic remobilisation into shears and veins.

Examples are Mittersill (Austria), and Damingshan and Guangxi Zhuang (China).

F) PLACER DEPOSITS

These superficial deposits are heavy mineral concentrations in alluvial, eluvial, or marine sediments derived from proximal bedrocks sources of tungsten. They are mostly small and only amenable to artisanal exploitation.

As examples, we have Heinze Basin (Burma), Dzhida district (Siberia), and Bodmin Moor (England).

G) BRINE AND EVAPORITE DEPOSITS

This type of superficial deposit is tungsten-bearing brines in recent lakes and/or the saline deposits of paleolakes in arid continental regions. It features tungsten-rich bottom muds of brine-charged lakes and sabkha/playa basins.

As examples, we have Searles Lake (the USA), and other examples in the CIS and the USA.

H) PEGMATITE DEPOSITS

These bedrock deposits are dyke-like masses around granitic bodies. They can be described as simple unzoned to complex strongly zoned types with more varied mineralogy. Their features may be transitional with greisens and be hosted by skarns.

As examples, we have Okbang (South Korea), Kular and Priskatel (CIS), and Wodgina (Australia).

I) BRECCIA DEPOSITS

These bedrock deposits are near-vertical bodies of fragmented rock formed by hydraulic fracturing or steam-dominated volcanic explosions, which are bordering I- or A- type granitic intrusions. In addition, they are associated with vein/stockwork and porphyry deposits and commonly zoned.

Examples of this type of deposit are Doi Ngom and Khao Soon (Thailand) and Washington breccia pipe (Mexico).

J) PIPE DEPOSITS

This type of bedrock deposit may be cylindrical or irregular, elongated or bulbous masses, or quartz that arise at the borders of granitic intrusions. Mineralisation, most commonly wolframite, is usually intermittently distributed in high-grade shoots or pockets, containing as much as 20% wolframite, however, deposits are likely to be small (Werner, 1998).

An example of this type of deposit includes the Wolfram Camp deposits (Queensland, Australia).

K) HOT SPRINGS DEPOSITS

These superficial deposits are siliceous or ferro-manganiferous precipitates that are deposited by hot groundwater and hot springs. They are combined with bedrock tungsten deposits. Their features are somewhat high grade but small tonnage.

Examples of this type of deposit include Golconda in the USA, Uncia in Bolivia, and Rotorua-Taupo area in New Zealand.

3.5. EXTRACTION METHODS AND PROCESSING

3.5.1. EXTRACTION

The extraction techniques used to mine tungsten are similar to a large number of other metals of similar occurrence. The majority of tungsten is mined from underground mines. Furthermore, although several tungsten mines have used surface (open-pit) methods, in the majority of cases, these mines were converted into underground mines in order to access deeper ores.

A) SURFACE MINING

Open-pit mining is, more often than not, safer and cheaper to operate than underground mining, and is used if the near-surface ore body occurs in enormous quantities or when it occurs in steeply-dipping lodes, sheeted veins systems, pipes, or makes up the majority of the country rock, as in disseminated or porphyry-style deposits. This type of mining almost never exceeds 100 metres in tungsten mine operations before going underground. Some superficial tungsten deposits, such as placer deposits, are amenable to strip mining or dredging operations (Pitfield & Brown, 2011).

Another type of surface mining is the hydraulic mining, which is usually used in old mine tailings that still contain valuable amounts of tungsten or other valuable metal. This type of mining uses one or more monitors that deliver a very high-pressure jet of water that erodes the material, which then gravitates into a sluice, where it is collected and pumped to the treatment plant.

B) UNDERGROUND MINING

When surface mining is, or becomes, inordinately expensive, we change to underground mining. For example, if the deposit is too deep or if its form is such that underground mining is more efficient. The ratio of waste to ore (strip ratio) is a major factor in the decision to mine. Once this ratio becomes large, surface mining is no longer economic.

The ore is mined in stopes[40] on a number of roughly horizontal levels at various depths below the surface. A contemporary underground mine is a highly-mechanised operation with mine safety and environmental protection being top priority.

The gentle dipping to an almost horizontal ore zone at the Panasqueira tungsten mine, in Portugal, requires more roof support, and so employs “room and pillar stopping”. Around 85% of the available ore can be mined in this way; the other 15% has to remain underground as pillars to prevent the mine roof from collapsing (Pitfield & Brown, 2011).

3.5.2. PROCESSING

Concerning the processing methods of tungsten ores, three main phases can be identified: ore beneficiation, hydrometallurgy, and pyrometallurgy.

A) ORE BENEFICIATION

This phase usually occurs at the mine site in order to increase the tungsten content. First, the tungsten ore is **crushed** and **milled** in order to liberate the tungsten mineral grains. The slurry, containing tungsten minerals and ROM, is then concentrated to 65%, or more, of WO_3 using different methods, including gravity separation, froth flotation[41], and magnetic and

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[40] Voids created by the process of extracting the ore.

[41] A separation process that relies upon difference in surface “wettability” of different minerals. Hydrophilic particles will fall to the bottom of the cell and hydrophobic particles will be carried on froth bubbles to the surface of the cell.

electrostatic separation, depending on the characteristics and composition of the ore. In some plants, there may be a **pre-concentration stage** before other conventional processing methods. This stage normally includes an ore sorting process, in which a continuous stream of rock particles is subjected to a "sensing" stage. Afterwards, these rock particles are separated using an air blast. If the dark tungsten ore minerals are contained within white quartz, the "sensing" stage may be composed of a photometric method. Following this stage, wolframite ore may be concentrated by gravity, and occasionally in combination with magnetic separation[42]. Gravity methods normally entail the use of spirals, cones, and/or vibrating tables. The consequent tungsten concentrate, which contains more than 65% of WO_3, can be smelted directly with charcoal or coke in an electric furnace, in order to produce ferrotungsten (FeW), which is used in steel production as an alloying material. The recycling of tungsten is vital in high speed steel production, with an average melt containing 60 to 70% scrap. (Pitfield & Brown, 2011)

B) HYDROMETALLURGY

The primary raw materials, currently processed by hydrometallurgical methods, are concentrates of scheelite or wolframite containing between 65 to 75% of WO_3. Secondary raw materials, such as recycled (oxidised) scrap and residues that contain between 40 to 95% of tungsten, are also a crucial source for tungsten processing (Pitfield & Brown, 2011).

The production of tungsten metal from the wolframite and scheelite concentrates, and tungsten scrap, needs a conversion of tungsten minerals to an intermediate compound that can be easily purified and then reduced. In modern plants, tungsten concentrates are processed chemically into an ammonium paratungstate (APT) intermediate. In this process, wolframite is first digested by sodium hydroxide pressure leaching.

Tungsten scrap is, in general, easier to convert to APT than ore concentrates, therefore it doesn't contain detrimental elements such as F, As, and Si. For this conversion, tungsten scrap is first oxidised by heating it in air, or oxygen-enriched air, in a rotary furnace in order to aid dissolution in the alkaline leach process. Dissolution is achieved either by sodium hydroxide pressure digestion or an oxidising alkaline melt, or by electrolysis.

C) PYROMETALLURGY

The calcination[43] of APT under oxidising conditions converts it to WO_3. However, under slightly reducing conditions, calcination results in tungsten blue oxide. Additional treatment in a furnace is required in order to convert either oxide into tungsten metal powder and to use this powder in the production of tungsten carbide or the various tungsten alloys.

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[42] In this process, because wolframite is not very magnetic, it will be attracted to a strong electromagnet, while gangue minerals that are not, will be left behind.

[43] Thermal treatment process used to bring about the decomposition of a material, or the removal of a volatile phase.

3.6. SPECIFICATIONS AND USES

Tungsten is traded and used in a variety of forms, and its properties are considered an essential component in a wide variety of products for different applications.

Consumption of tungsten in the future will primarily depend on the performance of sectors that use hard metals (tungsten carbide and cemented carbide), especially in machine tools. Additional development of specialist steel alloys and ‘superalloys’, for a variety of applications, requiring high degrees of wear and temperature resistance, may also require significant quantities of tungsten. Consumption in this area will depend on developments in the aerospace, industrial turbines, and similar industries.

3.6.1. SPECIFICATIONS

According to Pitfield & Brown (2011), and GTP, the main tungsten forms (Figure 6) are as follows:

- **Ammonium paratungstate (APT):** a white, finely divided crystalline salt that is the main intermediate, and also the main tungsten raw material, traded in the market. It is produced by the evaporation of purified ammonium tungstate solution to obtain pure tungstate crystals. As already mentioned, APT is normally calcined to tungsten blue oxide. Formula: $(NH_4)_{10}(W_{12}O_{41}) \cdot 5H_2O$.
- **Ammonium metatungstate (AMT):** a tungsten chemical in the form of highly soluble hydrated crystals, which are free of alkali and other metallic impurities. It is produced from APT in an electrolytic cell. Formula: $(NH_4)_6(H_2W_{12}O_{40}) \cdot nH_2O$.
- **Tungsten trioxide (WO_3):** also called tungstic oxide, is a thermally stable and water insoluble tungsten compound. This light-yellow powder can be synthesised by oxidative calcination of APT. It can also be produced by calcination of tungstic acid. Although this form is still used, is being largely replaced by blue tungsten oxide (TBO) as a forerunner for tungsten metal and tungsten carbide production.
- **Tungsten blue oxide (TBO):** a dark blue or black powder that is not a well-defined chemical compound, but a mixture of constituents. It is produced by heating APT at closely controlled temperatures in reducing conditions. Formula: $WO_{2.29}$.
- **Tungsten metal powder (W):** produced from yellow or blue tungsten oxide in hydrogen reducing furnaces. Although it is used in a solid form, tungsten is sometimes used as a powder. This metal powder is not smelted directly, because tungsten has the highest melting point of any metal, but is pressed into bars, and then sintered at a high temperature (between 1800-2500^{o}C).

- **Tungsten-heavy-metal alloys (WHAs):** this category of tungsten alloy, which normally contains between 90 to 98% by weight of tungsten mixed with Ni, Fe, Cu, and/or Co. All these metals serve as a binder to hold the tungsten particles in place after sintering[44].
- **Tungsten carbide (WC) and semi-carbide (W_2C):** both of these forms of tungsten are produced by the reaction of the tungsten metal powder with pure carbon powder at 900 to 2200°C in a furnace (carburisation). By melting the tungsten metal and carbon together, a eutectic composition of WC and W_2C is formed. This melt (WC) is cast and quenched to form extremely hard solid particles with a feather-like crystal structure. The solid particles are crushed and classified into various mesh sizes. This is the most important tungsten compound as it holds important properties: it is about three times stiffer than steel and extremely hard (8.5 to 9 on Moh's scale), with a high melting point (2870°C), etc.
- **Ferro-tungsten (FeW and Fe_2W):** this steel-greyish alloy is formed by combining iron and tungsten. There are two grades, one with 75 to 82% of tungsten content and another with 70 to 75% of tungsten content. Because of its highest melting point, it is an extremely robust alloy.
- **Non-ferrous tungsten alloys:** these alloys include composites with Cu, Ag, Ni, and rare metals. The combination of tungsten or tungsten carbide with the aforementioned metals produces somewhat hard, heat-resistant metals, with exceptional wear resistance, and strong and sturdy physical properties at elevated temperatures, and good electrical and thermal conductivity.
- **Superalloys:** these high-performance alloys feature excellent mechanical strength and creep resistance at high temperatures, good surface stability, and corrosion and oxidation resistance. Their base alloying metal is, normally, Ni, Co, or Ni-Fe. Although tungsten is present in these superalloys, it is just a minor component of a number of nickel-based (Hastelloy®) and cobalt-based (Stellite®) superalloys.

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[44] Method of consolidating a powder into a solid by heating it at a temperature below its melting point, which is enough for the particles to adhere to each other.

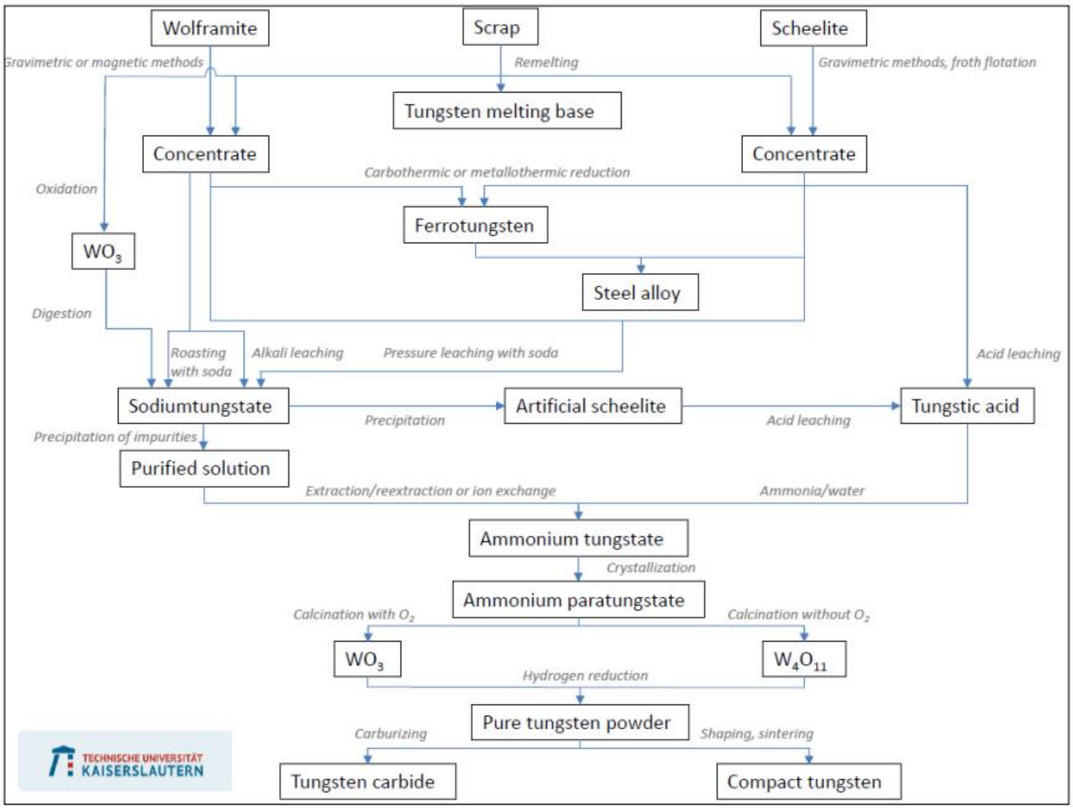

Figure 6 - Flowchart of the production of tungsten compounds (Cuesta-Lopez *et al.*, 2016).

3.6.2. USES

Due to tungsten's properties, such as very high melting point, very high density, extreme strength, etc., a variety of different uses for this metal exist (Figure 7), though its main global uses are in hard metals, steel and other alloys, mill products, and chemical and other specialist applications.

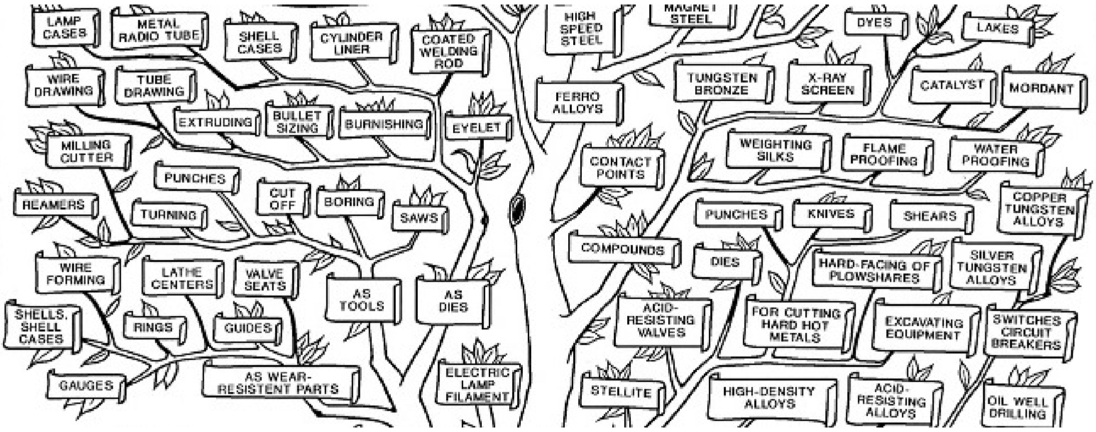

Figure 7 - Different uses of tungsten in different areas (ITIA, n.d.a).

A) HARD METALS

These metals include tungsten carbide and cemented carbides, which are formed from tungsten carbides and cobalt, or other metals such as Ti, Ta, and Nb. These very hard metals are normally used for cutting, drilling (including a new ‘painless’ dental drill), and wear-resistant parts or coatings.

Tungsten carbide is, as previously mentioned, a very important tungsten compound. It is used in the metal-working (40%), mining (30%), and petroleum (20%) industries, and its main applications are machine tools, armour-piercing ammunition, sports equipment, and domestic items, such as the rotating ball in the tips of ballpoint pens (Brown & Pitfiled, 2014). Fine and ultra-fine tungsten carbide hard metals are becoming more and more important as they last longer than conventional tungsten carbide and can be used for specialist applications (drilling of holes in electronic circuit boards).

Cemented carbides have widespread applications in high tech tools, wear parts, and mining and stone-cutting tools. The majority of wear parts and mining tools are made solely from tungsten carbide-cobalt hard metals without the inclusion of any other carbide.

It is also vital to note that the addition of titanium carbide and tantalum carbide to hard metals produces excellent cutting tools for the machining of steel, and has revolutionised productivity in several industries.

B) STEEL AND OTHER ALLOYS

Tungsten was one of the first elements to be alloyed with steel with the purpose of improving its properties. Specialist steel alloys are, to a large extent, put to use in metal cutting and specialist engineering applications, where hardness and strength are vital requirements, especially over a wide temperature range.

Tungsten is a common heat-resisting alloying element in high-speed steel (HSS), a type of tool steel. It is capable of operating at temperatures up to 700^{o}C, enabling HSS to cut faster than high carbon steel. There are two expansive categories of HSS, according to their chemical composition: T-type (tungsten-based) and M-type (molybdenum-based). Super high-speed steels, such as M-48, have very high wear and/or temperature resistance, and are used for high cutting speeds, dry, or semi-dry cutting.

Superalloys containing tungsten have specific applications in the aerospace, industrial gas turbine, and marine turbine industries due to their high corrosion and wear resistance in a large range of environments.

Heavy-metal alloys (WHAs) are mostly W-Ni-Fe alloys, although the addition of Co increases strength and ductility. Their unique properties, such as high density and high strength, allow them to be used for a variety of defence and civilian applications, such as X-ray and radiation shields, etc.

Tungsten-copper (WCu) alloys are dense, high performance, and easily machinable materials, with good thermal and electrical conductivity, which means they are good for use in the electrical and aerospace industries, in applications such as electrical contacts and high voltage switches, etc. (Brown & Pitfiled, 2014)

Nickel-tungsten (WNi) alloys are extremely resistant to decomposition when heated, and continuously remain stable at room temperature. This is a rather new technology; however, it possesses potential applications in coating shock absorbers, print rolls, and connectors for portable electronics (Nanomaterials, 2009).

Other tungsten alloys, such as molybdenum-tungsten (MoW), tungsten-rhenium (WRe), tantalum-tungsten (TaW), and niobium-tungsten (NbW), which have superior properties with regards to strength, corrosion resistance, temperature stability, etc. are used for specialist applications in the glass, aerospace, and electrical industries. (Brown & Pitfiled, 2014)

C) MILL PRODUCTS

Mill products are a term used in the industry to refer to tungsten wire, sheets, or rods. The pure metallic tungsten properties, such as high melting point, conductivity, and ductility, make it ideal for electronic applications (incandescent light bulb filaments, vacuum tubes, and heating elements). Unalloyed tungsten is also used in electronic circuit interconnectors, filaments in vacuum-metallising furnaces, and for electrical contacts. Its high melting point is crucial for the use of tungsten in tungsten inert gas (TIG) welding, where it is frequently doped with La, Ce, Th, or Zr. Water-cooled tungsten tips are used for the non-consumable electrode vacuum-arc melting of alloys. (Brown & Pitfiled, 2014)

According to RSC, although pure metallic tungsten was extensively used for the filaments of old-style incandescent light bulbs, many countries have gradually stopped using them due to the fact that they are not very energy efficient, and they produce much more heat than light. Furthermore, in the EU market, they have also been phased out due to the EC, which in 2005, established a framework for eco-design requirements for energy using products (EC, 2005).

D) CHEMICAL AND OTHER SPECIALIST APPLICATIONS

Several tungsten compounds, such as APT, AMT, or WO_3, have varying uses. APT can frequently be used as a colouring agent in the porcelain industry, or in catalysts, phosphorus, and absorbent gels; AMT is normally used as a reagent for chemical analysis during medical diagnosis, or as a corrosion inhibitor; and WO_3 can be used as a catalyst or as a pigment in ceramics and paints.

Other substances containing tungsten, such as sodium tungstate, can be used in the manufacture of organic dyes and pigments, catalysts, and the fireproofing of textiles, etc. Tungsten hexafluoride (WF_6) gas is used in the production of semiconductor circuits and circuit boards through the process of chemical vapour deposition.

3.7. RECYCLING AND SUBSTITUTION

In the last decade, the price of tungsten has been gradually increasing. As a result, economic and environmental imperatives exist to use tungsten in the most efficient way possible, to seek replacements for less-demanding applications and allow us to recycle it more effectively.

3.7.1. RECYCLING

According to the Critical Raw Materials Profiles (EC, 2014b), recycling is a fundamental element of the world's tungsten supply, and it is estimated that 34% of total world supply is from recycled sources – Figure 8. The tungsten processing industry is capable of treating nearly every kind of tungsten-containing scrap and waste to recover tungsten and, if present, other valuable constituents.

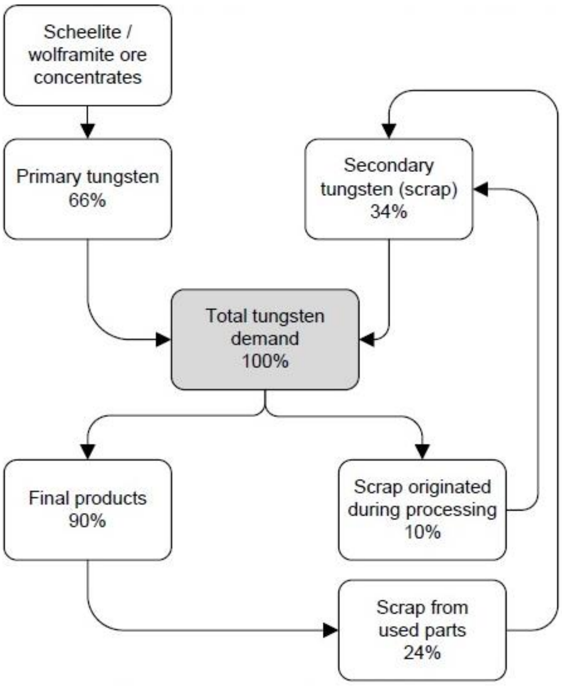

Figure 8 - Flowchart of primary vs. secondary tungsten (EC, 2014b).

A) OLD SCRAP

EoL scrap exists in tungsten-bearing products that are no longer being used, such as cemented carbide parts, tungsten metal and tungsten alloy parts, old superalloy scrap, and tungsten-bearing catalysts. On average, it is estimated that 10 to 25% of old scrap is recycled globally (UNEP, 2011).

B) NEW SCRAP

This is generated during the processing of tungsten concentrates, scrap and chemicals to make metal powder, carbide powder, or chemicals, and during the fabrication of tungsten products from these materials. The recovery rates of new scrap are pretty high, and metal losses are kept to a minimum by internal recycling of the scrap generated. These losses are estimated at around 2 to 6% of tungsten in raw materials consumed (Pitfield & Brown, 2011).

According to Shedd (2011), new scrap can be classified as “soft” or “hard” scrap. Soft scrap are fine particles, such as baghouse dust from steel and alloy manufacturing, cutting or grinding sludges, etc. On the other hand, hard scrap is composed by solid pieces, such as cemented carbide parts, excess alloy, etc.

The alloy industries that produce large quantities of new scrap are also the same ones that produce parts by cast or wrought processes. Around 40 to 60% of the melt becomes new scrap during the casting of corrosion-resistant alloys (Shedd, 2011), which is always recycled, either in-house or sold to be recycled elsewhere.

C) UNRECOVERED SCRAP

Scrap tungsten is not recovered in several applications as a result of the absence of an efficient collection system, or due to the fact it isn’t always economic to recycle due to contamination. Tungsten is lost, when in use, as a result of the wear of cemented carbides parts and hard-faced products, arc erosion of electrical contacts and electrodes, and the oxidation of alloys under high-temperature conditions.

D) RECYCLING METHODS

The most frequently used tungsten recycling methods are the metallurgical and hydrometallurgical techniques, which enhance recovery and lessen costs of this metal, and are capable of treating all types of scrap and removing impurities.

Contaminated cemented carbide scrap, tungsten grindings, and powder scrap can be oxidised and chemically processed to APT in a similar way to that used for the processing of tungsten ores. If present, other metals, such as cobalt, tantalum, and niobium, can also be recovered, but separately (ITIA, n.d.c). Also, tungsten in HSS is frequently recycled, and a typical melt contains 60 to 70% scrap, including internally generated scrap (Brown & Pitfield, 2014).

3.7.2. SUBSTITUTION

As a result of tungsten’s unique properties, substitutes for most applications, particularly where optimum performance is required at high temperatures, result in a loss of performance or an increased cost; however, there are some potential substitutes for tungsten (Table 7).

Table 7 - Potential substitutes for tungsten-containing products (Brown & Pitfield, 2014 and EC, 2014b).

TUNSGTEN APPLICATIONS	POTENTIAL SUBSTITUTES
Cemented tungsten carbides & hard metals	Cemented carbides based on molybdenum carbide and titanium carbide, ceramics, depleted uranium or hardened steel.
Mill products	Molybdenum can replace tungsten in these products.
Tungsten steels	Molybdenum steels.
Light bulb filaments	Compact fluorescent lamps, low-energy halogen light bulbs, carbon nanotube filaments and LEDs.

According to the EC (2015), there are different substitutability scores for the different tungsten compounds, as shown in Table 8.

Table 8 - Use vs. substitutability index (EC, 2014b).

USE	SUBSTITUTABILITY INDEX[45]
Tungsten alloys	0.7
Superalloys	1.0
Fabricated products	1.0
Alloy steels (mostly tool steel)	0.7
Cemented carbides	0.7

3.8. WORLD AND EUROPEAN RESOURCES, RESERVES, AND PRODUCTION

This subchapter does not consider future issues and supply-demand scenarios, hereby only representing a “snapshot” in time. The minerals market is constantly changing, and new reserves are continually added in response to drivers, like demand and advances in technology.

3.8.1. WORLD

A) RESOURCES AND RESERVES

The world tungsten resources have been estimated at 7Mt, including tungsten metal and deposits, which haven’t been proven to be economically workable. It is believed that around

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[45] As already mentioned before, this index measures the difficulty to substitute the material. Values are between 0 and 1, with 1 being the least substitutable.

30% of the resources are in wolframite-group minerals (76.5% of WO_3) and 70% are in the form of scheelite (80.5% of WO_3) ores. (Brown & Pitfield, 2014)

In January 2017, the USGS (Shedd, 2017) estimated that the world reserves of tungsten metal stood at around 3Mt, and those occur in five locations in China (62%), in two locations in Russia (8%), in two locations in Canada (4%), in seven locations in the USA (4%), in four locations in Bolivia (2%), and in several locations in the ROW (20%). Some occurrences in the ROW have been discovered, for example O'Callaghans (Australia) and others have been found to contain more than what was previously thought, for example, Hemerdon (UK) – Figure 9.

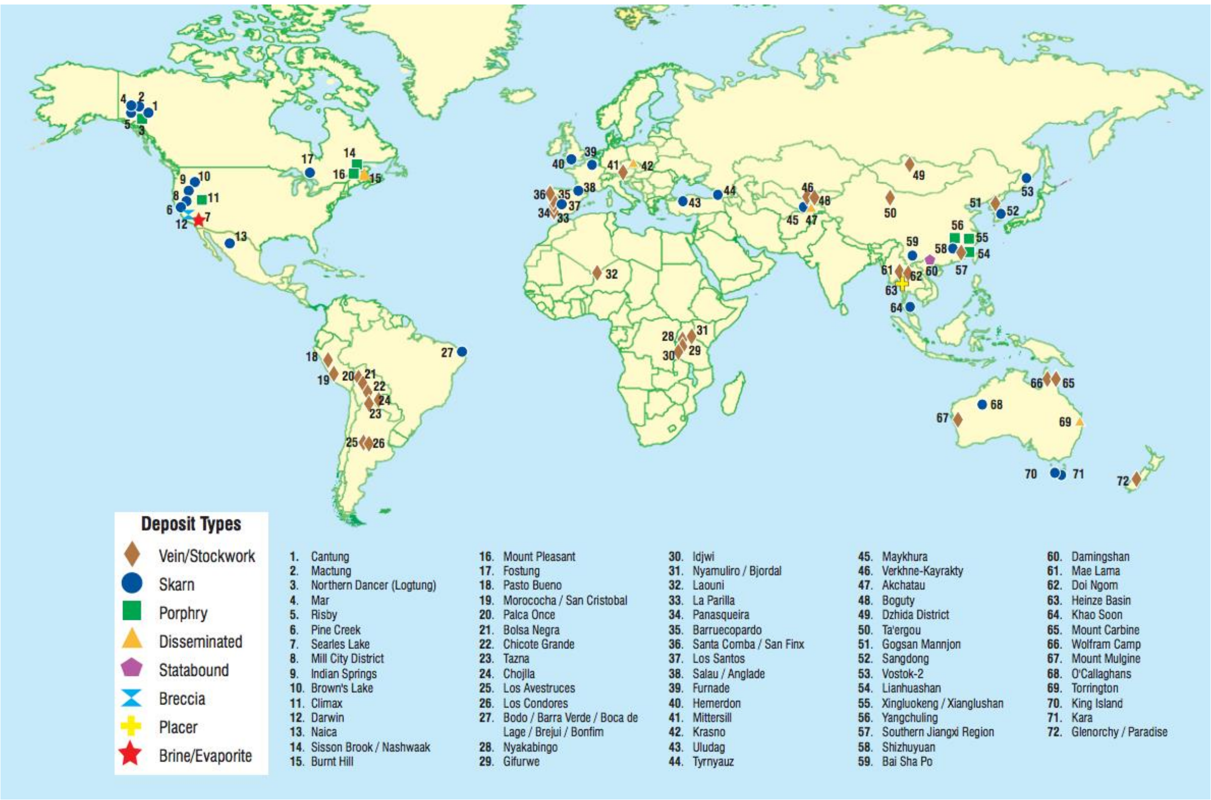

Figure 9 - Location and type of major tungsten deposits in the world (Schmidt, 2012).

B) PRODUCTION

In 2014, the total production was nearly 86,000 tonnes of tungsten (metal content of concentrates), a 26% increase when compared to 2010 (BGS, 2016a).

Tungsten is currently produced in twenty-one countries (not including the USA), from which only ten produce more or equal to 500t of tungsten (metal content) – Chart 6. On the chart it is clear to see that the world's main producers, in 2014, were China (80%), Russia (7%), and Canada (3%). For Portugal, Chart 6 below considers wolframite and scheelite, and for Brazil it mainly considers scheelite.

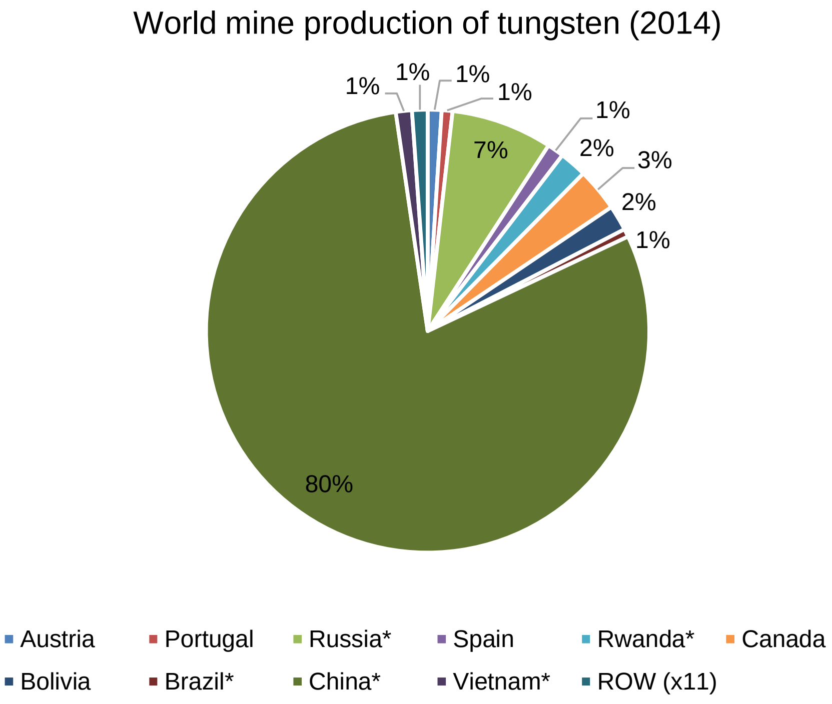

Chart 6 - World mine production of tungsten in 2014, not including the USA (*means estimated) (BGS, 2016a).

The concentration of production in China is a somewhat new development. China's share of the total global production more than doubled from 29% in the eighties to 62% in the nineties. In the 2000s, global production decreased. However, China's share of the total global production increased to 77%. Between 2000 and 2010, the majority of the increase of total global production was in China, increasing up to 80% in 2014 (Brown & Pitfield, 2014).

China is the most important supplier of tungsten (primary and secondary tungsten), as well as its largest consumer, responsible for 51% of the world's total consumption in 2011, along with the USA (14%), Europe (13%), Japan (11%), and other countries (11%). (Roskill Consulting Group, 2012)

3.8.2. EUROPEAN

A) RESOURCES AND RESERVES

In the EU-36, there are three major tungsten deposits currently in use, located in Austria (Mittersill deposit), Portugal (Panasqueira deposit), and Spain (Los Santos deposit). According to Shedd (2017), these three main deposits hold a reserve of an estimated 45,000 tonnes in tungsten content, as of 2016.

In terms of percentage, Austria has 22%, Portugal has 6% and Spain holds 72% of the EU-36's reserves in 2016.

B) PRODUCTION

In 2014, the total EU production was 2,600 tonnes of tungsten (metal content of concentrates), a 19% increase compared to 2010. Tungsten is currently produced in three main European Union countries: Spain (40%), Austria (33%), Portugal (26%), as well as other EU-36 countries (1%) – Chart 7. For Portugal, Chart 7 below considers wolframite and scheelite. (BGS, 2016b)

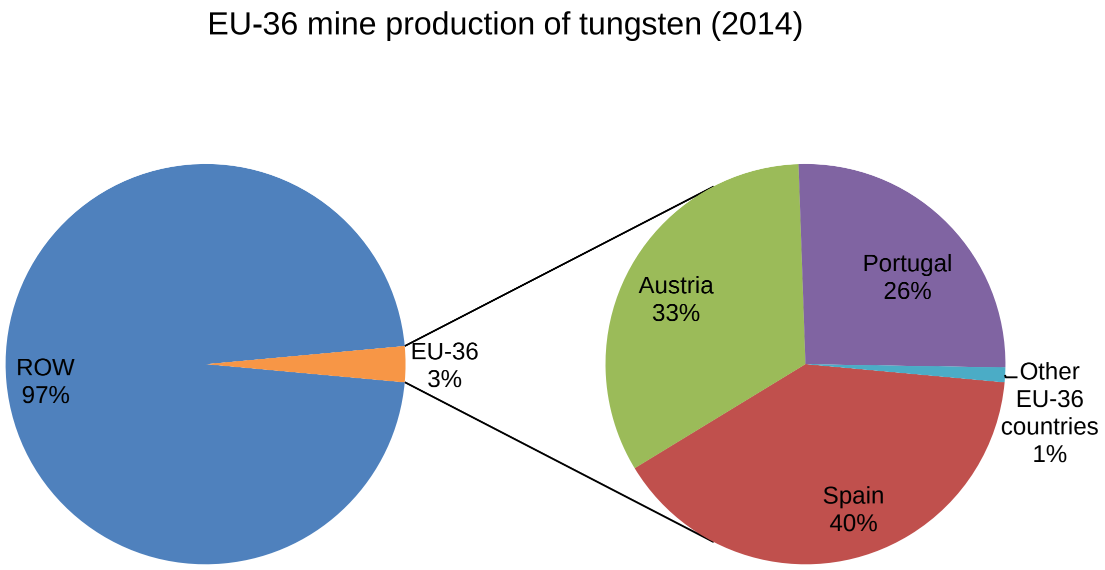

Chart 7 - EU-36 mine production of tungsten (metal content) in 2014 (adapted from BGS, 2016b).

As a whole, these three countries represent approximately 3% from the world's production. For that reason, the EU's import dependency on tungsten ores and concentrates is estimated at 74%, and its main sources of imports into the EU are, in 2012, from Russia (98%) and Bolivia (2%) which is equivalent to approximately 15,000 tonnes (EC, 2014b).

Regarding exports, the EU exports of tungsten ores and concentrates, in 2012, went mainly to the USA (65%), Brazil (15%), Japan (7%), and several other countries, which is equivalent to approximately 3,700 tonnes of tungsten ores and concentrates (EC, 2014b).

The values, in tonnage, of the exports and imports of these top three EU-36 producer countries, as of 2014, are represented in Table 9.

Table 9 - Exports and imports of the EU-36's top three producers of tungsten in 2014 (adapted from BGS, 2016b).

Tungsten form	**Country**					
	Austria		**Portugal**		**Spain**	
	Exports	**Imports**	**Exports**	**Imports**	**Exports**	**Imports**
Ores & concentrates	-	-	1,070t	-	1,460t	4t
Metal	2,000t	997t	70t	70t	350t	620t
Carbide	-	1,340t	-	76t	-	38t

3.9. SUPPLY CHAIN

After mining, the tungsten ore is concentrated, normally geographically close by, in order to minimise losses. Following this stage, the concentrated ore is mixed with in-process and EoL scrap, and pre-treated to remove impurities. Then, after this stage, APT is most frequently produced, which is the most usual tungsten intermediate used to manufacture other tungsten chemicals and products. (EC, 2014b)

All the **mining**, **concentration**, **pre-treatment**, **purification, production of high-purity ATP, manufacture end-products,** and **End-of-Life (EoL)** stages of this metal occur within the EU to some extent (Figure 10). The recovery process of EoL or manufacture end-products, such as hard metals, tungsten alloys, chemicals, etc., re-enter into this supply chain in the pre-treatment stage (EC, 2014b).

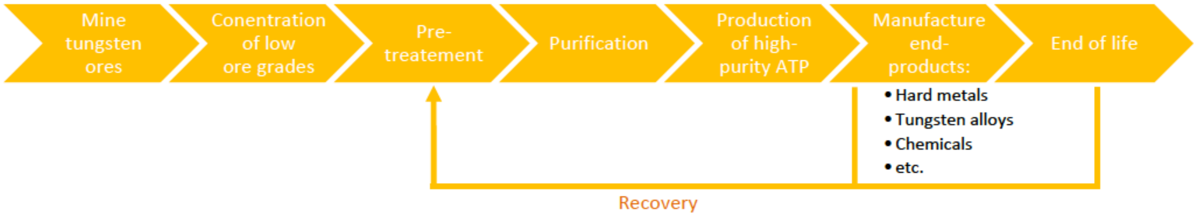

Figure 10 - Value chain of tungsten (EC, 2014b).

3.10. FUTURE SUPPLIES

A recent increase in prices for most forms of tungsten, and worries over security of supply, particularly from China, have caused a revival in the reopening of inactive mines in South Korea (Sandong), Australia (King Island), Spain (Barruecopardo), and Canada (Mactung), as well as the development of new mines in Australia (O'Callaghan's and Cookes Creek), the United Kingdom (Hemerdon), and Canada (Northern Dancer and Sisson Brook) for example. The resources of the selected major tungsten deposits are estimated at 2,250,000 tonnes of tungsten content (Brown & Pitfield, 2014).

3.11. WORLD TRADE

Different forms of tungsten are traded, primarily as ores and concentrates, as intermediate products (APT), and as tungsten oxide or trioxide. Although China is the biggest producer of tungsten ores and concentrates, it does not export a large amount of material in these forms, preferring to process the raw material into either tungstates (mainly APT) or other tungsten compounds. The main exporting and importing countries are shown in Chart 8 and Chart 9 respectively, as of 2016, where the world trade value of the four main traded tungsten forms reached for imports exceeded 1 billion dollars, and for exports close to 1 billion dollars.

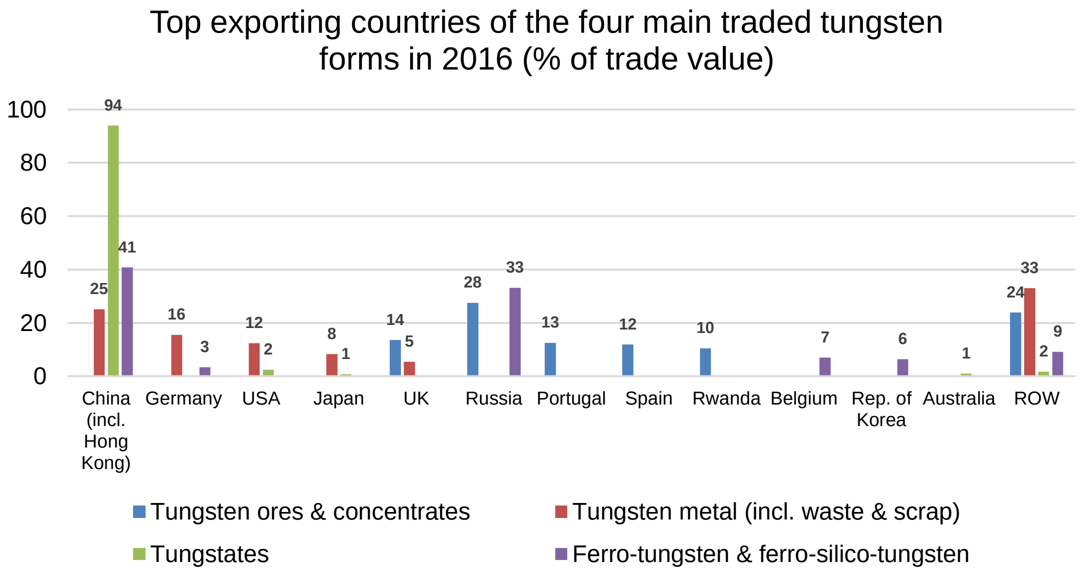

Chart 8 - Main tungsten exporting countries in 2016 (% of trade value) (data from UN COMTRADE, n.d.).

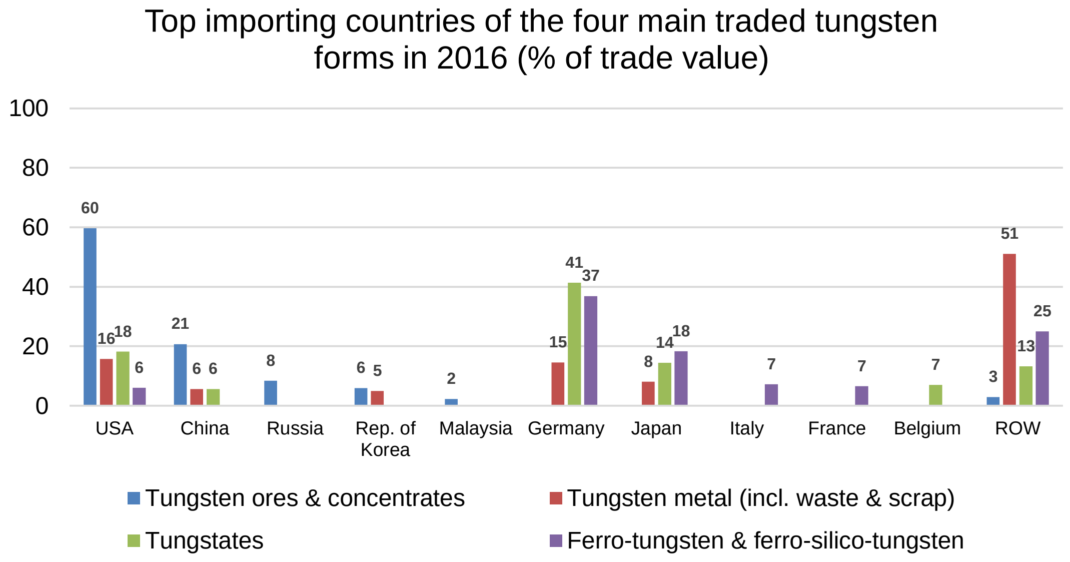

Chart 9 - Main tungsten importing countries in 2016 (% of trade value) (data from UN COMTRADE, n.d.).

As a result of its high economic significance, worries regarding access to raw tungsten materials, and doubt over the ability of European and American producers to compete with China in the sale of tungsten products, the European Commission has identified tungsten as one of its 20 critical raw materials (EC, 2014a).

As a consequence, the EU considers there to be a risk of supply shortage with an associated potential impact on the EU’s economy. This means strategies to reduce the risk of supply shortage are being considered, which include the diversification of supply sources, resource efficiency, substitution, and recycling. Several countries, including China, the USA, Japan and Russia, maintain stockpiles of critical raw materials, including tungsten in case of a risk of supply shortage (Brown & Pitfield, 2014).

3.12. PRICES

In the late seventies and the eighties, there was a considerable growth in the availability of tungsten concentrates and intermediate products from China, at lower prices than any other country in the world, which led to oversupply, and therefore a significant fall, in tungsten prices. As a consequence, economic production could not be sustained and world output decreased.

In current years, with recovering demand and prices, Chinese producers were able to react more rapidly, allowing China’s output to grow much quicker than the rest of the world. The subsequent imposition of production and export quotas in China has pushed prices up further, and encouraged the exploration of new deposits, the development of new mines outside China, and even the remining of old mines and its tailings.

According to the China Tungsten Industry Association, China is held responsible for about one third of the world’s total consumption, which is expected to increase. This increase in Chinese demand, along with stricter controls by the Chinese government on their tungsten exports, has contributed to an increase of more than 300% in the price of tungsten since 2004 (Pitfield & Brown, 2011).

Tungsten is traded either on undisclosed supply contracts between primary producers, secondary processors, and tertiary manufactures, or via traders.

For all the primary traded forms, tungsten prices demonstrate a similar trend, with a very sharp increase during the latter part of 2004 through to the early part of 2006 (Pitfield & Brown, 2011).

Following this, and up to now, the prices of the Chinese concentrates and the European APT and ferro-tungsten have, in general, remained stable between 2006 and 2008, with a fall at the end of 2008, due to the global financial crisis (GFC), followed by increases between 2009 to 2011[46] (reaching the highest peak in the early periods of 2011, due to capacity constraints/speculation after the GFC). Since 2011, the prices of tungsten gradually decreased, up until early 2015 (Chart 10).

During 2016, the prices for ferro-tungsten have, in general, risen, up to 31st May, where the price for ferrotungsten was 25.52 USD/kg (Infomine, n.d.).

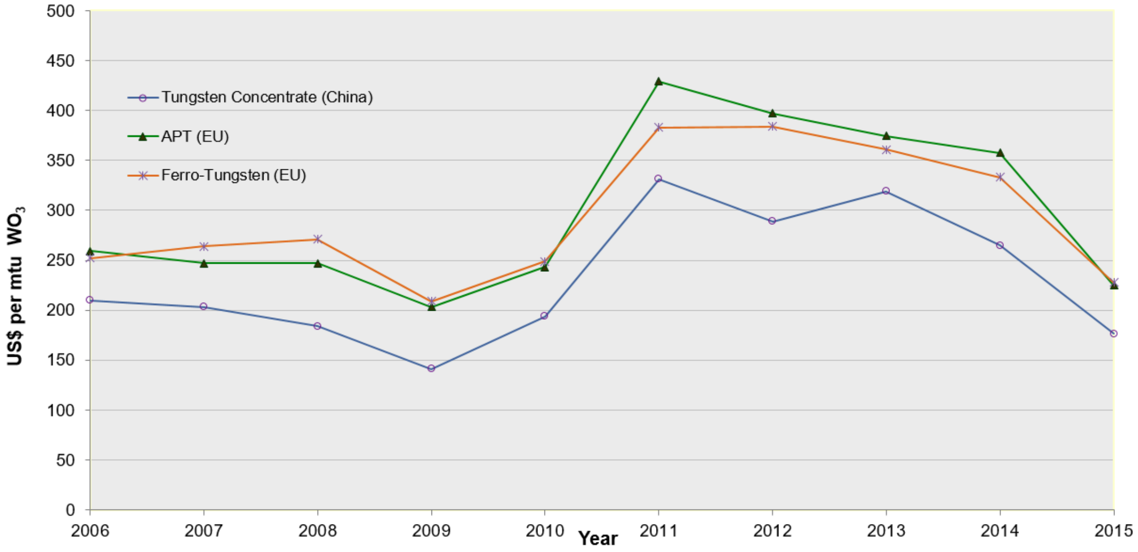

Chart 10 - Historical tungsten pricing (annual mean averages) from 2006 to 2015 (ITIA, n.d.b).

In Chart 10, the prices of tungsten concentrates produced by mines, and the intermediate tungsten powders produced by the secondary processors, are quoted in terms of metric tonne units. A metric tonne unit (mtu) is the equivalent of 10kg of contained WO_3. 10kg of WO_3 contains 7.93kg of tungsten metal.

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[46] These increases occurred because China set strict controls on its tungsten industry by restricting the amount of exploration and mining licences issued within the borders, applying production quotas and imposing export taxes and quotas.

UNIVERSITY OF COIMBRA
FACULTY OF SCIENCES AND TECHNOLOGY
Department of Earth Sciences

CHAPTER 4.

STUDY AREA FRAMEWORK

CHAPTER 4. STUDY AREA FRAMEWORK

4.1. GEOGRAPHICAL LOCATION

The Panasqueira mine (40º09'16''N, 7º44.49''W) is located in the central region of Portugal, more precisely on the edges of the municipalities of Covilhã and Fundão (Beira-Baixa region) and Pampilhosa da Serra (Coimbra region). The perimeter of the mining concession, conditioned to the southeast by Zêzere river, includes the parishes of São Jorge da Beira, Aldeia de São Francisco de Assis (Covilhã municipality), Barroca (Fundão municipality), Dornelas do Zêzere, and Unhais-o-Velho (Pampilhosa da Serra municipality) – Figure 11. It lies on the southern-edge of the Estrela Mountain[47], in the Açor Mountain and to the north-west of Gardunha Mountain.

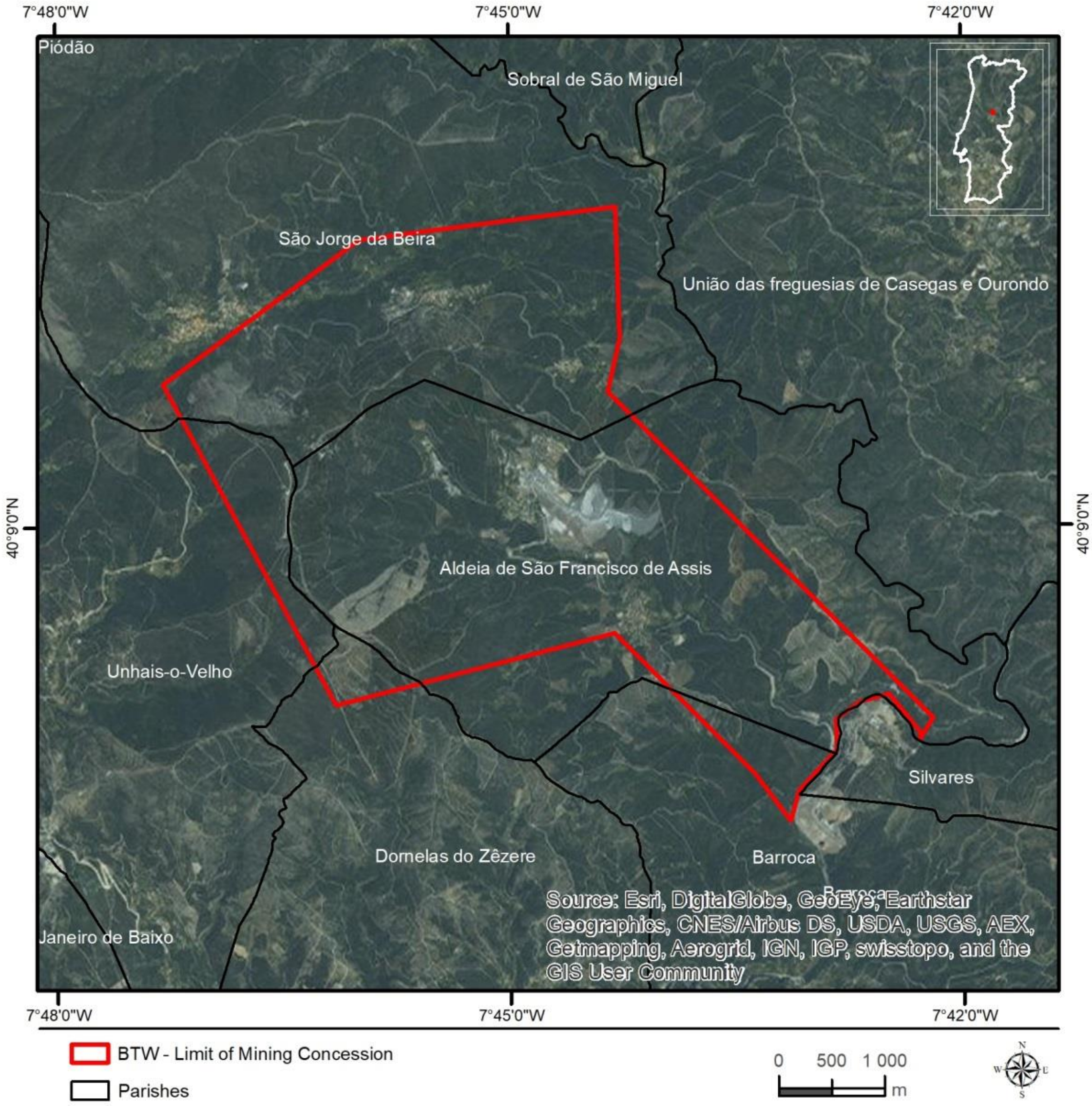

Figure 11 - Location of the mining concession limit (produced in ArcMap, ESRI version 10.1).

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[47] Highest continental Portuguese mountain range 1,993m.

The Panasqueira mining concession (“Contract of Exploitation No. C-18”), owned and operated by Sojitz Beralt Tin & Wolfram (Portugal), S.A.[48] (BTW), covers an irregular shaped area trending NW-SE, and is approximately 7.5km in length and 1.5km in width at the south-eastern end and 5.0km at the north-western end where, currently, all the mine workings are concentrated to the Barroca Grande site. The total area of the mining concession is about 19 km^2 (red line in Figure 12). However BTW also owns the surface rights of a total area of approximately 8.76km^2 (yellow line in Figure 12), of which roughly 7.29km^2 is within the concession. Outside of the concession area, BTW owns Rio and Argemela, measuring 0.68 and 0.78km^2 respectively. (Wheeler, 2016).

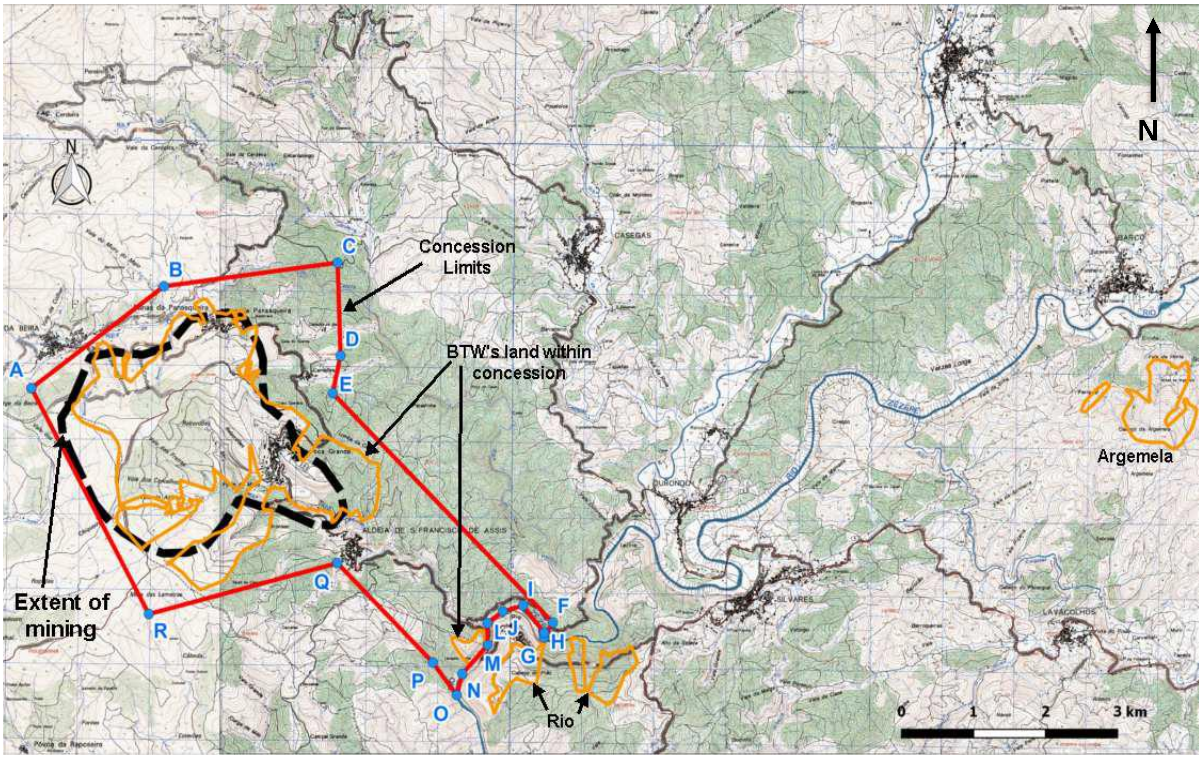

Figure 12 - BTW's limits of mining concession and surface rights (Wheeler, 2016).

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[48] Indirect wholly-owned subsidiary of Almonty Industries Inc. who owns 100% interest in the Panasqueira mine.

4.2. GEOLOGICAL FRAMEWORK

4.2.1. REGIONAL SETTINGS

A) OVERALL MINERAL OCCURENCE IN PORTUGAL CONTINENTAL

From a geological point of view, Portugal can be considered a diverse and complex territory (Figure 13), with its characteristics providing it with important potential in various mineral resources.

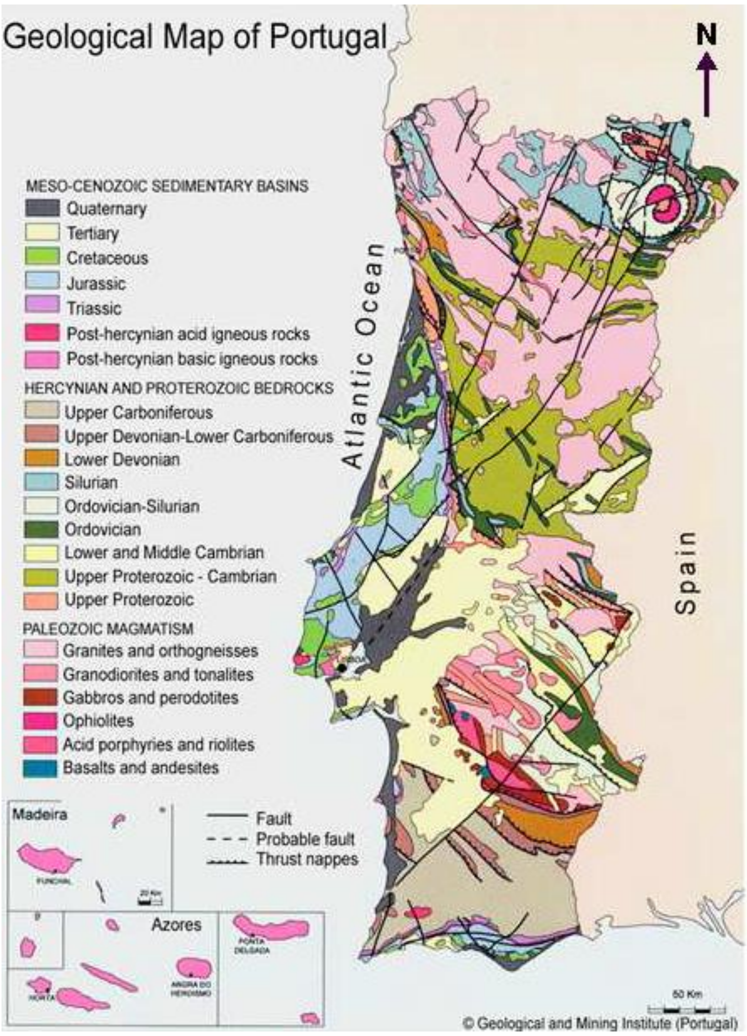

Figure 13 - Geological map of Portugal (Wheeler, 2016).

The Portuguese territory can be subdivided into two main groups: the **Hesperian Massif,** in which occurs, predominantly, metallic mineral resources; and the **Epi-Hercynian Covering,** which includes non-metallic mineral resources, such as sands, gypsum, clay, kaolin, limestone, diatomite, and salt.

The **Hesperian Massif** (Figure 14) occupies around 70% of the national territory, and constitutes the fundamental nucleus of ancient lands of the Iberian Peninsula, occupying the central and western zone of this Peninsula. This Massif is a great horst, whose lateral blocks were depressed, brought about marginal zones with Mesozoic and Cenozoic lands, affected later by the alpine orogeny. This Massif consists essentially of a rocky substrate, related to the variscan orogen, composed of sedimentary rocks, igneous and metamorphic, consolidated mainly within the variscan movements. These movements are responsible for their overall orientations and the promotion of extensive intrusion of granites phenomena with the resulting metamorphism. According to Ribeiro *et al*. (1979) and Quesada (1992), this massif is divided into four geotectonic units within the Portuguese borders (DGEG, 2012):

- **Galicia–Trás-os-Montes Zone:** in this zone, two mafic and ultramafic polymetamorphic massifs occur (Bragança and Morais). The minerals, which are present in these massifs are Cr, Pt, possibly Cu, Ni, and Co with potential for W, Sn, U and, probably, polymetallic sulphides in the surrounding formations from the Silurian period;
- **Central Iberian Zone**: this zone is characterised by the Schist-Greywacke Complex, which includes a flysch-type series dating from Late Precambrian eon to Cambrian period, and is related to deep sea sediment formation. Continental formations from the Carboniferous period occur in the Douro-Beiras sector, where several coal mines have been exploited (Douro Carboniferous Belt). This geotectonic unit has important mineralisations of W and Sn, which are normally associated with the contact between granite and metasediments, as well as the existence of precious metals, frequently associated with As and Sb. This zone, apart from the contact with the Ossa-Morena Zone, is also in contact with a Spanish zone, the West Asturian-Leonese Zone at the northern part, which in turn is in contact with the Cantabrian Zone to the east.
- **Ossa–Morena Zone:** this is the most complex and diverse unit, which begins with a polymetamorphic Precambrian, followed by Cambrian and Silurian formations, and ends with a flysch sequence from the Late Devonian period. In this geotectonic unit, base metals occur, which are associated with the Cambrian-Ordovician volcanic sedimentary complex, and W and Sn in the Stª Eulália granite complex, as well as the potential for chrome, nickel, cobalt, and platinum in the basic and ultrabasic rocks on the north and south margins of this zone;
- **South Portuguese Zone:** in this unit a Volcanic Sedimentary complex (VS) from the Late Devonian – Early Carboniferous period occurs, overlain by a Culm flysch sequence. The acid volcanic rocks in the VS complex constitute the metallotect of the massive polymetallic sulphides that are characteristic of the Iberian Pyrite Belt, which is the most important metallogenetic province in Portugal, where the Lousal, Aljustrel, Neves Corvo, and S. Domingos mines are located.

The **Epi-Hercynian Covering** is divided into the western and southern Meso-Cenozoic borders and also the basins of the Tagus and Sado rivers.

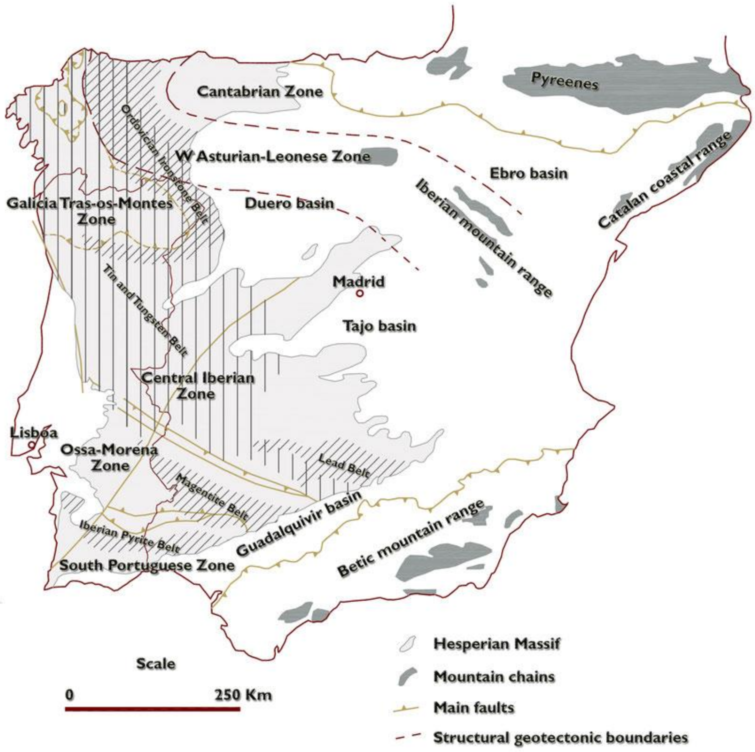

Figure 14 - Iberian Hesperian Massif with prominent metallogenic provinces and structural geotectonic boundaries (Quesada, 1992 and Schermerhorn, 1981 in ProExMin, n.d.).

B) TUNGSTEN AND TIN OCCURENCES IN PORTUGAL

Regarding tungsten and tin deposits, there is an Iberian metallogenetic province of those deposits (Tin-Tungsten Belt), which, in Portugal, overlays the Galicia – Trás-os-Montes and Central Iberian zones that are located in the central and northern regions of Portugal (Figure 15).

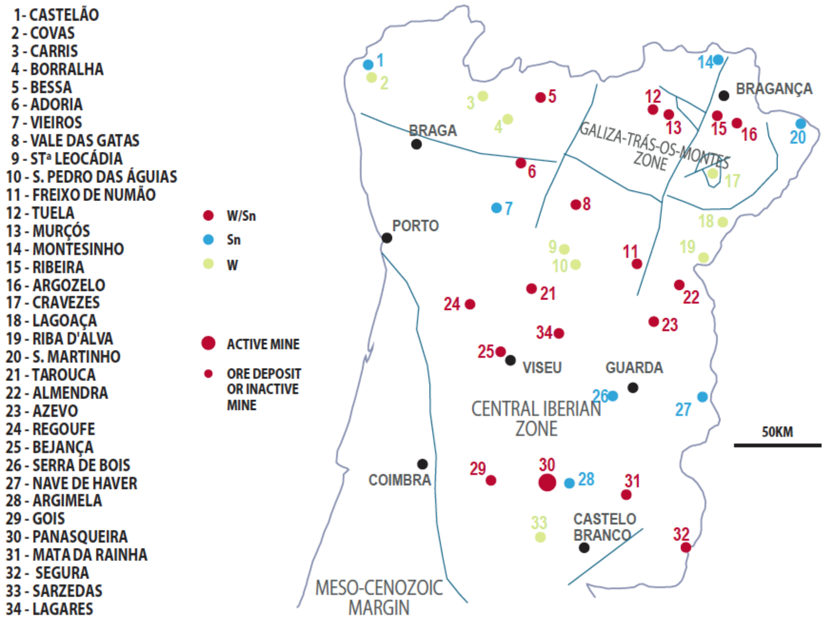

Figure 15 - Geotectonic units and main W-Sn deposits in Portugal (DGEG, 2012).

The primary deposits or occurrences of W-Sn are, for the most part, either directly or indirectly linked with granites, with different typology: aplite-pegmatites, intra and extra-batholithic stockworks, and hydrothermal vein type. They are generally found in contact metamorphic aureoles, sometimes a great distance from the granite outcrops, in which case their relationship with fairly deep, non-outcropping granitic domes, such as **Panasqueira**, Argemela, Góis, Borralha, Vale das Gatas, Ribeira, Argozelo, etc is assumed. According to Conde *et al*. (1971), the hydrothermal vein type W-Sn deposits can be divided, based on particular aspects of their paragenesis, into: **tin deposits** (Sn), like Montesinho (no. 14 in Figure 15), with greisen differentiations, mineralised in cassiterite, poor in sulphides and sporadically with beryl; **tungsten deposits** (W), such as Borralha (no. 4 in Figure 15), which are often associated with molybdenite, wolframite, scheelite, and rare cassiterite mineralisations with abundant sulphides; and **tungsten-cassiterite deposits** (W-Sn), such as Ribeira and Panasqueira (no. 15 and 30 respectively in Figure 15), which are often mineralised in wolframite and cassiterite, and rich in sulphides and carbonates.

In Portugal, the most promising areas for the occurrence of large deposits of W-Sn have different types of geo-structural settings (DGEG, 2012):

- Monotonous schist series, where the existence of non-outcropping greisenised granitic domes is presumed (e.g.: Schist-Greywacke Complex of Beiras - SGC);
- Structural alignments of regional dimension, containing various types of Sn-W deposits and small outcropping or sub-outcropping domes of differentiated granitoids (e.g.: WNW-ESE alignment);
- Granitic areas, containing multiple intrusions differing in terms of mineralogy, metallogeny, and chronology;
- Circumscribed granitic massifs, with differentiated composition from regional granites and its metamorphic aureoles (e.g.: NW-SE circumscribed massifs in the Arouca region);
- Secondary alluvial-type Sn-W deposits of reduced economic interest due to their small size (e.g.: Nave de Haver and Gaia).

Concerning skarns with scheelite, it is important to mention the Douro Scheelite Belt, which is where the SCG and the sin-tectonic granites make contact. It is a zone of interest for an eventual economical extraction. Other zones of potential interest are the Trancoso – Figueira de Castelo Rodrigo Belt and the Serra de Arga zone, where small deposits of scheelite stratoid type occur in skarns. (DGEG, 2012).

Regarding regional tectonic settings in the Iberian Peninsula, there are fundamentally two main variscan deformation phases: D1 and D3. The structures formed during the D1 phase are characterised by folds of predominant orientation NW-SE, and vertical axial plane. The folds of great amplitude and the ductile shearings are contemporaneous of this stage. The

D3 phase develops according to intracontinental ductile shearing, and it encompasses the authochtonous, parauthoctonous, and allochthonous terrains, resulting in wide folds of small amplitude, vertical axial planes, and sub-horizontal axes, according to NW-SE compression, associated with these shearings (Pinto, 2014).

4.2.2. LOCAL SETTINGS

About 280 million years ago (during the Paleozoic era, in the Permian period), magma ascended into the crust and crystallised into a granite. It also mobilised fluids that widened and filled cracks in the pre-existing rocks (schists and greywackes of Beiras), where the mineralogical associations were formed, until today, in the vein-type deposit of Panasqueira.

The Panasqueira deposit, as previously mentioned, is related to non-outcropping greisenised granitic domes, where a monotonous schist series occurs, the so-called Beiras Group, which belongs to the Schist-Greywacke Complex (SGC), situated to the south of the Estrela Mountain, and in particular, the belt running E-W between Góis and the Spanish border, which covers the Góis (Sn-W Góis Mining Field), Panasqueira, Argemela, and Mata da Rainha mines.

During the early compressive stages of the Variscan Orogeny, the SGC was exposed to lower greenschist grade regional metamorphism. The rocks were folded into a sequence of tight, upright isoclinal folds, normally striking NW-SE and accompanied by a sub-vertical slaty cleavage, sub-parallel to bedding during the primary deformation event. (Wheeler, 2016).

The Estrela Mountain batholith[49], a post tectonic intrusive body, does not outcrop on the Panasqueira concession; nonetheless, greisenised granite, believed to be the roof of the batholith, has been intersected in various exploration diamond drill holes and in a range of stoped areas north of the deposit. It is assumed that the granite is the principal source of the mineralising fluids accountable for the economic wolframite vein system. The roof rocks vary from a more or less strongly greisenised granite to muscovite-quartz unit with associated pyrite, chalcopyrite, and is also cut by the later tungsten bearing quartz veins. The greisenised granite dome is covered by approximately 15 metres of extensive unmineralised quartz (silica cap), which does not hold economic value, and is believed to have been installed in the void left by the contraction of the intrusive material. (Wheeler, 2016)

Diabase dykes (dolerite veins in Figure 16) are present in large numbers in this region, but seldom intersected in underground workings. The dykes had no effect on the tungsten mineralisation, and are cut by the tungsten vein system. The dykes may invade pre-existing faults, are sub-vertical to vertical, and range in thickness from around 0.5-3.0m. It is reported that they can be traced for more than a 1km strike at the surface. The rock is finely grained

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[49] Large emplacement of an intrusive igneous rock formed from cooled magma at deep Earth's crust levels.

and micro-porphyritic and mainly consists of labradorite and amphibolitised pyroxene. (Wheeler, 2016)

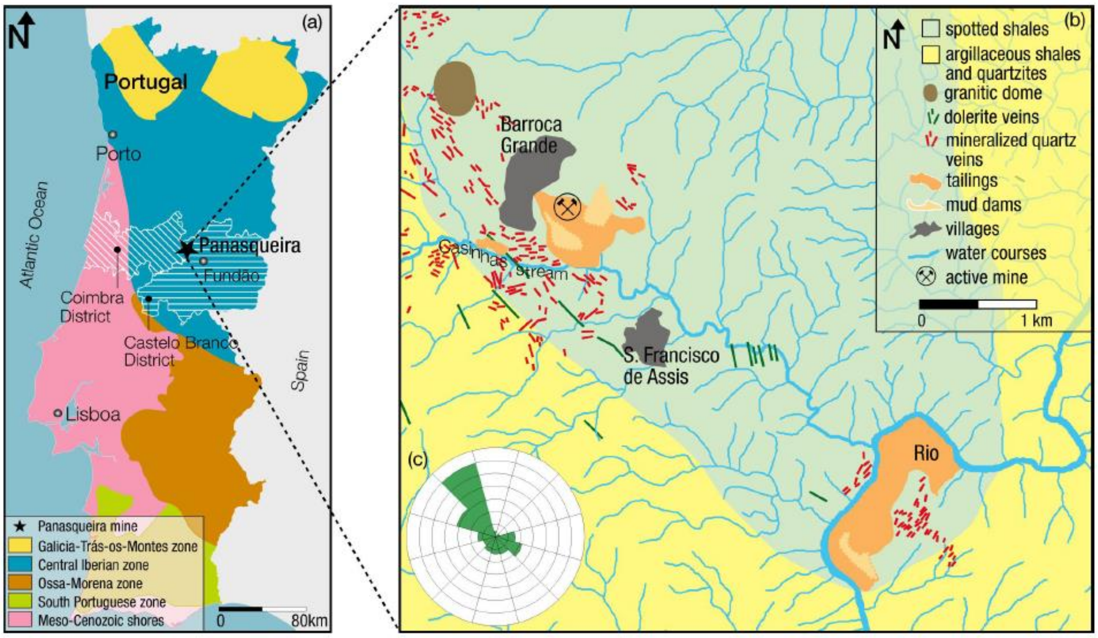

Figure 16 - (a) Panasqueira location in Portugal with its geological units; (b) main geological features of the study area; (c) wind rose of the prevailing winds on top of the Barroca Grande tailing (Candeias *et al.*, 2014).

Regarding local tectonic settings, the Panasqueira Granite is a syn-D3 granite (or syn-tectonic), which means it is contemporary to the formulation of the D3 folds, occupying their hinge zones with NW-SE orientation.

The flyschoid facies, present on the SGC, allows us to verify the first phase of deformation (D1), with large folds of axis oriented NNE to ENE, and the second phase of deformation (D2), with formation of shale with an axial plane NW-SE, sub-vertical. Phase D1, masked by phase D2, presents an ante-variscan (ante-D1) age, and the second phase corresponds to D1 variscan (Pinto, 2014).

4.2.3. MINE SETTINGS

The first relevant studies, regarding the geology of the Panasqueira W-Sn-(Cu) deposit, were developed by Décio Thadeu, where he described it as being a region dominated by metamorphosed sedimentary formations, where, however, there are numerous eruptive manifestations, both basic and acidic (Thadeu, 1951). The deposit lies in a folded metasedimentary sequence, known as the Neoproterozoic-Cambrian aged Schist-Greywacke Complex, Group of Beiras (SGC), which is composed by a several thousand metre thick sequence of low marine flyschoid schists, greywackes, lenticular, thinly bedded mudstones, shales, and arenites (Wheeler, 2016).

In fact, the Panasqueira deposit, which is a typical vein-type deposit, consists of a series of stacked, sub-horizontal, hydrothermal quartz veins, which overlap and fill the joints of fractures occurring in the host-rock, related with a non-outcropping, partially greisenised, leucogranitic dome[50] (containing ore minerals, such as wolframite, cassiterite, and chalcopyrite), which intrudes into the spotted shales – Figure 17. These veins vary in thickness from 1 to 150cm, although the average thickness of the veins currently being mined is between 30 and 40cm (DGEG, 2012).

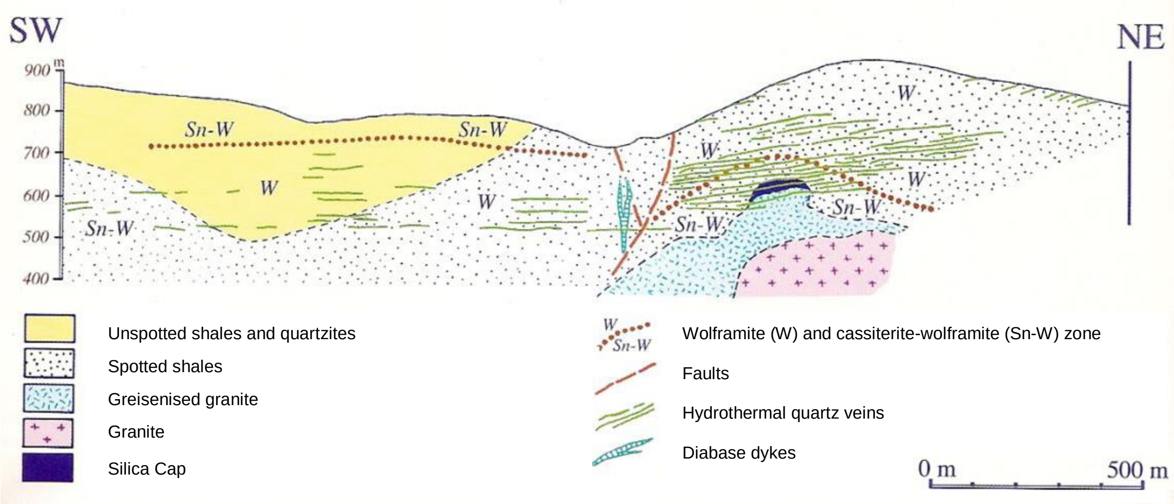

Figure 17 - Schematic geological section of the Panasqueira deposit (modified from Pinto, 2014).

A second set of non-wolframite bearing quartz veins (containing minor chalcopyrite and pyrite) also exists at the Panasqueira deposit, and the set is called “Seixo-Bravo”. The largest concentration of veins occurs immediately after the greisenised granite, and frequently, when one vein thins out, another occurs close to it. There is also a considerable dilution during mining works because the veins are so thin, which is why the mine goes to great lengths to not exceed the 2.2m stope height (Wheeler, 2016).

Besides the main minerals being mined, such as wolframite (tungsten), cassiterite (tin), and chalcopyrite (copper), various other minerals occur, such as sphalerite, topaz, apatite, fluorite, pyrite, pyrrhotite, marcasite, siderite, arsenopyrite, and muscovite, not to mention many others (DGEG, 2012).

A) MINERALISATION AND VEIN MORPHOLOGY

The mineralisation is coarse-grained and very erratically distributed in the quartz veins. Only in the deep area of the Panasqueira mine, close to the greisen, is a more disseminated “fly-dirt” style of mineralisation developed (Wheeler, 2016). This mineralisation and joint

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[50] This granite, also known as Panasqueira granite, is an S- type, peraluminous granite, composed of a two mica porphyroid facies, with K-feldspar megacrysts, which includes hydrothermal accessory minerals, such as zircon, monazite, apatite, ilmenite, and pyrite, grades upwards into an equigranular greisen rich in quartz, muscovite, and topaz, which are the main endomagmatic minerals (Clark, 1971; Kelly & Rye, 1979).

development is associated with the granite intrusion, which, according to Noronha (2017), played an important role in the ore forming processes by supplying heat to drive the mineralising system, rather than being the source of fluids or metals.

During the first stages of variscan deformation in the region, steep folds were formed, NW-SE, which created a sub-vertical slaty cleavage. These folds developed and formed a sub-horizontal fracturing system, also called diaclasing (Sanches, 2015). The veins horizontality was controlled by the granitic intrusion represented in Figure 18.

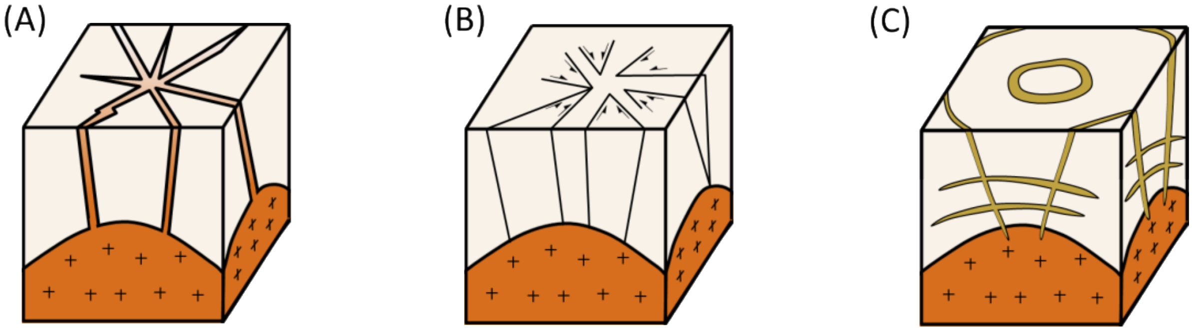

Figure 18 - Schematic view of the maximum, medium, and minimum compression in the formation of the post-tectonic granitoid dome (Sanches, 2015).

According to Pinto (2014), in the ascending phase of the intrusive mass, the fluid pressure was amply high, causing a network of radial fractures, which opened around the eruptive centre, intruding residual granitic magma into these fractures (Figure 18-A). In the following stage, when the pressure of the rising magma and the resistance of the host rock to the intrusion were equal, there was a decrease of fluid pressure and, as a result, shearings occurred, which were bisected by the radial direction. The fluids then greisenised the interior of the granite dome (Figure 18-B). Finally, the intrusive mass entered into the solidification phase, and, by cooling, the contraction of the apical zone occurred, forcing the reopening of the sub-horizontal fractures, which gave rise to the mineralised veins that are exploited in the Panasqueira mine (Figure 18-C).

Wolframite mineralisation occurs as very large crystals (due to extremely slow rates of crystal growth and slow velocities of the mineralising fluids) are usually concentrated towards the margins of the flat-lying quartz veins or, sometimes, close to the central portion of the flat-lying quartz veins (Wheeler, 2016) - Figure 19.

Figure 19 - Flat-lying white quartz vein with abundant wolframite (Wheeler, 2016).

The mode of occurrence of wolframite crystals includes pods (5-20cm), large (10-40cm) and small scattered crystals, mixed (mixture of the three last types), selvedge wolframite (3-10cm), fibrous wolframite (1cm wide, 5-10cm long), and barren (5-10cm). A characteristic quartz-mineralised vein type is the eel-tail morphology that can be found in the Panasqueira deposit, which results from wedge entanglement resulting from pressure variation during the genesis of the vein. Although the ends of the eel-tail veins aren’t connected, sometimes, a connection can occur and form a structure called a “bridge” (Pinto, 2014) - Figure 20.

(a) (b)

Figure 20 – (a) Typical eel-tail (b) Bridge type quartz veins (adapted from Pinto, 2016).

B) PARAGENETIC SEQUENCE

The paragenetic sequence of the Panasqueira deposit is, as already mentioned, complex, but, as accepted by most authors, primarily four stages of mineral formation occur and generally follow the sequence specified in Table 10.

Table 10 - Mineral paragenesis of the Panasqueira deposit (adapted from Wheeler, 2016).

Stage	Event	Minerals	Temperatures[51]
1	Oxide-silicate	Quartz, wolframite, cassiterite.	230°C-360°C
2	Main sulphide	Pyrite, arsenopyrite, pyrrhotite, spharelite, and chalcopyrite.	230°C-360°C
3	Pyrrhotite alteration	Marcassite, siderite, galena, and Pb-Bi-Ag sulphosalts.	230°C-360°C
4	Late carbonate	Dolomite and calcite.	120°C or lower

A brief description of each stage is presented below:

Stage 1: the most important stage, from an economic point of view, due to the formation of the main marketable products at the Panasqueira deposit (wolframite and cassiterite). Quartz, muscovite, tourmaline, topaz, arsenopyrite, molybdenite, and bismuth are formed in this stage; the rare phosphate minerals called panasqueirite and thadeuite, which only occur at the Panasqueira mine, are also formed in this stage.

Stage 2: where the sulphide minerals are formed, namely, pyrite, chalcopyrite, sphalerite, pyrrhotite, and galena; the end of this stage corresponds to the final deposition of quartz, muscovite, and mostly apatite; some arsenopyrite has been deposited in this stage.

Stage 3: characterised by the pyrrhotite alteration, which consequently results in marcasite and mainly siderite, due to the iron released; a second generation of pyrite, magnetite, and hematite occurs; it is also in this stage that the alteration of stannite occurs by reacting with siderite, forming covellite, chalcopyrite, and cassiterite; the sulphosalts are deposited in this stage (Pinto, 2014).

Stage 4: mainly late carbonate deposition (calcite and dolomite), siderite, and fluorite; some sulphides can also be formed in this stage.

C) MINERALOGY

An assemblage of sixty-five minerals is reported to occur in the Panasqueira deposit (Kelly & Rye, 1979), and can be gathered into eleven mineral groups based on their chemical composition (Table 11).

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[51] According to Kelly & Rye, 1979.

Table 11 - Mineralogy of Panasqueira deposit (adapted from Wheeler, 2016).

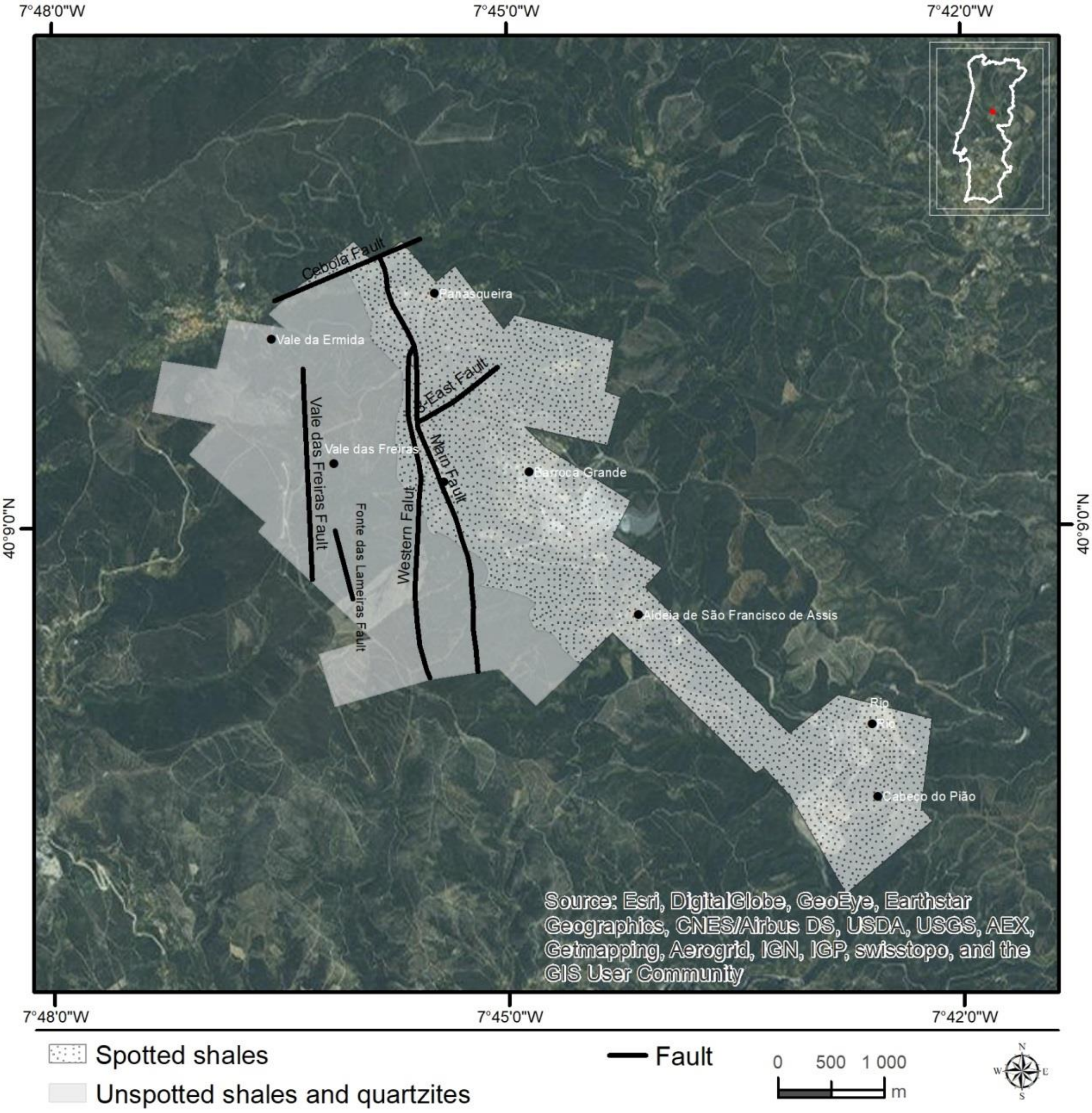
Mineral Group	Mineral
Arsenates	Arseniosiderite, scorodite, and pharmacosiderite.
Arsenides	Lollingite.
Carbonates	Ankerite, calcite, dolomite, and siderite.
Halides	Fluorite.
Native elements	Antimony, bismuth, gold, and silver.
Oxides	Cassiterite, goethite, hematite, magnetite, and rutile.
Phosphates	Althausite, amblygonite, apatite, isokite, panasqueirite, thadeuite, vivianite, wagnerite, and wolfeite.
Silicates	Beryl, bertrandite, biotite, chlorite, quartz, muscovite, topaz and tourmaline.
Sulphates	Gypsum.
Sulphides and Sulphosalts	Acanthite, arsenopyrite, bismuthinite, chalcocite, chalcopyrite, canfieldite, covellite, cubanite, freibergite, galena, gudmundite, mackinawite, marcassite, matildite, molybdenite, pavonite, pentlandite, pyrite, pyrrhotite, pyrargyrite, spharelite, stannite, stephanite, stibnite, and tetrahedrite.
Wolframates	Hydrotungstite, scheelite, tungstite, and wolframite.

D) TECTONIC VS. MINERALISATION

The area of the purported “Couto Mineiro” of Panasqueira is also intersected by various faults and fractures, locally well-defined in both the type of filling and in its location. According to Thadeu (1951), there are three fault systems in this region of Portugal, which, according to Wheeler (2016), can be compacted into two main fault systems (Figure 21):

- NNW-SSE system: which includes the so-called Main fault, the Western fault, the Vale das Freiras fault, and the Fonte das Lameiras fault;
- ENE-WSW system: which includes the so-called Cebola fault and the 8-East fault.

This last fault system (ENE-WSW) is believed to have been initiated with strike-slip movements during the Variscan Orogeny, and reactivated during the Alpine Orogeny.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 21 - Main fault system at Panasqueira mine (modified from Thadeu, 1951).

In Figure 21, with the mining concession area at the time (1951), the main faults are represented, as well as the two major types of lithology, which occur in this area. The western half of the concession contains unspotted shales, schists, and quartzites, and the eastern half contains spotted shales, schists, and quartzites (Wheeler, 2016).

According to Reis (1971), all the mineralisations are bound north by the Cebola fault, and therefore, they occur towards the south of this fault. The mineralisation of wolframite (W), chalcopyrite (Cu), and arsenopyrite (As) occurs to the eastern side of the Main fault, especially in the Panasqueira and Barroca Grande sites, whereas the mineralisation of tin (Sn) occurs towards the western side of the Main fault, especially in Vale das Freiras and Vale da Ermida sites.

All the mineralisations in this area are mainly aligned NW-SE, which is the same direction as the fault system, meaning that the mineralisations are structurally controlled by this fault system, and therefore the mineralisations aren't connected to the ENE-WSW fault system. This means that there isn't a genetic-temporal relationship between these mineralisations and the ENE-WSW fault system.

The natural occurrence of different types of mineralisations (e.g.: tin in the west side and tungsten in east side), can possibly be associated with the dispersion model, or occurrence form of the hydrothermal veins, considering the variation of the metals which occur there. That occurrence form or dispersion model can be interpreted as a radial variation, bound by faults. In Figure 22 a representation of this model, produced using CorelDRAW X6 software, is visible, where we have a concentration in the middle, along the sites where cassiterite (Sn) is abundant: Vale da Ermida, Vale das Freiras, Alvoroso, Corga Seca, Veia Branca, and Giestal sites. Assuming the radial dispersion and the tungsten occurrence in the surrounding areas of the Sn centre at the Panasqueira, Barroca Grande, and Lomba da Cevada sites, we can propose this dispersion model, where the meeting point of the tin (Sn) and tungsten (W), at Rebordões, can be identified.

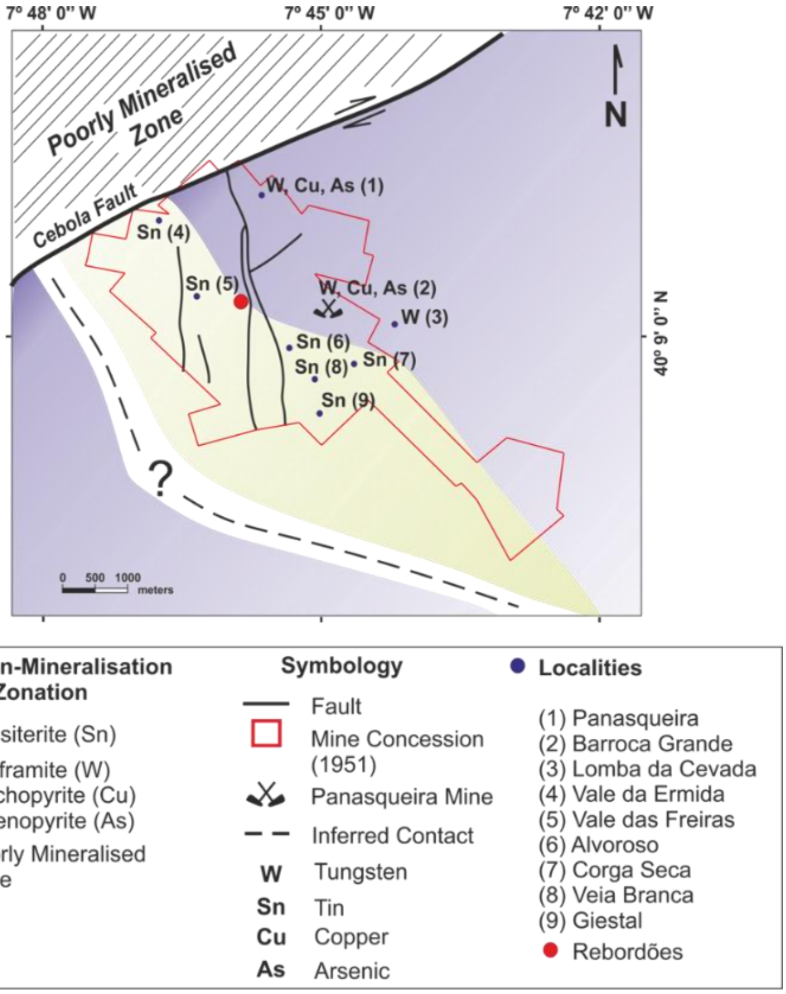


Figure 22 - Proposed model for the radial dispersion of the two major mineralisations in the Panasqueira deposit.

UNIVERSITY OF COIMBRA
FACULTY OF SCIENCES AND TECHNOLOGY
Department of Earth Sciences

CHAPTER 5.

PANASQUEIRA MINE

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5.1. HISTORICAL REVIEW

Coinciding with the start of the industrial revolution, mining would become an important industry in Portugal, with the first mining concessions being granted in 1836. By the end of 19th century, approximately three hundred concessions had been awarded, although the main materials exploited were polymetallic sulphides (Aljustrel and S. Domingos), tungsten and tin (Panasqueira), and antimony and gold (Valongo/Gondomar) (DGEG, 2012).

The first prospecting licence for the Panasqueira deposit was granted in 1886, and only two years later the first reference to wolframite mineralisation arose (Cavey & Gunning, 2006). In 1898, the industrial process for this mine was kick-started for the exploitation of the Panasqueira deposit, which included the Cebola site (now known as São Jorge da Beira), the Bodelhão site (now known as Aldeia de São Francisco de Assis), and the Cabeço do Pião site. In the subsequent years, the exploitation extended to new areas, such as Vale das Freiras, Vale da Ermida[52] (Figure 23), and Barroca Grande. Following this, all the concessions were joined in what is called the “Couto Mineiro” of Panasqueira (Pinto, 2014).

Figure 23 - Old mine portal at Vale da Ermida site (author’s photography).

In 1904, the first mechanical processing plant was built near the Cabeço do Pião site in a place called Rio. Later on, in 1912, the general underground tunnels of the Panasqueira mine, with a length of 700m, were already open. Also in 1912, 5km of air cables were built in order to transport the ore from the exploitation sites, such as Barroca Grande, Rebordões, and Panasqueira, to the processing plant at the Rio site (Pinto, 2014). Exploitation at the Rio site finished when new wolfram-rich veins were discovered at the Panasqueira site.

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[52] At theVale da Ermida site, to this day, the remains of an old mine portal, and mine offices, are still visible.

Between 1914 and 1918 (WWI), the processing plant at the Rio site was extended. Between 1928 and 1934, the air cables were reinforced in order to increase the transport capacity to the Rio site, where all the mine tailings started being deposited in waste-rock dumps or fine tailings dams. The tin exploitation also started between these dates in Vale das Freiras, Alvoroso, and Corga Seca (Pinto, 2014).

In 1934, the regular exploitation of the so-called "Couto Mineiro" of Panasqueira started with the installation of a belt conveyer system, in the Barroca Grande site, for manual ore selection (hand picking plant). The full-mechanised underground exploitation started in 1974.

In 1996, the processing plant at the Rio site was transferred to the Barroca Grande site, which is still currently active. Two years later, in 1998, the processing plant was fully operational and a new fine tailings dam was built (FTD 2A) within the tailings disposal area.

Nowadays, the exploitation is all concentrated to the Barroca Grande sector, which incorporates the underground mine and portals (Rebordões), the processing plant, mine offices, and employee housing, along with the inactive, active, and new fine tailings disposal areas, the waste-rock dump, and a water treatment station.

The mine has continued to operate, apart from on two occasions; once at the end of the Second World War, and another in the mid-nineties, when the mine closed. For nearly the whole past century, 80 years to be exact, an estimated total of forty million tonnes of rock has been mined. This has produced around 128,000 tonnes of tungsten concentrate, 32,000 tonnes of copper concentrate, and 6,000 tonnes of tin concentrate. (Wheeler, 2016)

5.2. MINING METHODS

The mining methods used in the Panasqueira mine had to be carefully studied in order to adapt to the terrain's morphology, but also to maximise the exploitation of the mineral deposit. During the exploration, it is also common to face dilution[53], and, according to Rossi & Deutsch (2013), it can be divided into three types: one related to geological contacts (geological dilution), another related to the mixing of material types within a block (internal dilution), and finally the operational dilution (planned or unplanned dilutions) – Figure 24. Both of the planned and unplanned dilutions can be calculated using different factors, including the mining reserves (geological reserves and planned waste), the unplanned waste, the ROM and the total waste. As shown in Figure 24, the projected layout for mining involves an irregular geological body and expected dilution by the host rock. In real life, however, it is expected that there will be some further overbreak into the sterile rock – so real extraction involves both planned and unplanned dilution, which both have to be taken into consideration in a realistic ore reserve estimate.

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[53] All external material with grades lower than the cut-off grade that must be removed with the ore.

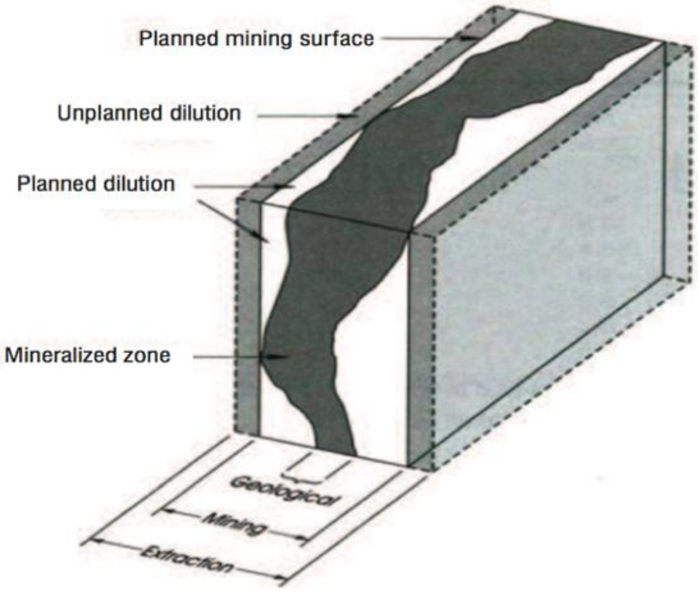

Figure 24 - Conceptual view of planned and unplanned dilution when mining a tabular deposit (ITIA, 2012).

Considering the Panasqueira deposit's morphology, security conditions, and more mechanised methods, in order to reduce labour costs, the company changed the mining method from largely long wall stoping[54] to a more mechanised room and pillar method, which has evolved over the past forty years. This mechanised method is possible due to the horizontal nature of the quartz veins and the very competent host rock. The minimum mining height of 2.2m is a critical factor to avoid big dilutions in the host rock (880% dilution factor). (Wheeler, 2016)

The stoping process starts with ramps being driven to access the mineralised veins in areas where the drilling has indicated quartz intersections = >18cm (indicated resources). When it is accessed, the vein is blocked out on a basic 100x100m pattern. Ores that exceed a 1.8m diameter are generally bored near drive/panel intersections, and allow ore to be dropped down to main haulage levels[55]. Chutes are installed in the bottom of the ore passes to facilitate the loading of the wagons. (Wheeler, 2016)

The underground mine of Panasqueira has currently four main levels, which are all connected by ramps (Level 0, 1, 2 and 3). There is also a planned Level 4, which is being studied. At the Panasqueira mine, they work with real elevation values, therefore the "depth" of each level is represented in mRL (metres Reduced Level), which means the datum plane is at sea level. The main water drainage level is the 530mRL, which is between level 2 (560mRL) and level 3 (470mRL). The underground crusher is below level 2 (560mRL) and

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[54] Stoping is a process of extracting a desired mineral ore from an underground mine, leaving behind an open space, known as a stope.

[55] An underground level, either along and inside the ore body, or closely parallel to it, and usually in the footwall.

above water drainage level (530mRL), and it feeds ore on the conveyor belt in the Santa Barbara hoisting ramp – Figure 25.

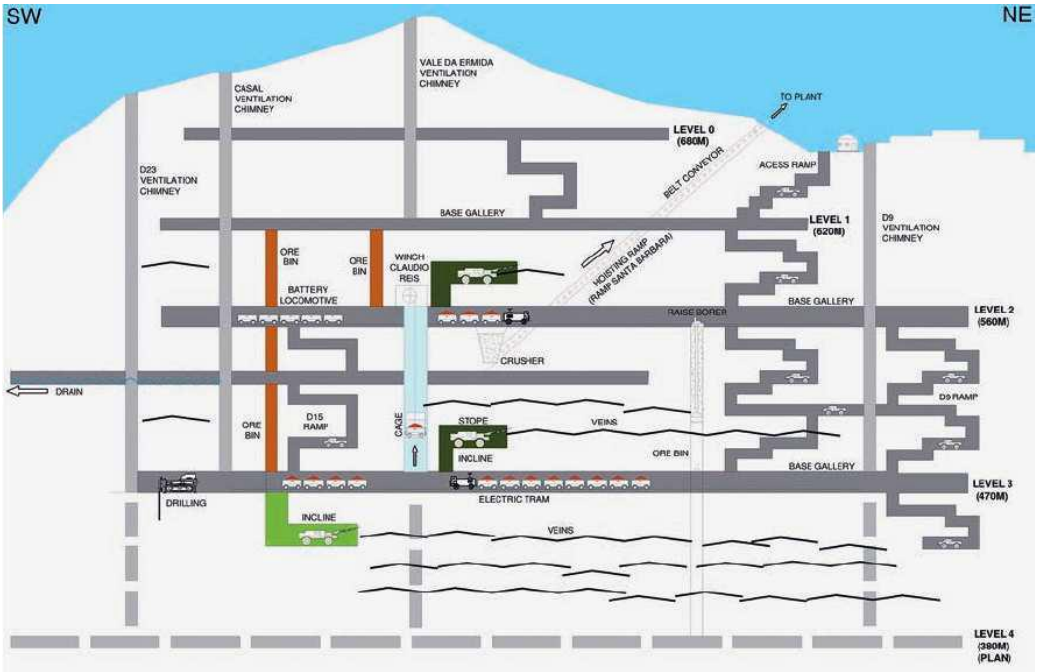

Figure 25 - Schematic profile of the underground shaft system of Panasqueira (Franco *et al*., 2014).

After completing the evaluation of the estimated resource using diamond drilling and face sampling, it is possible to move forward to the ore extraction. When sufficient ore has been delineated, in a first stage, additional 5m (W) x 2.2m (H) openings/galleries are excavated between, and parallel to, the drive and panels to create a regular series of 11x11m pillars. The pillars are then reduced in size to 11x3m pillars and then to 3x3m pillars (Figure 26).

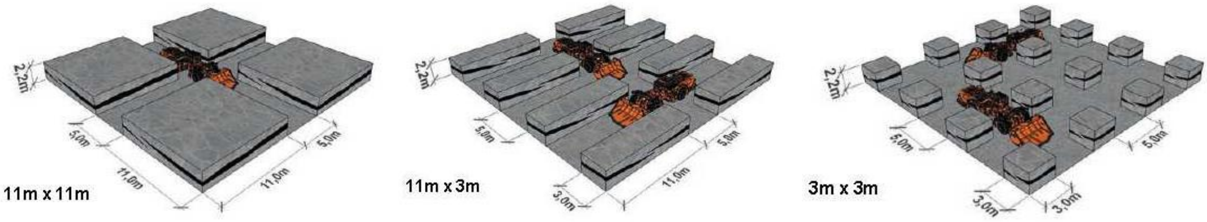

Figure 26 - Measurement of room and pillar method (adapted from Franco *et al*., 2014).

All those final pillars (3x3m unrecovered pillars) are aligned vertically on different levels, and usually begin to collapse within four or five months after completion, which gives plenty of time to “sweep” the fines from the floor, as a recovery process. Based on the room and pillar dimensions, an overall mining recovery of about 84% is applied to the large virgin blocks, which is divided into mining recovery of 33% from the 11x11m pillars and about 45% from the 11x3m pillars. The remaining mining recovery percentage (6%) is associated with the sweeping process, which recovers wolframite rich material that accumulates on the floor during the mining operations.

5.3. ORE PROCESSING AND RECOVERY METHODS

The ore fragmentation has to be taken as far as necessary so that the initial fragment is divided into grains small enough so that each corresponds to a mineral species. After fragmentation, the next step is the separation process, where we group individualised grains into classes. These classes are called concentrate (useful mineral species) and sterile (gangue). Panasqueira mine produces very high grade concentrates, which is almost pure wolframite (about 75% WO_3), helped by the coarse crystalline character of the ore. Wolframite (W), cassiterite (Sn), and chalcopyrite (Cu) are the economic minerals to be recovered as concentrates, being economic, efficient, and adaptable to the treatment of large capacities (BTW, 2015). The mill flow is divided into eight main circuits which will be explained next and shown in Figure 27.

5.3.1. RUN-OF-MINE (ROM) CIRCUIT

After the mine ore has been crushed in the underground jaw crusher into <100mm ROM, it goes through the Santa Barbara conveyor belt (1,200m long and 17% inclination) all the way up into four large coarse ore bins, three located under the mine office and another in front of it (Wheeler, 2016). Here the sterile material (gravel) of the ROM is dumped into the waste dump, by dumpers, or sold as aggregate.

5.3.2. CRUSHING, WASHING AND SCREENING (CWS) CIRCUIT

The ROM material enters in a closed circuit compounded by two vibrating sieves with 20mm aperture and two 18mm conical mills. The material over 20mm goes to the mills and returns to the sieves again. The material dropped from these sieves follows into a pair of secondary sieves with a 0.8mm aperture. Additional material with an aperture of 0.8mm is fed to the Heavy Media Separation (HMS) section. At the end of this circuit, the underflow is fed to the sand circuit and the overflow is fed to the sludge circuit. (BTW, 2015)

5.3.3. HEAVY MEDIA SEPARATION (HMS) CIRCUIT

Generally, these circuits account for approximately 80% of the original ore feed. The material coming from the CWS circuit (>0.8mm) goes in the HMS circuit, to a mix tank of water with Fe-Si. The ferro-silicon increases water density and aims to make the separation between ore (denser) and sterile (less dense) more efficient. The denser fraction is then sent again to the CWS circuit, and the less dense fraction (sterile) is going to the fine tailings dam through a belt conveyor, or transported by dumpers. (BTW, 2015)

5.3.4. SAND CIRCUIT

The fine material arrives at this circuit from the CWS (<3mm), and is then is divided according to its particle sizes (0 to 2.5mm) and passes on to different gravity shaking tables.

Those tables divide the material into three different fractions: the denser (pre-concentrate), the medium (mix), and the less dense (sterile). The sterile material goes to the fine tailings after passing through another classification. The mix material is bombed to a cyclone, which afterwards, is re-sent to the CWS circuit. Finally, the concentrate goes through a spiral classifier, where it is divided into two fractions: the overflow, which goes to another classifier, and the underflow, which represents the final concentrate. (BTW, 2015)

5.3.5. SLIME CIRCUIT

This circuit starts with a gravity concentration in a fluid medium, followed by froth flotation resulting in a fine concentrate of wolframite of a lower grade. The material is also divided into particle sizes (0 to 2.5mm) and passes onto gravity shaking tables, which divide the material into three different fractions: the denser (pre-concentrate), the medium (mix), and the less dense (sterile). Sulfuric acid is added onto the flotation cells (reduce pH), collector, and diesel (collector complement) in order to remove the sulphides. The floated material is then sent to a thickener and the sunken material is passed through a classifier, which then originates the overflow (bombed again to a thickener) and the underflow, which is the final product of this circuit: a fine tungsten concentrate of lower grade (60% WO_3). All the sterile material in this circuit goes to a thickener, and the denser material is bombed to the fine tailings. (BTW, 2015)

5.3.6. FINAL CONCENTRATION CIRCUIT

The material which feeds this circuit comes from two decks with an aperture of 2.25mm and 1.25mm. The fine material goes to a classifier, and the coarse material goes to flotation cells. After passing through some classifiers, the less dense material goes to a water tank, and the denser material goes to a thickener. They are then sent to separation tables, which divide the material, once again, into three fractions: concentrate, mix, and sterile. The sterile goes to a classifier, where the underflow will feed the copper circuit, and the overflow will be bombed to three cyclones. The mix returns to the beginning of this circuit, and the concentrate is divided into fines fraction and coarse fraction, and re-sent to the separation table, which divides it into two: the concentrate (more dense) and the “mix” (less dense). After passing through some classifiers, the material >0.85mm returns to the CWS, the material <0.85mm and >0.43mm is sent to a magnetic separator with two magnets (the first removes the Fe-Si and the second removes the wolframite), the material <0.43mm and >0.25mm is sent to a magnetic separator with three magnets (the first removes the Fe-Si, the second removes the siderite and the third removes the wolframite), and the material <0.25mm goes to a magnetic separator with three magnets (the first removes the Fe-Si, the second removes the siderite, and the third removes the wolframite).

All the non-magnetic material of all these classifications is sent to the tin circuit. (BTW, 2015)

The overall WO_3 plant recovery is about 81%, producing over 90% of the recovered mtus in a high-grade concentrate, as already referenced, of 75% WO_3, and the remainder in another high grade concentrate of 74% WO_3.

5.3.7. COPPER (Cu) CIRCUIT

This circuit includes a small ball mill and seven flotation cells. It normally treats about 5,000t per year (Wheeler, 2016). The main goal of this circuit is the recovery of the copper, which is present in the wolfram sterile material, resulting from the process of flotation on the final concentration circuit (chalcopyrite). This close circuit is also fed by the flotation material from the slime circuit (BTW, 2015).

Much of the arsenopyrite present in the ore is contained in the copper plant tailings, which then go to the fine tailings dam (arsenic discharged). The average arsenic grade in the copper tailings is about 20%, with a copper circuit recovery of 77%. In 2016, about 380t of Cu concentrate were produced, with a medium grade of 28% Cu (Wheeler, 2016). Copper is considered as a sub-product of the exploitation.

5.3.8. TIN (Sn) CIRCUIT

The goal of this circuit is to recover tin and wolframite, which had not been removed in the final concentration circuit. The material from the final concentration is sent to some magnetic classifiers, which discard the siderite, whilst cassiterite and pyrite go for further treatment, using tables to eliminate the finer gangue particles, and flotation in a mechanical cell to eliminate the remaining finer sulphide particles. The recovery of wolframite from the tin concentrate using magnetic separation occurs in this circuit, and is put into the final concentration circuit (BTW, 2015). Every year, approximately 70 tonnes of Sn concentrate are produced, with a grade of about 73% Sn (Wheeler, 2016). Tin is considered as a product of the exploitation.

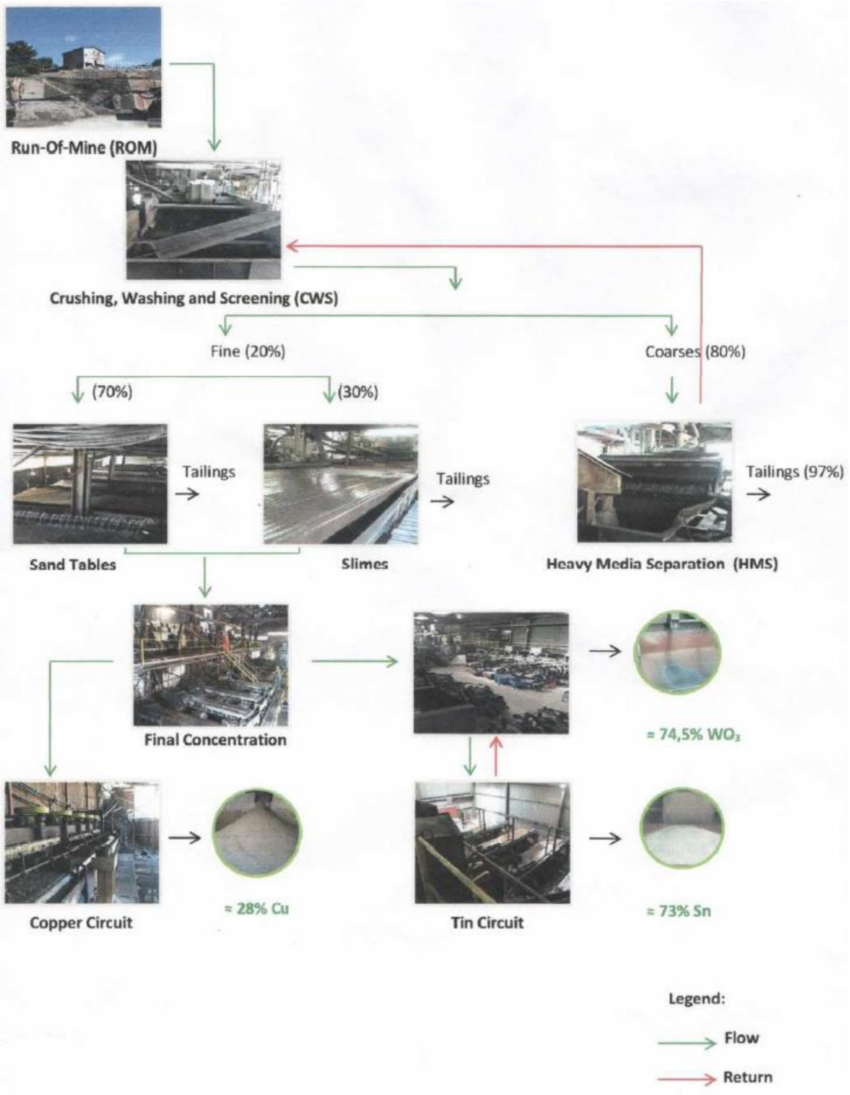

Figure 27 - Simplified flowsheet of the ore processing and recovery (Wheeler, 2016).

5.4. MAIN TYPES OF LANDFILL MINING

Landfills of mining waste can be classified according to their size or the characteristics of the waste deposited. Regarding the first aspect, there are two types of landfills, the small landfill, for deposits of less than 10m in height and a volume of less than 25,000m^3, and the large landfill exceeding any of these dimensions (height > =10m or volume > =25,000m^3).

Regarding the characteristics of the waste, two situations are distinguished, landfills of sterile material and landfills of non-sterile material. Landfills of sterile material are normally defined as coarse granular residues of sterile waste-rock associated with low-grade ores and slags (waste-rock dumps). Landfills of non-sterile material are usually defined as very fine-grained residues from the beneficiation and processing of the high-grade ores, known as fine tailings dams or ponds. (Meira & Bastos, 2001 and Carvalho, 2016)

In this study, we only considered the landfills of non-sterile residues, the so-called fine tailings dams.

5.5. FINE TAILINGS DISPOSAL AREAS

Based on the geographic location of the two main tailings/waste dump sites of the Panasqueira mine, the revised mining concession was divided into two subsections: the Rio site (old mine/plant) and the Barroca Grande site (active mine/plant). It is also expected that smaller tailings will be present at some of the old locations, such as the Vale da Ermida or Panasqueira sites. These fine tailings are derived from the crushing, milling, and recovery processes of the ore, which are conveyed by pipelines into lagoons, the so-called slime dams or ponds, or fine tailings dams or ponds. Note that the tailings resources have no cut-off applied (Wheeler, 2016).

5.5.1. RIO SITE

This location was part of BTW’s mining concession until 2006, when the Portuguese government signed an agreement that removed the site, and all its associated environmental liabilities. It included the old mill and treatment station, a large coarse waste dump (composed of schists and quartz - majority of the material in the dump) and an old fine tailings dam, situated at the top of the waste-rock dump (Figure 28). These tailings piles (Rio tailings) are estimated to exceed 8Mt of material (Wheeler, 2016).

Although it doesn’t belong to the BTW’s mining concession, it belongs to BTW’s surface concession. Some studies have been held here, in order to investigate the fine tailings’ internal structure, its geochemical distribution, and associated mud (particle size) distribution (Grangeia *et al*., 2009), or even to analyse the feasibility of an eventual re-mining and restructure of the Rio Tailings deposit (Salom, 2017).

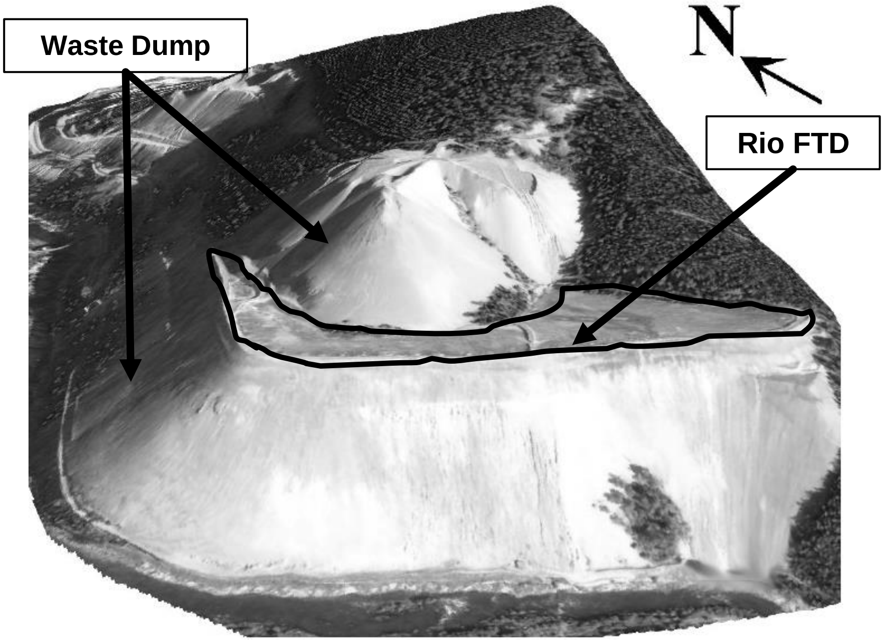

Figure 28 - Current surface topography of the so-called Rio tailings (modified from Grangeia *et al*., 2009).

5.5.2. BARROCA GRANDE SITE

Regarding fine tailings in this area, there are two different fine tailings dams (FTDs): FTD 1 and FTD 2A with an elevation of around 600m and 700m respectively (Figure 29). There is also a new FTD being built, which is expected to be ready to receive the tailings by 2019 (FTD 2B).

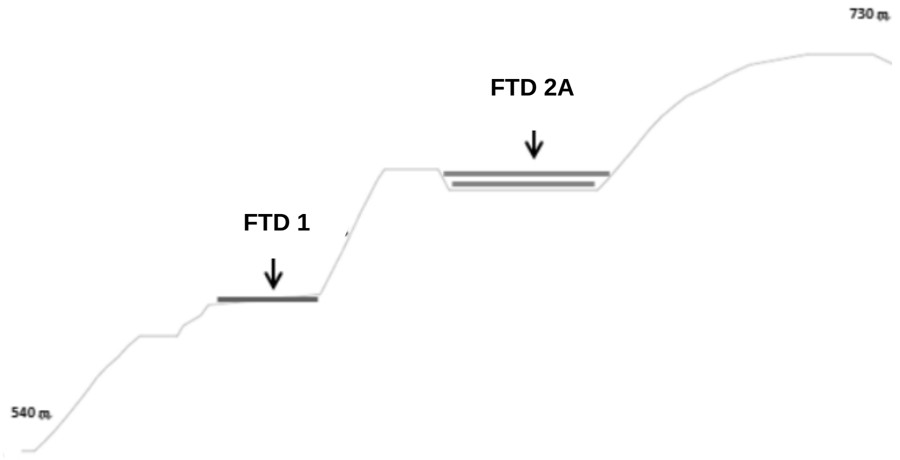

Figure 29 - Topographic draft of the Barroca Grande fine tailings (adapted from Gonçalves, 2014).

These tailings are the biggest liability, as they contain precipitate from the water treatment plant, as well as the copper circuit tailings with up to 25% arsenic with an average density of between 1.4 to 1.8g/cm^3, depending of the sampling site. (Wheeler, 2016) Concerning waste dumps in this area, there is a huge continuous pile of waste material (Barroca Grande dump), which includes a waste-rock dump, and three fine tailings dams (FTD) – Figure 30. All of those waste dump materials are very benign and marketable as aggregate (an example of recovery of this waste is the REMINE H2020 project[56] coordinated by University of Beira Interior). This dump lies adjacent to, and above, the Bodelhão Creek, which flows south-easterly to the Zêzere river.

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[56] Reuse of Mining Waste into Innovative Geopolymeric-based Structural Panels, Precast, Ready Mixes and in situ Applications.

Figure 30 - Profile view of the Barroca Grande site from north-west (BTW, 2014).

A) FTD 1

Fine tailings dam 1 has been inactive since 1985, and has, approximately, a 750m perimeter, 35,000m^2 area, 50m maximum depth, and an elevation of around 600m. The maximum volume, which is completed, is about 731,600m^3 (BTW) which, according to Wheeler (2016), is equivalent to 1,817Kt[57] of material – Figure 31.

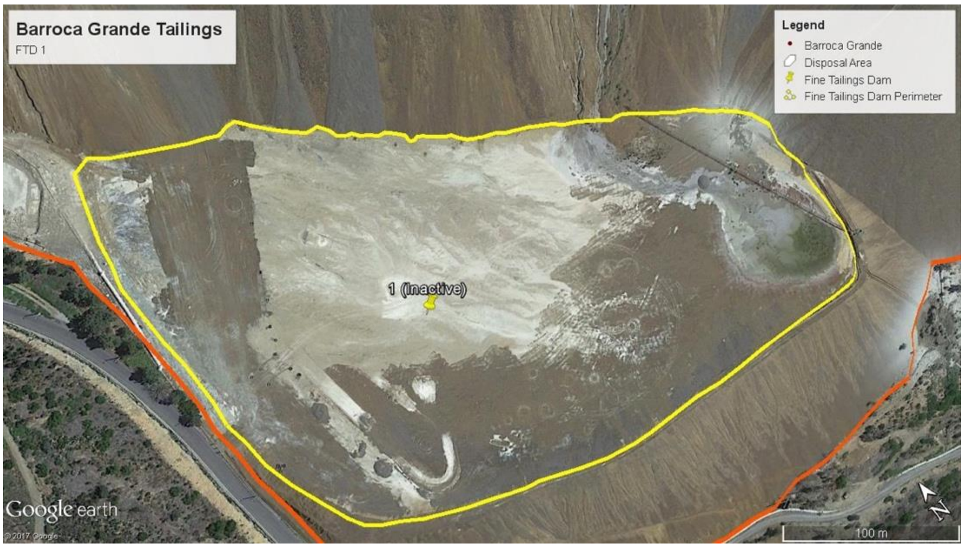

Figure 31 - Bird's eye view of the inactive fine tailings dam 1 as of May 2013 (Google Earth Pro version 7.1.5).

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[57] As of 30th September 2016.

B) FTD 2A

Fine tailings dam 2A has been active for almost twenty years (since 1998), and it had, at the end of 2013, approximately, a 1km perimeter, 69,000m^2 area, 50m maximum depth, and an elevation of around 700m. The maximum volume capacity, which is almost fulfilled, is about 1,545,000m^3 (BTW) which, according to Wheeler (2016), is equivalent to 3,347Kt[58] of material – Figure 32 and Figure 33. This dam, apart from sand and slimes, receives sludge from the water treatment plant, as well as the copper circuit tailings with up to 25% of arsenic (Wheeler, 2016).

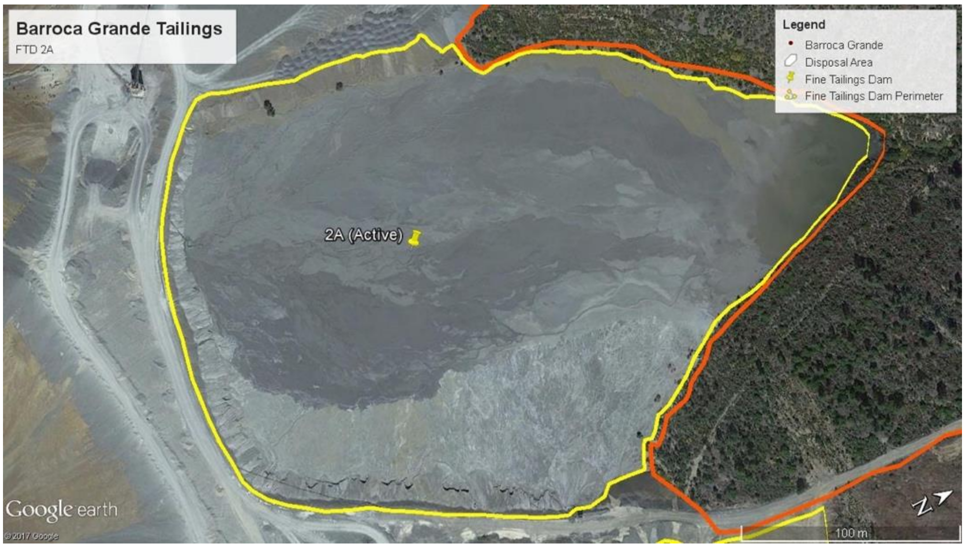

Figure 32 - Bird's eye view from the current fine tailings dam 2A as of May 2013 (Google Earth Pro version 7.1.5).

Figure 33 - Panoramic view of the current fine tailings dam 2A as of May 2016 (author's photography).

The estimated tonnage of ROM (waste dump) and fine tailings disposal (FTD 2A), per year, at the current disposal area in the last 6 years is represented in Table 12.

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[58] As of 30th September 2016.

Table 12 - Values of the processed ROM and fine tailings at the Panasqueira mine in the last 6 years (BTW).

Year	ROM (tonnes)	Fine Tailings (tonnes)
2011	904,619	53,112
2012	830,135	46,554
2013	789,442	49,296
2014	774,965	50,456
2015	517,505	39,555
2016	642,573	35,087

C) FTD 2B

The new fine tailings dam (FTD 2B), which will start receiving tailings by 2019 has, approximately, a 1.6km perimeter, 135,000m^2 area, and 70m maximum depth. The maximum volume capacity of this new dam is about 1,800,000m^3 (BTW) - Figure 34.

Figure 34 - Close-up view of the new fine tailings dam 2B as of May 2013 (Google Earth Pro version 7.1.5).

UNIVERSITY OF COIMBRA

FACULTY OF SCIENCES AND TECHNOLOGY

Department of Earth Sciences

CHAPTER 6.

MATERIALS, METHODOLOGIES, AND TECHNIQUES

CHAPTER 6. MATERIALS, METHODOLOGIES, AND TECHNIQUES

The proposed research plan is to study the geochemistry of two fine tailings dams (FTD 1 and 2A) at Barroca Grande in the Panasqueira mine (Portugal), in order to physically and chemically characterise their fine tailings. To complete this characterisation, we used four different types of analyses in order to obtain the results of the mineral and chemical content of these fine tailings dams (LDPS, XRD, SEM, and XRF). The adopted methodologies used to characterise the residues were the **selection of the sampling site**, **sampling**, **sample preparation**, and finally the respective **analyses** we wanted to do.

6.1. SELECTION OF THE SAMPLING SITE AND SAMPLING

The sampling sites selected were the two fine tailings dams at Barroca Grande in the Panasqueira mine, one inactive (1) and the other currently active (2A). In this disposal area, where all the waste from the extraction process goes, there is also a new fine tailings dam (2B), although the deposition has not started here yet.

The **sampling** process consisted of two different types of sampling, either doing a horizontal analysis or a vertical analysis:

A) SURFACE SAMPLING (HORIZONTAL ANALYSIS)

In order to carry out this type of sampling, held in May 2016, we previously selected 12 different sites, spaced approximately 10 to 15 metres from each other, on the currently active fine tailings dam of the Panasqueira mine (2A – Barroca Grande Tailings), which has been active for the past 20 years – Figure 35 and Figure 36. Around 5 to 7 kilograms of soil were collected per sample. These samples were collected superficially at a depth of up to 30 centimetres, with the help of a shovel, and they were then packed into suitable plastic bags. This type of sampling was also fundamental, as it allowed comparison with other studies, as they were both collected superficially.

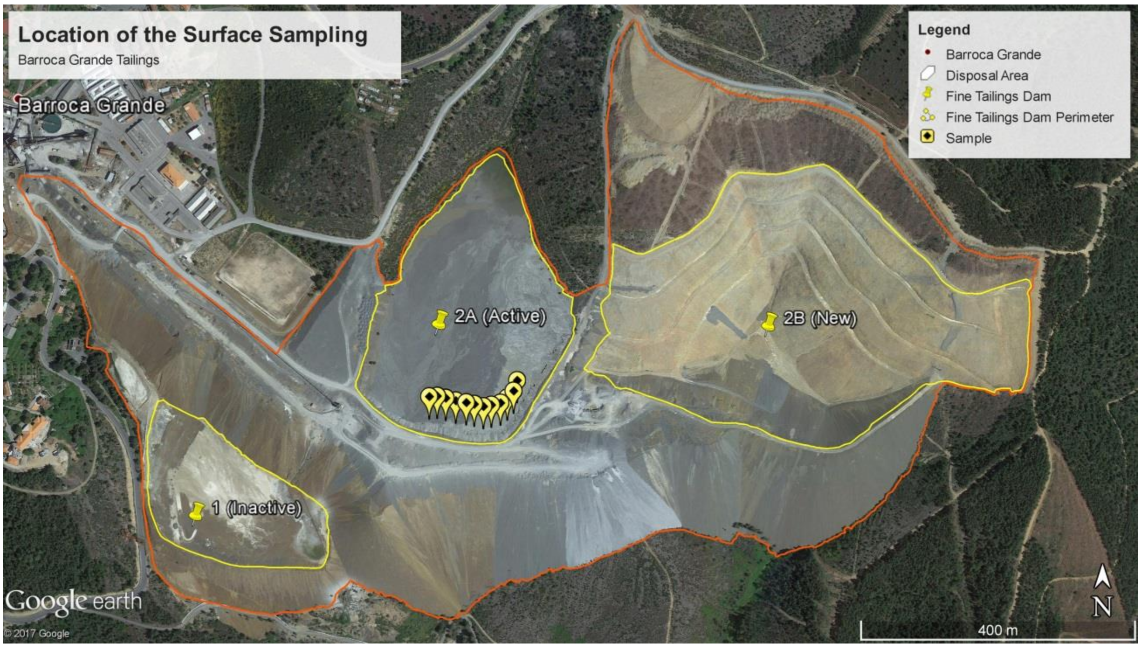


Figure 35 - Bird's-eye view of the location of the surface sampling at Barroca Grande Tailings as of May 2013 (Google Earth Pro version 7.1.5).

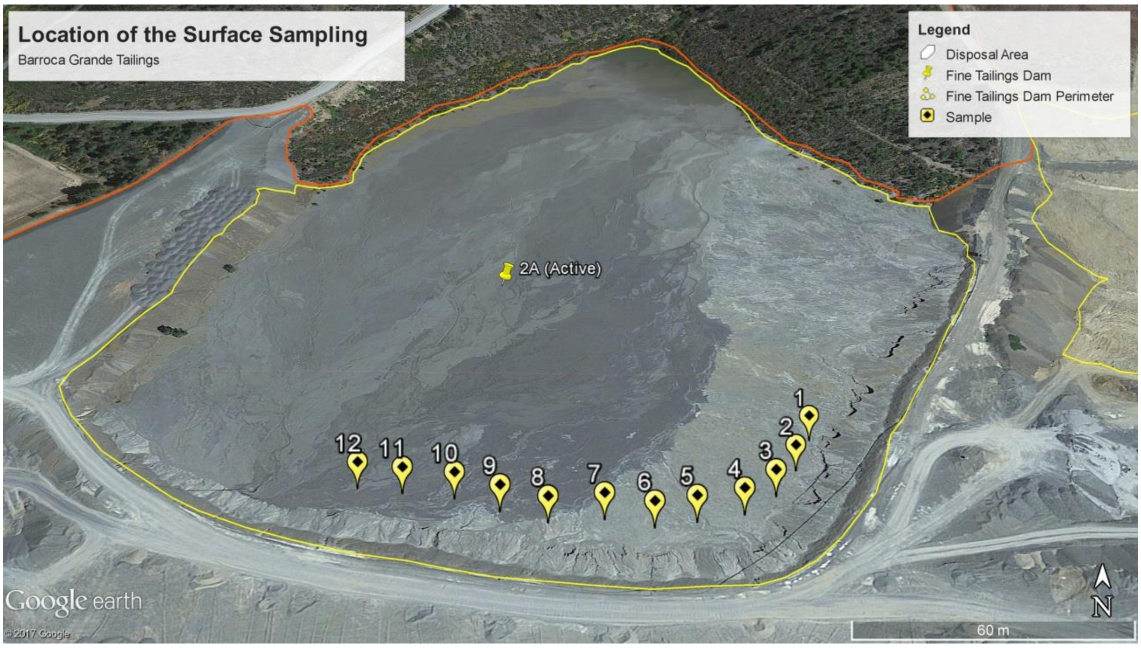


Figure 36 - Close-up view of the location of the surface sampling at the currently active fine tailings dam (FTD 2A) at Barroca Grande as of May 2013 (Google Earth Pro version 7.1.5).

B) BOREHOLE LOGGING (VERTICAL ANALYSIS)

To carry out this type of sampling, which took place in September 2016, four different sites were previously selected (Figure 37): two in the currently active fine tailings dam (FTD 2A), spaced approximately 100 metres from each other (Figure 38), and two at the inactive fine tailings dam (FTD 1), which were also spaced approximately 100 metres from each other (Figure 39).

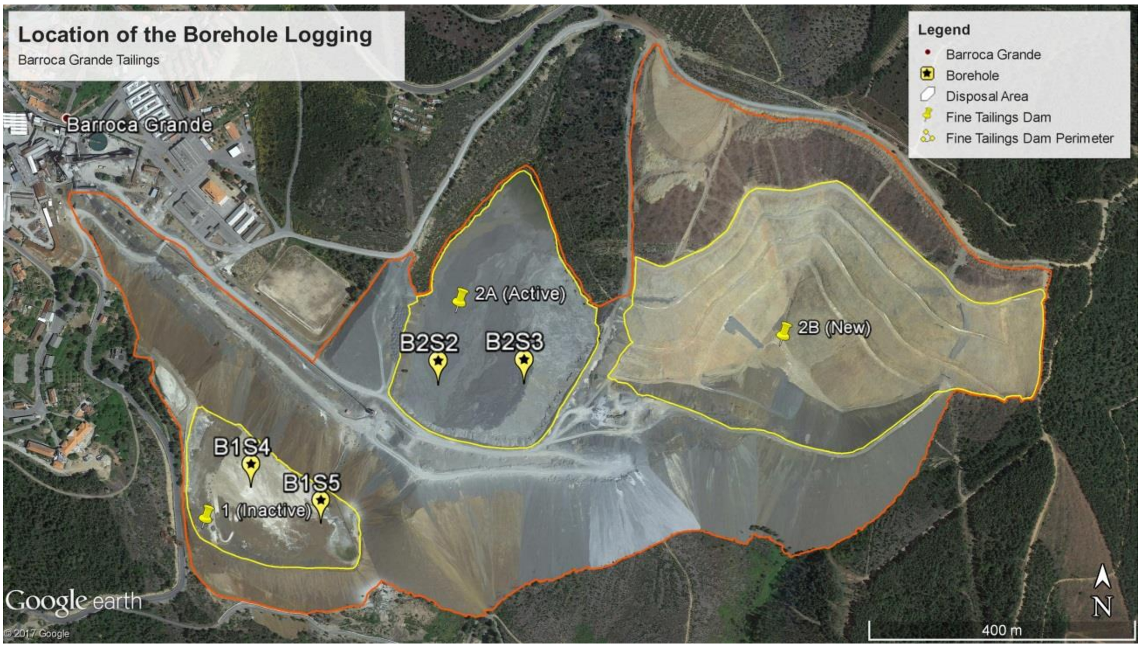


Figure 37 - Bird's-eye view of the location of the borehole logging at the Barroca Grande Tailings as of May 2013 (Google Earth Pro version 7.1.5).

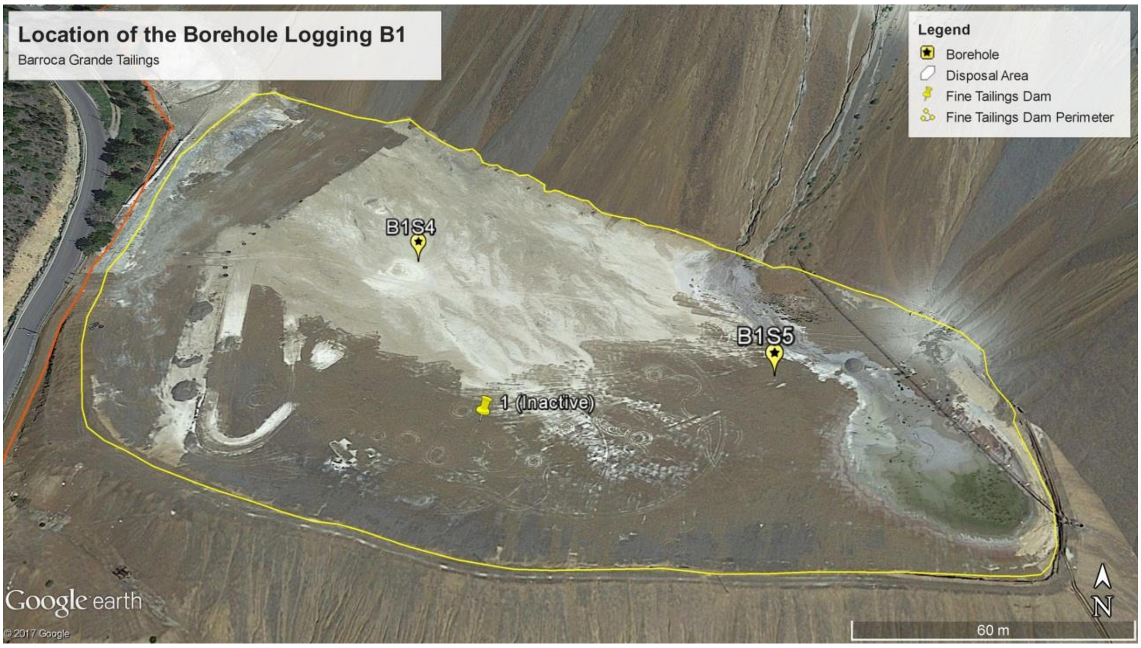


Figure 38 - Close-up view of the location of the borehole logging B1 in the inactive fine tailings dam (FTD 1) at Barroca Grande as of May 2013 (Google Earth Pro version 7.1.5).

Figure 39 - Close-up view of the location of the borehole logging B2 in the currently active fine tailings dam (FTD 2A) at Barroca Grande (Google Earth Pro version 7.1.5).

These borehole samples (B1S4, B1S5, B2S2 and B2S3) were collected from a borehole, with a depth of 4 metres, by percussion drilling (without diamond tip). However, samples were only preserved from the depths between 1 and 4 metres, thus the first metre wasn't considered.

For every metre that was drilled, only around 50cm were used for this study, and were stored in PVC tubes, with a 6.4cm diameter, and sealed with cling film. These PVC tubes were then cut in half before the analysis took place. As a result, only three halves per borehole were used in this study – Table 13. These 12 segments weighed between 400 to almost 1000 grams each, depending on which borehole segment we considered. (APPENDIX III)

Table 13 - Measurements of the borehole samples.

Fine Tailings Dam 1 (Barroca Grande)		**Fine Tailings Dam 2A (Barroca Grande)**	
B1S4 (1 - 4m)	**B1S5 (1 - 4m)**	**B2S2 (1 - 4m)**	**B2S3 (1 - 4m)**
B1.S4.2.2: 1.58 - 2m	**B1.S5.2.2:** 1.59 - 2m	**B2.S2.2.2:** 1.5 - 2m	**B2.S3.2.2:** 1.5 - 2m
B1.S4.3.2: 2.63 - 3m	**B1.S5.3.2:** 2.33 - 2.66m	**B2.S2.3.2:** 2.5 - 3m	**B2.S3.3.2:** 2.5 - 3m
B1.S4.4.2: 3.33 - 3.67m	**B1.S5.4.2:** 3.63 - 4m	**B2.S2.4.2:** 3.5 - 4m	**B2.S3.4.2:** 3.5 - 4m

6.2. SAMPLE PREPARATION

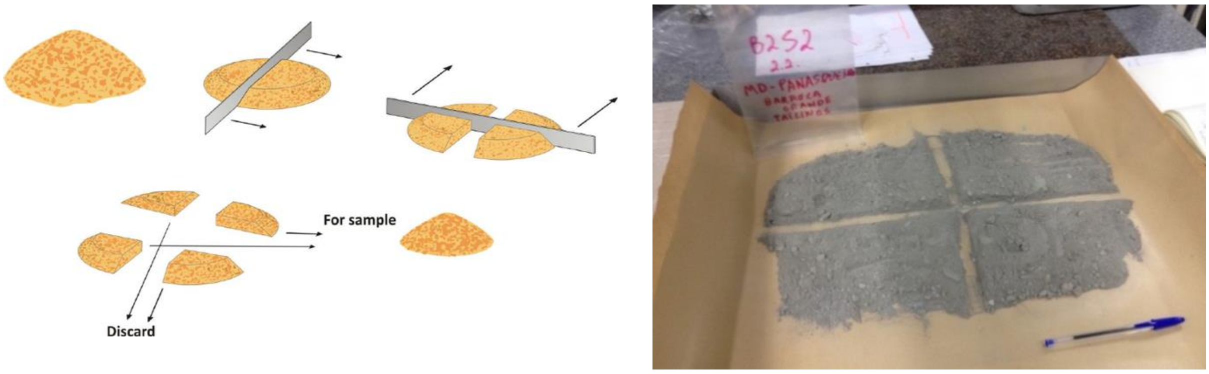
After the sampling process, the samples were prepared, according to the general laboratory techniques, before being subjected to any kind of physical or chemical analysis, in order to be characterised. The goal of this preparation was: to facilitate the transportation and storage of the samples; to separate the constituents and/or removal of undesirable constituents in the sample; and to increase the surface area of the sampled particles in order to render the chemical decomposition more effective.

To prepare these fine samples, we used a spatula for the homogenisation and quartering process, a drying cabinet for the drying process, a porcelain mortar and pestle, and an agate mortar for the milling process, two sieves (<1mm and <0.125mm) for the sieving process, a wet shaking table, in order to obtain the mineral concentration, and a balance and a pellet press for the pressed pellet preparation. Each one of these materials was used with a different purpose and according to the analysis we wanted to carry out.

All the homogenising and quartering, drying, milling, and sieving preparation processes were done in the Laboratory of Sample Preparation and Mineral Separation (LSPMS-UC), and the mineral concentrate process was done in the Laboratory of Ore Treatment (LOT-UC), both of which belong to the Department of Earth Sciences, Faculty of Sciences and Technology, University of Coimbra. The pressed pellet preparation process was done in the Laboratory for Wear, Testing & Materials at the Pedro Nunes Institute (LED&MAT-IPN).

6.2.1. HOMOGENISING AND QUARTERING

All the surface samples (S1 to S12) and six of the borehole samples (B1.S5.2.2, B1.S5.3.2, B1.S5.4.2, B2.S2.2.2, B2.S2.3.2, and B2.S2.4.2) were homogenised and reduced so that the portion to be characterised, or sent for chemical analysis, was representative of the entire sampled material. This results in a uniform distribution of particles throughout the sample. As previously mentioned, we used a spatula for the homogenisation and reduction process. After we mixed all the sediments in different directions, we did the cone and quarter method in order to reduce the sample. The cone and quarter method ‘involves pouring the sample into a cone, flattening the cone, dividing the flattened cone into four equal divisions (quartering), and then removing two opposite quarters’ (Schumacher *et al.*, 1990). This process continued until a suitable sample volume was achieved – Figure 40.



(a) (b)

Figure 40 - (a) Illustration of the cone and quartering method (Alakangas, 2015) (b) Application of the quartering method on the borehole sample B2.S2.2.2.

6.2.2. DRYING

Although all the surface samples (S1 to S12) and six of the borehole samples (B1.S5.2.2, B1.S5.3.2, B1.S5.4.2, B2.S2.2.2, B2.S2.3.2, and B2.S2.4.2) were relatively dry, we decided to dry them at around 50^{o}C just to be certain they were completely dry. We chose the temperature of 50^{o}C because it's the ideal temperature to keep volatile constituents (never over 50-60^{o}C), which was the case. For that purpose, we used a ventilated stove for the drying process (Figure 41). Regarding the borehole samples, although we left them drying inside the same ventilated stove without any temperature set, they had already been dried at room temperature.

Figure 41 - Ventilated stove with the 12 surface samples.

6.2.3. MILLING

To perform this method, we used two different materials: a manual porcelain mortar and a mechanic agate mortar (Agate & General Stonecutters, Ltd. mortar machine) with the purpose of reducing the grain size of the samples. This method is applied when the analytical method to be used requires finely powdered samples. With the porcelain mortar, we reduced all the samples before they were sieved at 1mm (Figure 42a). Using the agate mortar, we also reduced all the samples after they were sieved at 1mm, and before sieving them at 0.125mm (Figure 42b). The samples, which were milled by those two mortars, were all the samples from the surface sampling (S1 to S12) and six samples from the borehole logging (B1.S5.2.2, B1.S5.3.2, B1.S5.4.2, B2.S2.2.2, B2.S2.3.2, and B2.S2.4.2).

(a) (b)

Figure 42 - (a) Manual porcelain mortar (b) Mechanic agate mortar.

6.2.4. SIEVING

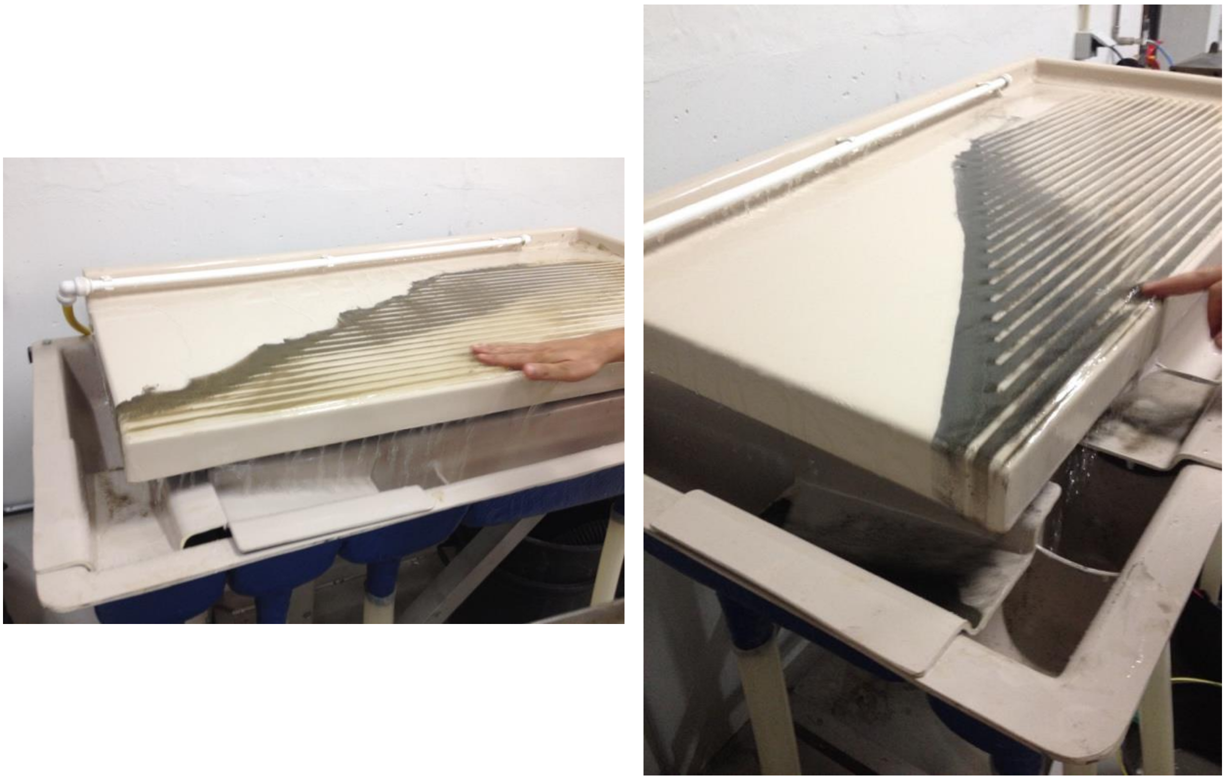
The soil samples consisted of materials of very different granulometry, ranging from very coarse to finer particles. Depending on the type of analysis we wanted to do, and on the type of analyser we used, we sieved the samples at 1mm (Retsch test sieve – Figure 43a) and re-sieved them at 0.125mm (Endecotts test sieve – Figure 43b). The only analyses which required the re-sieving process at 0.125mm were those we did using the XRF with the Panalytical analyser, in order to produce the pressed pellets for the analyser. The samples, which were sieved and re-sieved, were all the samples from the surface sampling (S1 to S12) and six samples from the borehole logging (B1.S5.2.2, B1.S5.3.2, B1.S5.4.2, B2.S2.2.2, B2.S2.3.2, and B2.S2.4.2).

(a) (b)

Figure 43 - (a) Sieving process using 1mm Retsch test sieve (b) Sieving process using 0.125mm Endecotts test sieve.

6.2.5. MINERAL CONCENTRATE

For this sample preparation, we only used three samples, one from the surface sampling (S10) and two from the borehole logging (B1.S5.4.2 and B2.S2.3.2), in their pure state, as they were of sufficiently fine material for the gravity separation process. With the help of a wet shaking table (Holman-Wilfley Ltd. shaking table), we were able to separate them into three different types of material: sterile, mix, and concentrate. However, we only wanted to analyse the concentrate in the SEM-EDS/WDS analyser, in order to complement the XRD analysis. The principle of separation is the motion of particles, according to their specific gravity and size, moving in a slurry across an inclined table, which moves backwards and forwards virtually at right angles to the slope, in conjunction with the riffles which hold back the particles closest to the deck. This motion and configuration causes the fine high specific gravity particles to migrate closer to the deck and be carried along by the riffles in order to be discharged at the uppermost point of the table, while the low specific gravity coarser particles move or remain closer to the surface of the slurry and ride over the riffles, discharging over the lowest edge of the table (Falconer, 2003) – Figure 44.

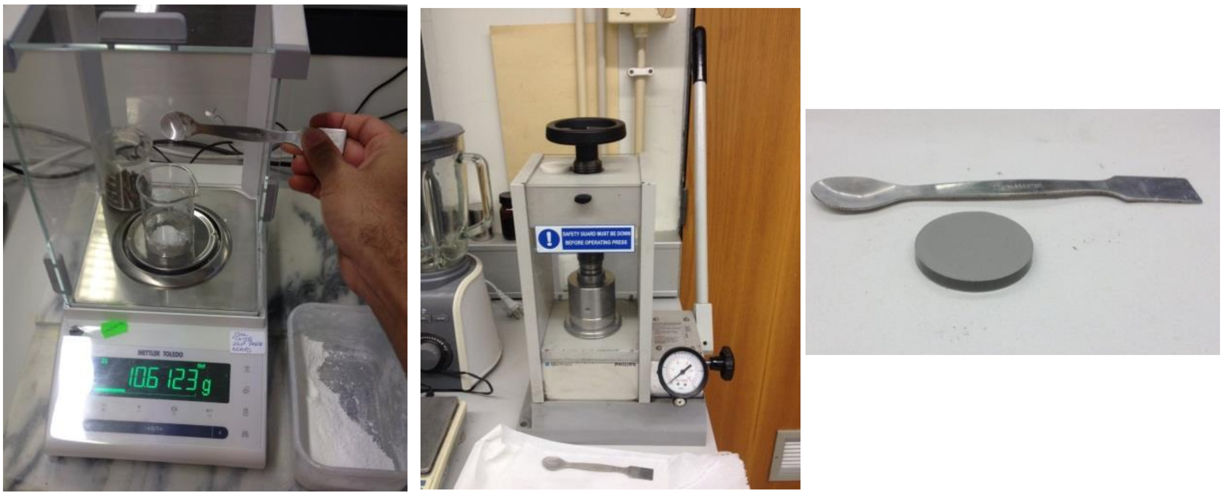


(a) (b)

Figure 44 - (a) Gravity separation using a wet shaking table (b) Accumulation of the denser particles.

6.2.6. PRESSED PELLETS

With all the surface samples (S1 to S12) and six samples from the borehole logging (B1.S5.2.2, B1S5.3.2, B1.S5.4.2, B2.S2.2.2, B2.S2.3.2, and B2.S2.4.2) already homogenised, dried, milled, and sieved twice (one at <1mm and another at <0.125mm), we were able to prepare pressed pellets for the XRF analyser Panalytical Axios mAX. To produce a pressed pellet, we took 10 grams of each prepared sample from the two types of sampling (surface and borehole) and added 2 grams of a binder (cereox[59]) for better stability of the pressed pellet, and for the settings which the analyser required (Figure 45a). After mixing these two components, we poured the mixture into a mould, then we pressed the mixture with the help of a mini pellet press (Philips Mini Press – Figure 45b), and finally the pressed pellet was ready for the analysis (Figure 45c).



(a) (b) (c)

Figure 45 - (a) Mettler Toledo Analytical Balance (b) Philips Mini Press (c) Pressed pellet.

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[59] Wax binder for XRF analysis (Licowax C Micropowder).

6.3. LASER DIFFRACTION PARTICLE SIZE ANALYSIS

Laser diffraction measures particle size distributions by measuring the angular variation in intensity of light scattered as a laser beam passes through a dispersed particulate sample. Large particles scatter light at small angles relative to the laser beam, and small particles scatter light at large angles (Malvern, n.d.). The main purpose of this analysis was to define the different grain size in each sample in order to determine the percentage, by weight, of each fraction in relation to the total mass of the sample.

6.3.1. BECKMAN COULTER

A) MATERIALS

For this analysis, we used the LDPS analyser **Beckman Coulter LS230 LS Variable Speed Fluid Module Plus** from the LS-UC[60]. This analyser is capable of giving the particle size percentage in clay (<4μm), silt (4-63μm), and sand (63-2000μm). This machine uses a laser source with a tungsten halogen lamp.

B) METHODOLOGIES AND TECHNIQUES

After the samples had been homogenised, dried, milled, and sieved at 1mm (equivalent to sand), they were prepared for this LDPS analysis. With this analyser, we only needed to add a few grams of the dry powdered sample into a fluid, in a motion container, which normally takes around ten minutes to produce the results (Figure 46). In this analysis, all twelve samples from the surface sampling (S1 to S12) and six from the borehole logging (B1.S5.2.2, B1S5.3.2, B1.S5.4.2, B2.S2.2.2, B2.S2.3.2, and B2.S2.4.2) were analysed.

Figure 46 - Introducing a sample into the Beckman Coulter LS 230 analyser.

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[60] Laboratory of Sedimentology from the Department of Earth Sciences, Faculty of Sciences and Technology, University of Coimbra.

6.4. X-RAY DIFFRACTION ANALYSIS

The XRD technique uses a portion of the sample, which is powdered and placed in a holder. Following this, X-rays of a fixed wave-length are used to irradiate the sample, and a goniometer is used to record the intensity of the reflected radiation.

In this analysis, we analysed the 12 samples from the surface sampling (S1 to S12) and 6 samples from the borehole logging (B1S5 and B2S2) in order to understand the mineralogy that occurs at the two fine tailings dams (FTD 1 and FTD 2A).

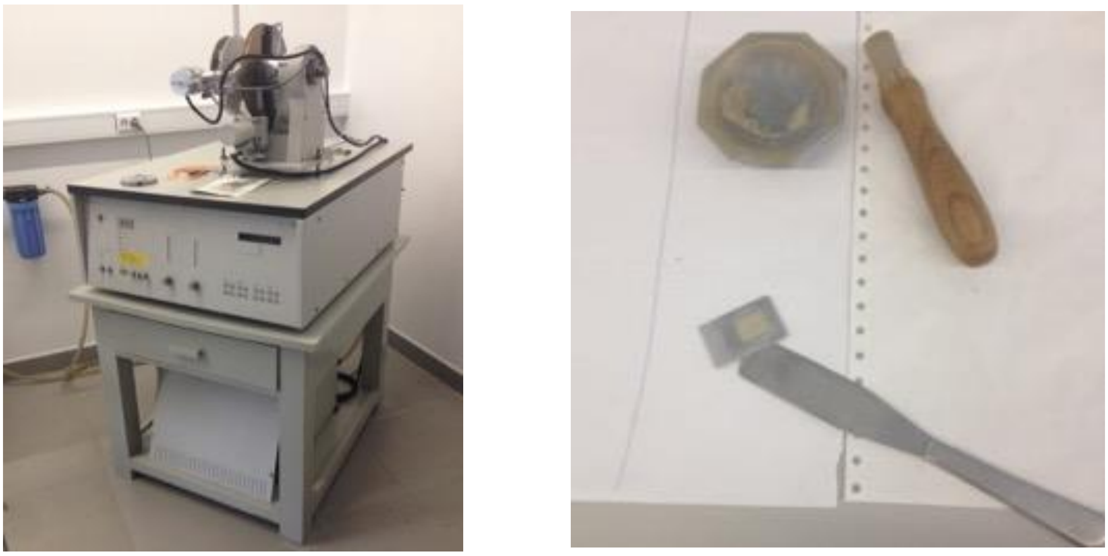
6.4.1. PHILIPS

A) MATERIALS

For the analysis itself, we used an XRD analyser **Philips PW3710 Automatic Powder Diffractometer** of the LGXR-UC[61]. This machine uses an air-cooled X-ray tube (Cu), with a voltage of 40kV and a current of 20mA.

B) METHODOLOGIES AND TECHNIQUES

The XRD diffractometer (Figure 47a) requires prepared samples; therefore, they were previously prepared using the homogenising, drying, milling, and sieving (1mm) processes. Even after the sample was prepared, we milled it in another agate mortar to be certain that it was completely powdered before we put it into a suitable sample holder (Figure 47b), which was loaded into the goniometer and prepared to be read by the analyser. The samples analysed were all the surface samples (S1 to S12) and six samples from the borehole logging (B1.S5.2.2, B1.S5.3.2, B1.S5.4.2, B2.S2.2.2, B2.S2.3.2, and B2.S2.4.2).



(a) (b)

Figure 47 - (a) Philips PW3710 XRD diffractometer (b) Preparation of powdered sample.

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[61] Laboratory of Geochemistry and X-Ray from the Department of Earth Sciences, Faculty of Sciences and Technology, University of Coimbra.

6.5. SCANNING ELECTRON MICROSCOPY ANALYSIS

This is a versatile analytical tool, which allows for material surface analysis to be carried out very accurately. Its high resolution allows accurate image quality at very high magnifications, and an X-ray analyser can simultaneously analyse elemental composition, even up to micrometre resolution (Top Analytica, n.d.).

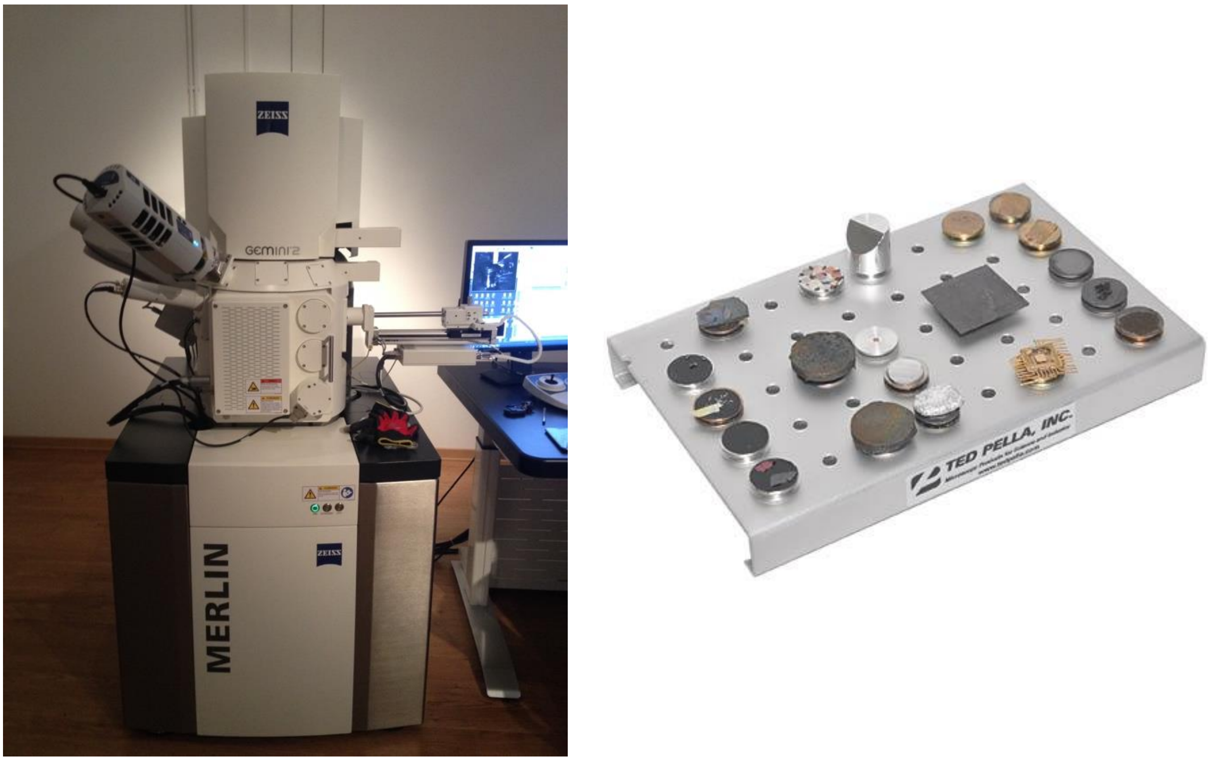
6.5.1. ZEISS

A) MATERIALS

For this type of analysis, we used a SEM-EDS/WDS analyser **Zeiss Merlin with the Gemini II column** from the LED&MAT-IPN[62]. This machine uses an X-ray source with a voltage of between 20 to 30kV and a current of up to 300nA.

B) METHODOLOGIES AND TECHNIQUES

For this analysis, the samples didn't require any previous preparation, as they were fine enough for the process of gravity separation, in order to get the mineral concentrate from the original sample. For this analysis, only three samples were selected, one from the surface sampling (S10) and two from the borehole logging (B1.S5.4.2 and B2.S2.3.2). The sample was then put into a sample holder, in order to be suitable for the analyser (Figure 48), which gave us the results.



(a) (b)

Figure 48 - (a) SEM Zeiss Merlin (b) Specimen sample holder.

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[62] Laboratory for Wear, Testing & Materials from the Pedro Nunes Institute.

6.6. X-RAY FLUORESCENCE ANALYSIS

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding it with high-energy X-rays or gamma rays. XRF is capable of qualifying any element, because this type of analysis is based on the measurement of the intensity of the characteristic X-rays emitted by the elements that constitute the sample we are analysing.

The purpose of this analysis was to trace the critical metals (Be, Mg, Cr, Co, Ga, Ge, Nb, In, Sb, W, and REEs) and the base metals (Ni, Cu, Zn, Sn, and Pb) that were more likely to appear in the samples collected at the fine tailings dams, at Barroca Grande. Two different XRF analysers were used (Thermo Fisher and Panalytical) to compare and obtain more accurate and precise results. It should be noted that the first analyser (Thermo Fisher) was used as a first test to guide us to what we wanted to trace, and the second analyser (Panalytical) was used with a more precise operation mode (Omnian and especially Pro-Trace) to give us the content in the aforementioned critical metals.

6.6.1. THERMO FISHER

A) MATERIALS

Thermo Fisher Scientific Niton™ XL3t GOLDD+ of the LG-UC[63], allowed us to analyse laboratory-grade samples, or even test the samples on site with little or no sample preparation, and use that geochemical data for research purposes, process control, quality assurance, and other operational decisions (concentration measurement, ore trading, etc.) in production and mineral processing. This analyser can also identify element concentrations at low levels, even at or below the averages naturally found in the Earth’s crust. It is the ideal tool for measuring elemental concentrations in ores, soils, sediments, tails, mill heads, etc. (Thermo Fisher, 2008). This machine has an X-ray source with an Ag anode, which has a voltage of 50kV and a current of 200µA.

B) METHODOLOGIES AND TECHNIQUES

With this analyser, we analysed all the samples (12+12) from both types of sampling. For the surface sampling, we used two different options, the TestAllGeo and the MiningCu/Zn, and for the borehole logging analyses, we only used the MiningCu/Zn option.

Each point that was read by this portable XRF analyser was divided into four different readings depending on the type of elements:

- ✓ 0-30 seconds – heavy elements;
- ✓ 30-60 seconds – low energy elements;
- ✓ 60-90 seconds – high energy elements;
- ✓ 90-120 seconds – light elements.

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[63] Laboratory of Geotechnics from the Department of Earth Sciences, Faculty of Sciences and Technology, University of Coimbra.

SURFACE SAMPLING:

In order to carry out a preliminary analysis of the 12 samples, using the operation mode called **TestAllGeo**[64], the samples were prepared using homogenisation and quartering, drying at 50°C, milling, and sieving at 1mm. They were then put into a proper recipient and sealed with cling film, before being put onto the support of the XRF analyser in order to be analysed – Figure 49. Using this option, each sample was analysed taking into consideration 37 different chemical elements.

Overall, 59 points were analysed, and each one took 120 seconds to scan, with an average of 5 points per sample. (APPENDIX IV)

(a) (b)

Figure 49 - (a) Prepared surface samples (b) Surface sample ready to be analysed.

In order to carry out a more specific analysis of the 12 samples, using the same analyser but with a different operation mode called **MiningCu/Zn**[65], they were physically prepared using only the homogenisation and quartering processes (Figure 50a). They were then put onto a tray and analysed by placing the portable analyser directly onto the surface of the sample, protecting it using the appropriate cover – Figure 50b. Using this option, each sample was analysed taking into consideration 33 different chemical elements.

Overall, 148 points were analysed, and each one took 120 seconds to scan, with an average of between 10 and 15 points per sample. (APPENDIX V)

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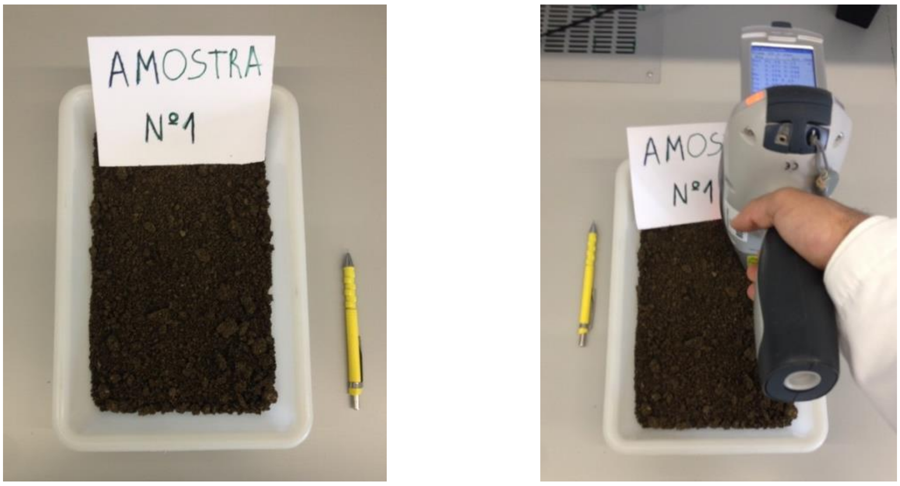
[64] Using this option, the manufacturers combined mining and soil modes. Mining mode offers a better calibration when some elements reach a high level, while soil mode offers a better scan of trace elements when diluted in a Si-Al matrix.

[65] It's ideal for detection of metal concentration in light matrices. A wide range of elements can be determined using this mode: Mg, Al, Si, P, S, Cl, As, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, W, Pb, Bi, Zr, Nb, Mo, Sn, Ba, Sb, Cd, Pd, Sr, Rb, Se, and Ag and Au.



(a) (b)

Figure 50 - (a) Prepared sample S1 (b) Sample S1 being analysed by the XRF portable analyser.

BOREHOLE LOGGING:

Three halves of these PVC tubes, from each borehole of the two fine tailings dams (FTD 1 and 2A), were analysed using this portable analyser and placing it directly onto the surface of the sample, protecting it using the appropriate cover. Therefore, a total of 12 halves were analysed from the four boreholes (B1S4, B1S5, B2S2 and B2S3) – Figure 51. These halves/samples were analysed using the sample type "soils & minerals", called **Mining Cu/Zn**, from this XRF analyser, and we tried to cover as much colour and grain-size differences as we could see, with the purpose of obtaining a wide variety of chemical elements. Using this option, each sample was analysed taking into consideration 35 different chemical elements. From those 35 chemical elements, there were only 3 we were unable to read, because they were under the Limit of Detection ("<LOD"): Sb, Pd, and Se.

In the end, 215 points were analysed, and each one took 120 seconds to scan, with an average of 10 points per sample. (APPENDIX V)

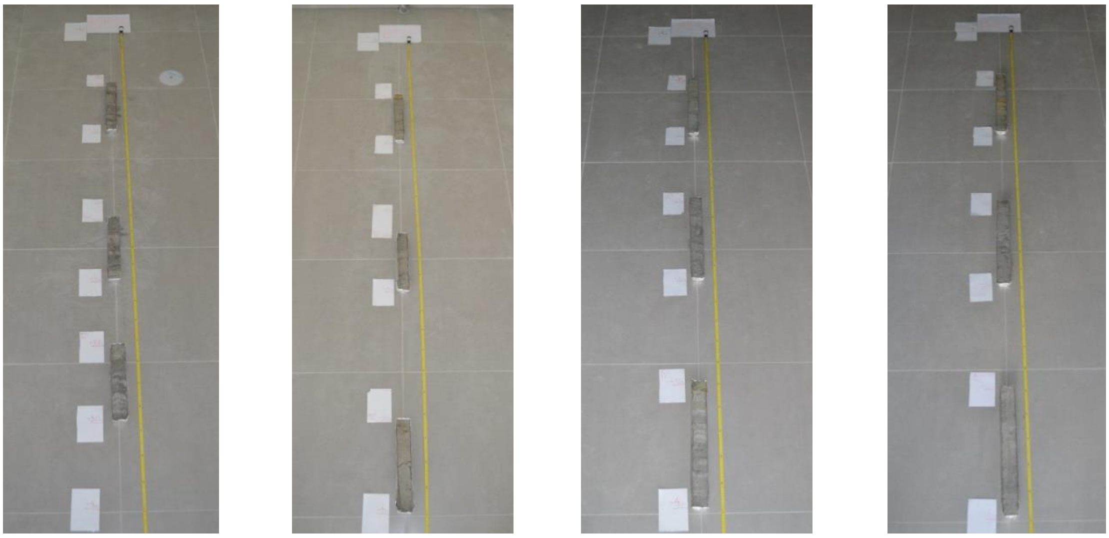


Figure 51 - Overview of the boreholes B1S4, B1S5, B2S2 and B2S3 (from left to right).

6.6.2. PANALYTICAL

A) MATERIALS

For this analysis, we used a **PANalytical Axios^{mAX}** Wavelength-Dispersive X-Ray Fluorescence spectrometer (WD-XRF) from LED&MAT-IPN[66], which allowed us to obtain more precise results from the samples, which were previously homogenised, quartered, milled, and sieved (up to 0.125mm), as well as prepared as pressed pellets. This XRF analyser can handle a wide variety of sample types, such as solids, pressed powders, fused beads, loose powders and liquids. The software is scalable according to the operation mode, and in the case at hand, we used two operation modes: Omnian and Pro-Trace. This machine as an X-ray source of Rh anode.

B) METHODOLOGIES AND TECHNIQUES

As previously mentioned, with this XRF analyser (Figure 52), we were able to use two operation modes: Omnian (standardless analysis[67]) and Pro-Trace (standard analysis[68]). The first one took around 25 minutes per sample, and we used it to identify the major elements[69] (more specifically the critical metal, Mg, which appears in the oxide form MgO) - APPENDIX VI - while the second one took around 1 hour per sample, and was used to detect trace elements[70], such as critical metals and semi-metals (Cr, Co, Ga, Ge, Y, Nb, Sb, La, Ce, and W) and base metals (Ni, Cu, Zn, Sn, and Pb) – APPENDIX VII. The samples selected for this analysis were all the surface samples (S1 to S12) and six borehole logging samples (B1.S5.2.2, B1.S5.3.2, B1.S5.4.2, B2.S2.2.2, B2.S2.3.2, and B2.S2.4.2).

Figure 52 - PANalytical Axios^{mAX} XRF spectrometer.

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[66] Laboratory for Wear, Testing and Materials at the Pedro Nunes Institute.
[67] Calibrated from the fabric with fundamental parameters and theory standards.
[68] With the help of the calibration lines method with the same matrix and standards.
[69] Elements that compose 95% of the Earth's crust (Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, and P) – SGS, n.d.
[70] Elements which are found at the 10 – 10,000ppm level in rocks, ores, soils, etc – SGS, n.d..

UNIVERSITY OF COIMBRA
FACULTY OF SCIENCES AND TECHNOLOGY
Department of Earth Sciences

CHAPTER 7.

RESULTS AND DISCUSSION OF RESULTS

CHAPTER 7. RESULTS AND DISCUSSION OF RESULTS

7.1. GRANULOMETRICAL DATA

7.1.1. LASER DIFFRACTION PARTICLE SIZE ANALYSIS

With this LDPS analysis, we proposed to do a preliminary characterisation of the grain size from the tailings of the two fine tailings dams considered in this study, using the laser diffraction technique and methodologies briefly described in Chapter 6, and using grain size scale, parameters, and descriptive terminology based on the GRADISTAT program[71] developed by Blott & Pye (2001) - Table 14.

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[71] Grain size statistics program developed by Blott & Pye (2001). For the sorting, skewness, and kurtosis, the geometric method of moments of the same authors was used.

Table 14 - Granulometric classification of the FTD 1 and FTD 2A (according to Blott & Pye, 2001).

Grain-size characterisation (FTD 1 and FTD 2A)																			
Type of sampling	**FTD**	**Sample**	**Depht**	**Sand (%)**	**Silte (%)**	**Clay (%)**	**Fines (%)**	**Mean**	**Classification (Blott & Pye, 2001)**	**Median**	**Classification (Blott & Pye, 2001)**	**Mode**	**Classification (Blott & Pye, 2001)**	**S.Deviation**	**Classification (Blott & Pye, 2001)**	**Skewness**	**Classification (Blott & Pye, 2001)**	**Kurtosis**	**Classification (Blott & Pye, 2001)**
			m	**2mm-63μm**	**63-4μm**	**<4μm**	**<63μm**	**mm**		**mm**		**mm**		**value**		**value**		**value**	
Surface Sampling	**FTD 2A**	**S1**	0.00-0.30	89.74	8.96	1.33	10.29	0.32	medium sand	0.46	medium sand	0.57	coarse sand	3.60	poorly sorted	-1.82	very fine skewed	3.98	leptokurtic
		S2	0.00-0.30	81.85	15.23	2.82	18.05	0.20	fine sand	0.31	medium sand	0.47	medium sand	4.46	very poorly sorted	-1.45	very fine skewed	1.81	platykurtic
		S3	0.00-0.30	70.47	26.00	3.56	29.56	0.13	fine sand	0.19	fine sand	0.57	coarse sand	5.13	very poorly sorted	-0.89	fine skewed	0.26	very platykurtic
		S4	0.00-0.30	50.89	41.76	7.35	49.11	0.06	very coarse silt	0.07	very fine sand	0.13	fine sand	5.50	very poorly sorted	-0.40	symmetrical	-0.55	very platykurtic
		S5	0.00-0.30	69.56	26.61	3.74	30.35	0.11	very fine sand	0.15	fine sand	0.43	medium sand	4.68	very poorly sorted	-0.92	fine skewed	0.50	very platykurtic
		S6	0.00-0.30	83.83	13.99	2.15	16.14	0.18	fine sand	0.24	fine sand	0.36	medium sand	3.76	poorly sorted	-1.44	very fine skewed	2.58	mesokurtic
		S7	0.00-0.30	87.14	11.38	1.55	12.93	0.21	fine sand	0.28	medium sand	0.43	medium sand	3.46	poorly sorted	-1.57	very fine skewed	3.34	mesokurtic
		S8	0.00-0.30	78.14	18.35	3.51	21.86	0.18	fine sand	0.31	medium sand	0.52	coarse sand	5.07	very poorly sorted	-1.26	fine skewed	0.94	very platykurtic
		S9	0.00-0.30	64.40	31.46	4.16	35.62	0.09	very fine sand	0.10	very fine sand	0.12	very fine sand	4.63	very poorly sorted	-0.70	fine skewed	0.45	very platykurtic
		S10	0.00-0.30	74.92	21.96	3.15	25.11	0.14	fine sand	0.19	fine sand	0.47	medium sand	4.56	very poorly sorted	-1.08	fine skewed	0.89	very platykurtic
		S11	0.00-0.30	86.04	13.38	0.65	14.03	0.17	fine sand	0.19	fine sand	0.19	fine sand	3.08	poorly sorted	-1.06	fine skewed	2.10	platykurtic
		S12	0.00-0.30	80.19	17.69	2.12	19.81	0.19	fine sand	0.30	medium sand	0.52	coarse sand	4.30	very poorly sorted	-1.29	fine skewed	1.48	very platykurtic
Borehole Logging	**FTD 1**	**B1.S5.2.2**	1.59-2.00	23.12	66.28	10.63	76.91	0.02	coarse silt	0.02	coarse silt	0.04	very coarse silt	3.80	poorly sorted	-0.33	symmetrical	-0.27	very platykurtic
		B1.S5.3.2	2.33-2.66	10.38	74.17	15.40	89.57	0.01	medium silt	0.01	medium silt	0.01	medium silt	3.35	poorly sorted	-0.09	symmetrical	-0.04	very platykurtic
		B1.S5.4.2	3.63-4.00	9.53	75.34	15.18	90.52	0.01	medium silt	0.01	medium silt	0.01	medium silt	3.29	poorly sorted	-0.19	symmetrical	-0.07	very platykurtic
	FTD 2A	**B2.S2.2.2**	1.50-2.00	60.97	32.85	6.17	39.02	0.08	very fine sand	0.11	very fine sand	0.43	medium sand	5.46	very poorly sorted	-0.67	fine skewed	-0.32	very platykurtic
		B2.S2.3.2	2.50-3.00	72.21	23.56	4.24	27.80	0.12	very fine sand	0.19	fine sand	0.43	medium sand	4.97	very poorly sorted	-1.04	fine skewed	0.43	very platykurtic
		B2.S2.4.2	3.50-4.00	54.59	38.59	6.83	45.42	0.06	very coarse silt	0.08	very fine sand	0.17	fine sand	5.49	very poorly sorted	-0.47	fine skewed	-0.51	very platykurtic

SURFACE SAMPLING

Regarding the 12 surface samples collected from FTD 2A, at a depth of between 0 to 0.30m, we verified that the samples were composed, in average, by 24% of fines[72] (<63µm), with a grain size ranging from very **fine sand to medium sand,** and occasionally coarse sand. The grains were mainly **very poorly sorted** and **fine skewed** (negative asymmetry), and presented mainly **very platykurtic** curves[73]. In Chart 11, the negative asymmetry is visible, mainly from all the 12 samples analysed, with the exception of sample S9 (which can be considered an outlier), as well as the very platykurtic curves from the samples S3, S4, S5, S8, S9, S10, and S12, with the exception of the mesokurtic curves, from S6 and S7, and the leptokurtic curve from sample S1.

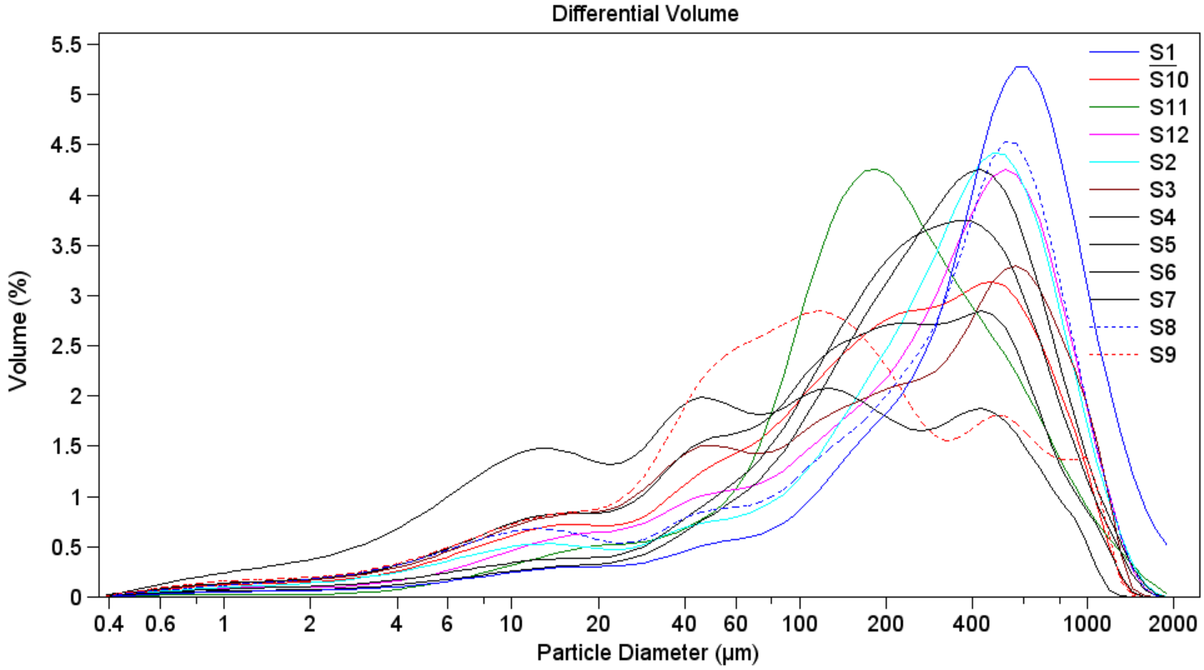

Chart 11 - Grain size distribution in the 12 surface samples from FTD 2A.

BOREHOLE LOGGING

Comparing the results from the 6 borehole samples, collected from a depth between 1 to 4 metres, we were able to verify that, in general, FTD 1 is composed of more fine grain (silt) than FTD 2A, which presented a coarser grain (sand), as already considered in the Ávila, *et al*. (2008) study. This was already established when we could literally see that the composition of the borehole samples from FTD 1 were finer than the others. We could also see this grain-size difference when, during the laboratory procedures, we compared the amount of material needed to constitute the same weight, which for the FTD 1 samples (lighter) required much more material than FTD 2A samples (denser).

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[72] Result calculated by adding the percentage of silt and clay.

[73] Regarding the "tailedness" of a curve, which can be "thin-tailed" (platykurtic), normal (mesokurtic), or "fat-tailed" (leptokurtic).

A) FTD 1

Taking into account the borehole B1S5, used to analyse this fine tailings dam, we were able to verify that the samples were composed of between 77 to 91% of fines[74] (<63µm), with a grain size ranging from **medium to coarse silt**. These grains were **poorly sorted** with **symmetrical skewness,** and presented **very platykurtic** curves. Chart 12 shows the very symmetrical "thin-tailed" shape of the curves, which is characteristic of the platykurtic curves, based on the samples B1.S5.3.2. and B1.S5.4.2. These present a similar shape, with a mode value of 14µm, which can indicate the presence of clay minerals. It contains finer grains compared to FTD 2A.

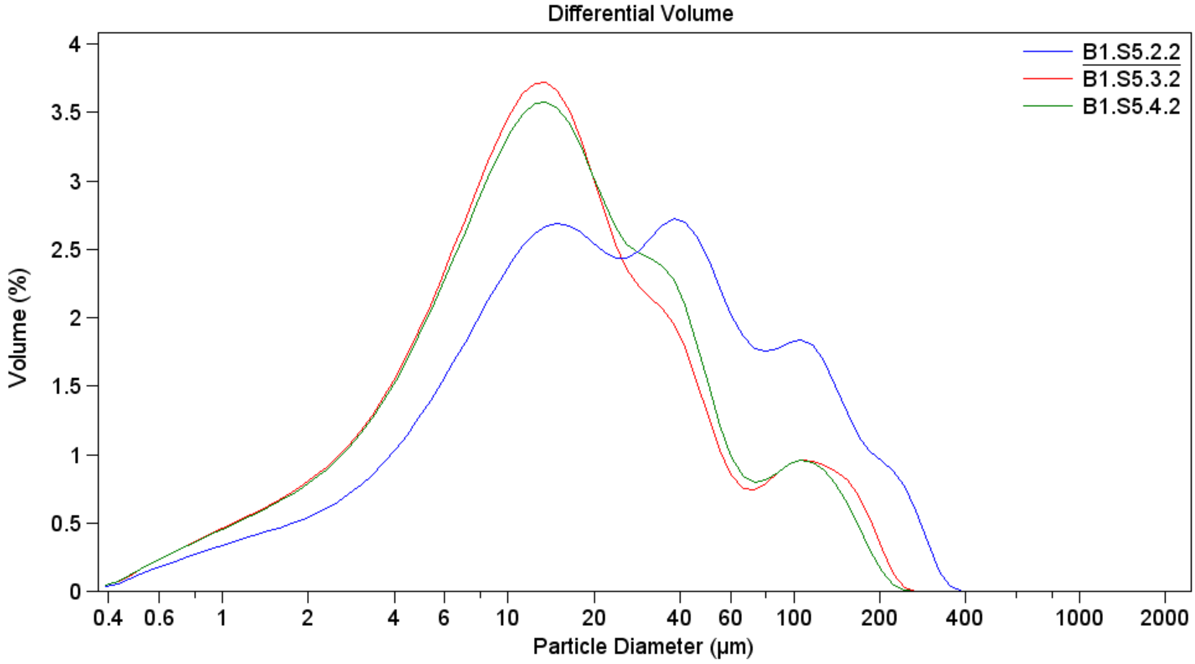

Chart 12 - Grain size distribution in the 3 borehole samples from FTD 1.

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[74] Result calculated by adding the percentage of silt and clay.

B) FTD 2A

Considering the borehole B2S2, we were able to verify that the percentage of fines[75] (<63µm) in these 3 borehole samples was between 28 to 45%, with a grain size ranging from **very fine sand to medium sand**. The grains were **very poorly sorted** with **fine skewness** and **very platykurtic** curves. On Chart 13, we can see the "thin-tailed" shape (very platykurtic) of the asymmetrical curves, with more dispersion of grain-sizes when compared to the borehole B1S5. The samples B2.S2.2.2 and B2.S2.4.2. present as identical in curve shape, and only sample B2.S2.3.2 appears to have a higher volume, ranging from 150µm to 400µm**.** The mode value can be seen as around 500µm, meaning FTD 2A has coarser grains compared to FTD 1.

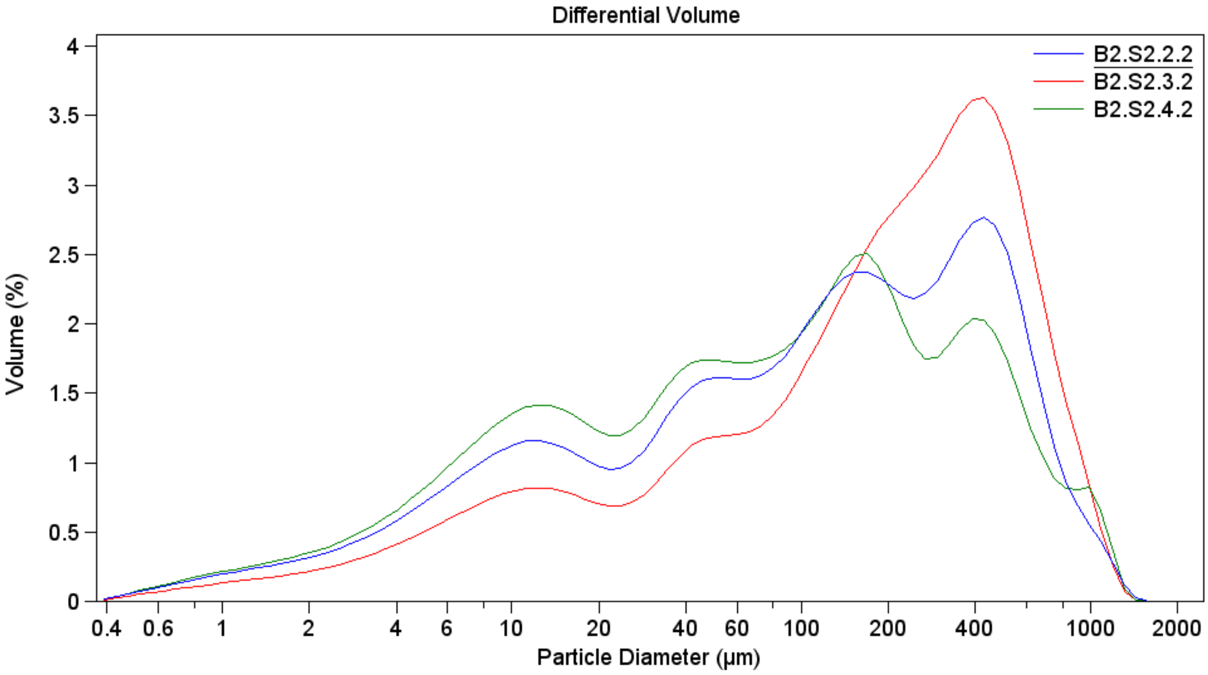

Chart 13 - Grain size distribution in the 3 borehole samples from FTD 2A.

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[75] Result calculated by adding the percentage of silt and clay.

7.2. CHEMICAL-MINERALOGICAL DATA

7.2.1. X-RAY DIFFRACTION ANALYSIS

Regarding mineralogy, we have already made reference to the wide, and sometimes unique, variety of minerals that occur in the Panasqueira deposit (Chapter 4). With the goal of knowing which types of minerals occur in the two fine tailings dams at Barroca Grande, we completed an XRD analysis using the methodologies and techniques described in Chapter 6. The two most abundant minerals are the silicates quartz and muscovite, which was to be expected, as the vein type deposit is composed of quartz integrated in the Schist-Greywacke Complex (SGC), where schist is the main lithology, which can verify the quartz and muscovite existence. These two minerals, plus halite, occurred in all the samples, from both of the fine tailings dams, which were analysed in this analysis (APPENDIX VIII). Other relevant minerals, which occurred in some of the samples, are clay minerals (silicates group), halite (halides group), pyrite (sulphides group), and forsterite (silicates group). The minerals' abbreviations used are according to Whitney & Evans (2010).

SURFACE SAMPLING

With regard to this type of sampling, we were able to verify that the majority of the mineralogy of these samples was composed by quartz, muscovite, albite, and clay minerals. Some other minerals were only identified in these surface samples, such as ilmenite (Ilm), magnesite (Mag), aragonite (Arg), zeolite (Zeo), smectite (Sme), anhydrite (Anh), calcite (Cal), aegirine (Aeg), and larnite (Lrn) – Table 15.

Table 15 - Main mineralogy of the surface sampling samples collected at FTD 2A – abbreviations according to Whitney & Evans (2010), vest.= vestigial (<2%).

SAMPLE	**Mineralogy**																						
	Qtz	**Ms**	**Ab**	**Clay min.**	**Hl**	**Py**	**Sme**	**Hem**	**Arg**	**Ilm**	**Fo**	**Lrn**	**Prh**	**Str**	**Mag**	**Aeg**	**Usp**	**Chr**	**Cal**	**Ap**	**Anh**	**Zeo**	**Lct**
S1	X	X	X	X	X				X	X					Vest.								
S2	X	X	X	X	X					X												X	X
S3	X	X	X	X	X	X							X										
S4	X	X	X	X		X	X		X			X											
S5	X	X	X	X	X	X																	
S6	X	X	X	vest.			X	vest.			X			X							vest.		
S7	X	X	X	vest.	X		X	X		X	X												
S8	X	X	X	X	X		X									X							
S9	X	X	X	X	X		X					X	X							X			
S10	X	X	X	X	X	X									X								
S11	X	X	X	X		X		X				X						X	X				
S12	X	X	X	X					X		X			X			X						

The diffractogram, on which the diffracted intensity of all these surface samples is shown as a function of the scattering angle 2ϴ, is represented in Chart 14, where the similarity of all their intensity peaks is visible, with the exception of sample S11, which can be considered an outlier (red line). On this chart, the characteristic peaks from quartz (Qtz) and muscovite (Ms) are also visible, representing the highest intensity peaks found at 26.6 (2ϴ) for quartz, and at 8.8 (2ϴ) for muscovite. It should be observed that, in between these two major peaks, there is another quartz peak with a lower intensity, although sometimes this can be higher than the muscovite peak. There are also other characteristic peaks from clay minerals (12.5, 2ϴ), albite (22.2, 2ϴ) and pyrite (47.5, 2ϴ).

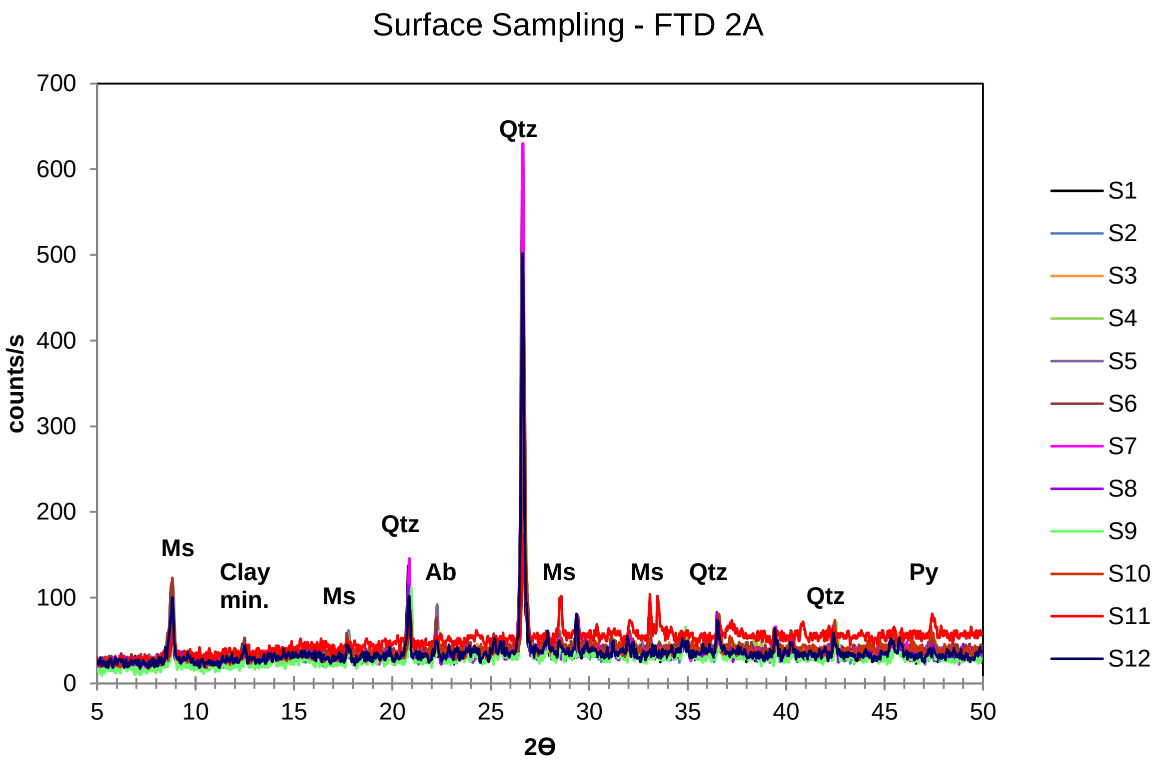

Chart 14 - Diffractogram of the surface samples – FTD 2A.

BOREHOLE LOGGING

Considering the borehole samples, which were collected from the different fine tailings dams (FTD 1 and FTD 2A), a significant increase in the quartz content from the old fine tailings dam to the new one occurred, which may possibly indicate an improvement in the recovery methods of the metals that are exploited there. Hematite (Hem) only occurs in the active fine tailings dam (FTD 2A), and siderite (Sd), prehnite (Prh), apatite (Ap), strontianite (Str), and leucite (Lct) only occur in the inactive fine tailings dam (FTD 1) – Table 16.

Table 16 - Mineralogy of the borehole logging samples collected at FTD 1 and 2A - abbreviations according to Whitney & Evans (2010), vest.= vestigial (<2%).

Sample	**Mineralogy**														
	Qtz	**Ms**	**Ab**	**Clay min.**	**Hl**	**Py**	**Usp**	**Fo**	**Chr**	**Sd**	**Prh**	**Ap**	**Str**	**Hem**	**Lct**
B1.S5.2.2	X	X	X	X	X	vest.		X							vest.
B1.S5.3.2	X	X	X	X				X		X	X	vest.	X		
B1.S5.4.2	X	X	X	X	X	X	X		X	X	vest.				
B2.S2.2.2	X	X	X	X	X	X	X	X	X						
B2.S2.3.2	X	X	X		X	X	X	X						X	
B2.S2.4.2	X	X	X	X	X	X	X								

Although the diffractograms of these borehole samples are very similar in shape – Chart 15 and Chart 16 - the results show that the fine tailings dams possess different mineralogy. Two major intensity peaks are also visible, which, once again, belong to quartz (26.6, 2Ө) and muscovite (8.8, 2Ө). The muscovite peak reaches its highest intensity values in FTD 1, when compared to FTD 2A. Apart from those two main peaks at both of the fine tailings dams, other peaks of quartz (Qtz) and muscovite (Ms) are visible, as well as other characteristic peaks, such as the clay minerals peak (12.5, 2Ө), albite (22.2, 2Ө), ulvöspinel (34.9, 2Ө), and halite (45.5, 2Ө).

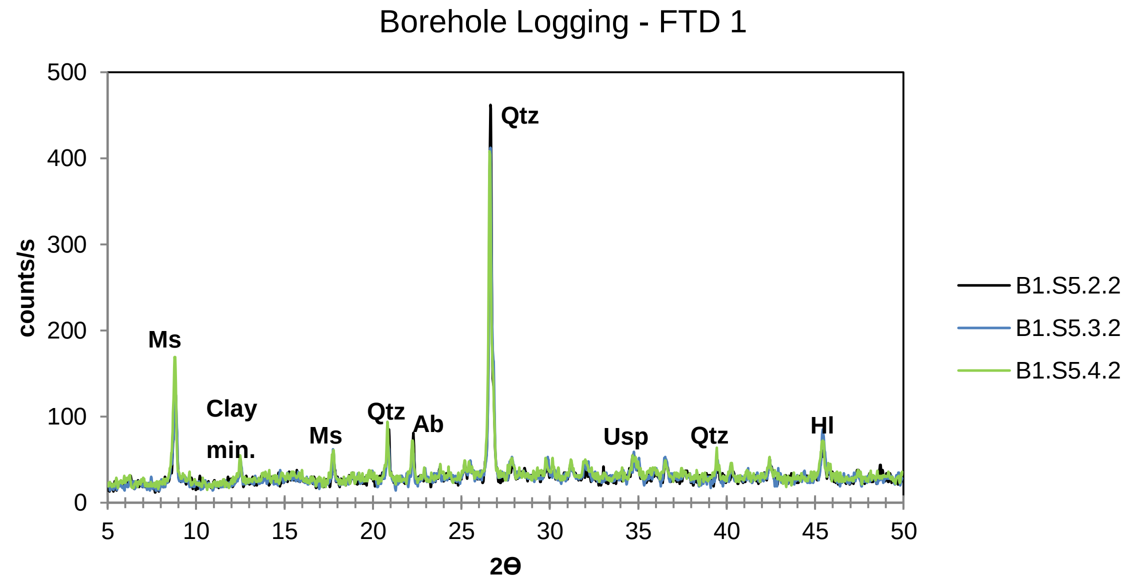

Chart 15 - Diffractogram of the borehole samples – FTD 1.

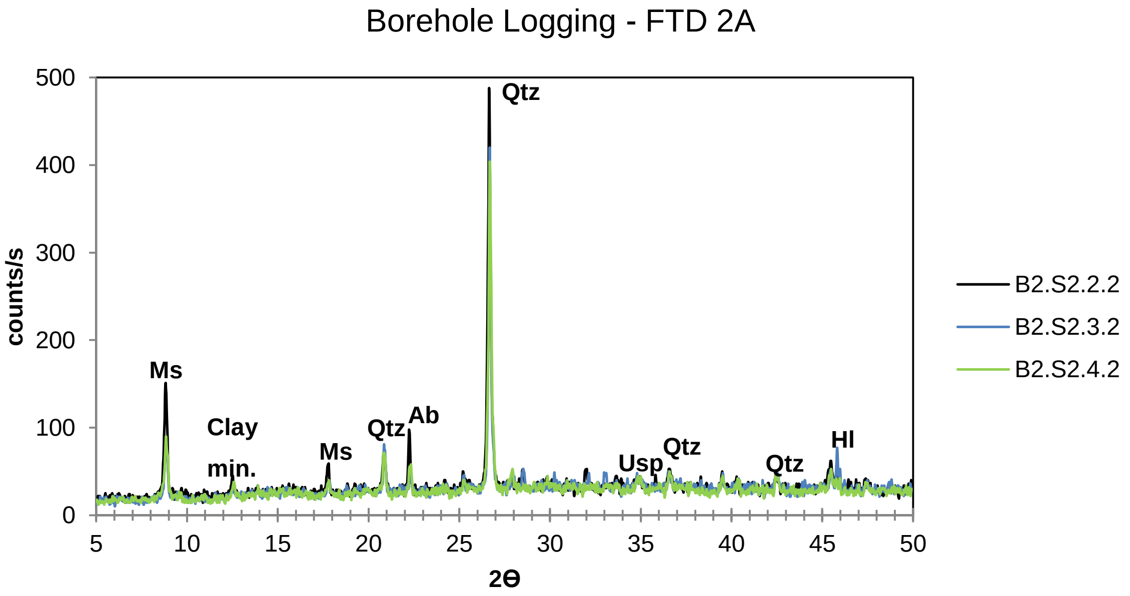

Chart 16 - Diffractogram of the borehole samples – FTD 2A.

7.2.2. SCANNING ELECTRON MICROSCOPY ANALYSIS

This SEM-EDS/WDS analysis was carried out in order to be a complementary and more precise analysis of the main mineralogy from the surface and borehole samples collected at two different fine tailings dams. Through an EDS layered image, we could identify the mineralogy dispersion in the selected samples (S10, B1.S5.4.2, and B2.S2.3.2). These samples were prepared by homogenisation and quartering, and by obtaining the mineral concentrate. It should be noted that for this analysis the samples were coated with a very thin gold (Au) layer to make them more conductive, therefore we ignored the Au presence in all of the samples analysed.

SURFACE SAMPLING

The sample selected to represent all of the 12 surface samples collected at FTD 2A was sample S10 (Figure 54). Looking at Figure 53, the two main particle sizes are visible, one more finely grained, between 50-90µm (majority), and other more coarsely grained, between 100-300µm (minority).

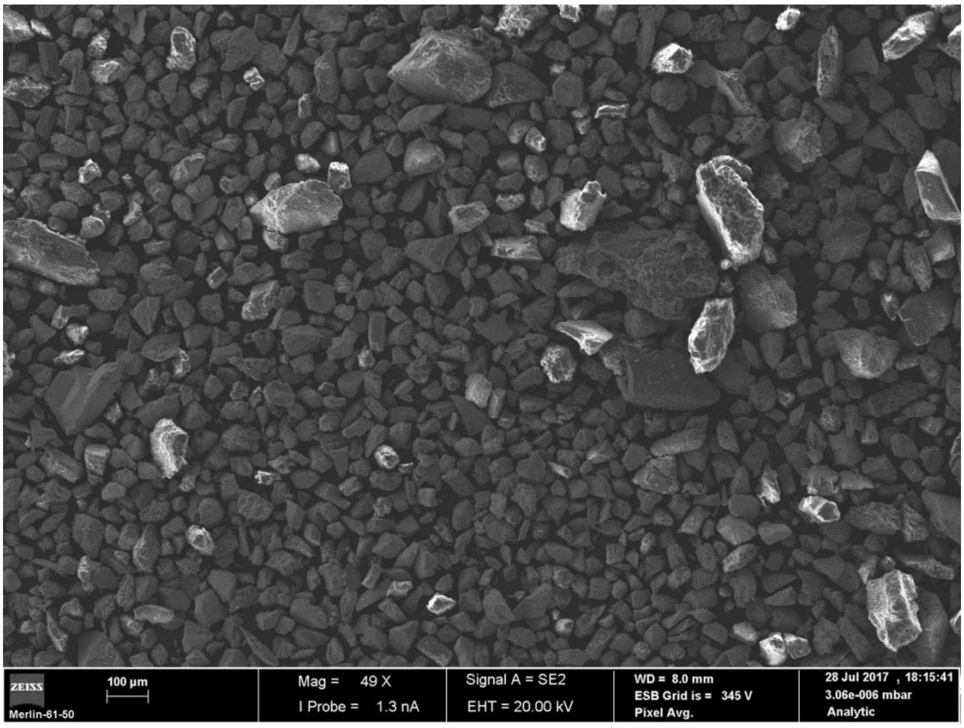

Figure 53 - SEM image of a selected region from the surface sample S10.

After we selected the grains we wanted to map, based on the morphological differences between them, we were able to obtain the spectrum charts of each point, where we can see the peak intensities, characteristic of each chemical element (APPENDIX IX). Following this, assuming the chemistry of the 8 points selected, we were able to produce an EDS layered image of the selected region and understand more about this sample’s mineralogy, which is represented in Figure 54.

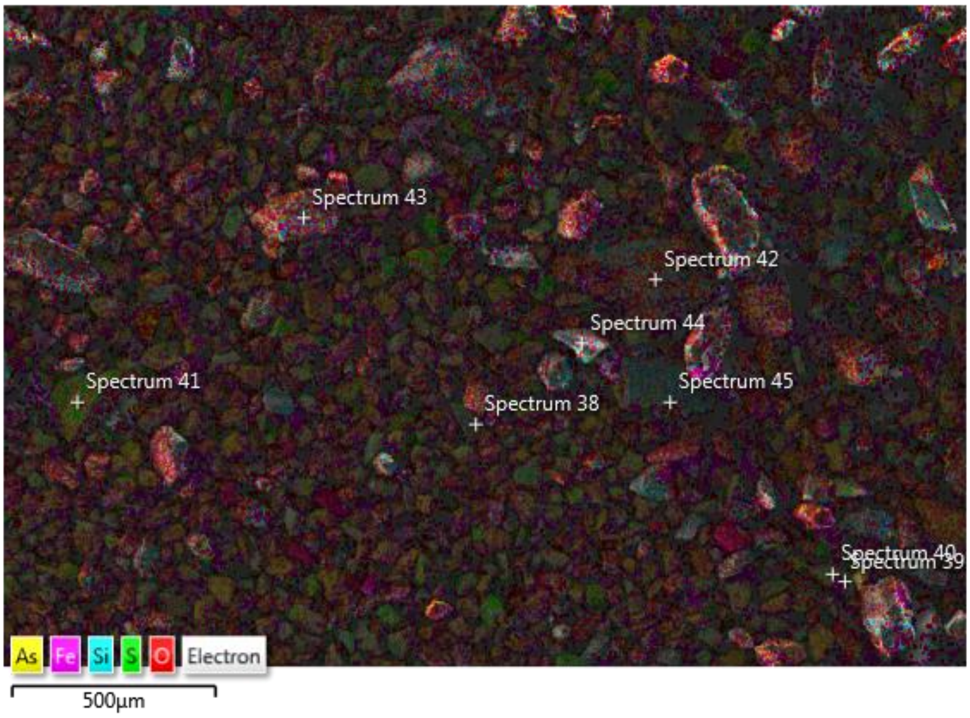

Figure 54 - EDS layered image of a selected region from the surface sample S10.

Apart from the silicates quartz (SiO_2) and muscovite ($KAl_2O_{10}(OH, F)_2$), in this selected region there were good quantities and dispersion of As, Fe, and S (arsenopyrite) and a low content in W and Cu. (APPENDIX IX)

Although presented as a low percentage, the magnesium (Mg) appears in Spectrum 42 and 43 (Figure 54), which was also verified by the XRD analysis of the selected sample (S10). Spectrum 38 (Figure 54) also presents a huge percentage of Cu, S, and Fe, which is characteristic of the minerals chalcopyrite ($CuFeS_2$) and pyrite (FeS_2), expected to occur at the sampling site.

BOREHOLE LOGGING

Regarding this sampling type, one representative sample was selected from each FTD. For FTD 1, the borehole sample B1.S5.4.2 was considered, and for FTD 2A the borehole sample B2.S2.3.2 was considered.

A) FTD 1

The selected sample B1.S5.4.2 from this fine tailings dam appear, in the selected area, to have a majority of fine and medium grains (50-100µm) and a minority of coarser grains (200-400µm), some of which have a slaty cleavage (Figure 55).

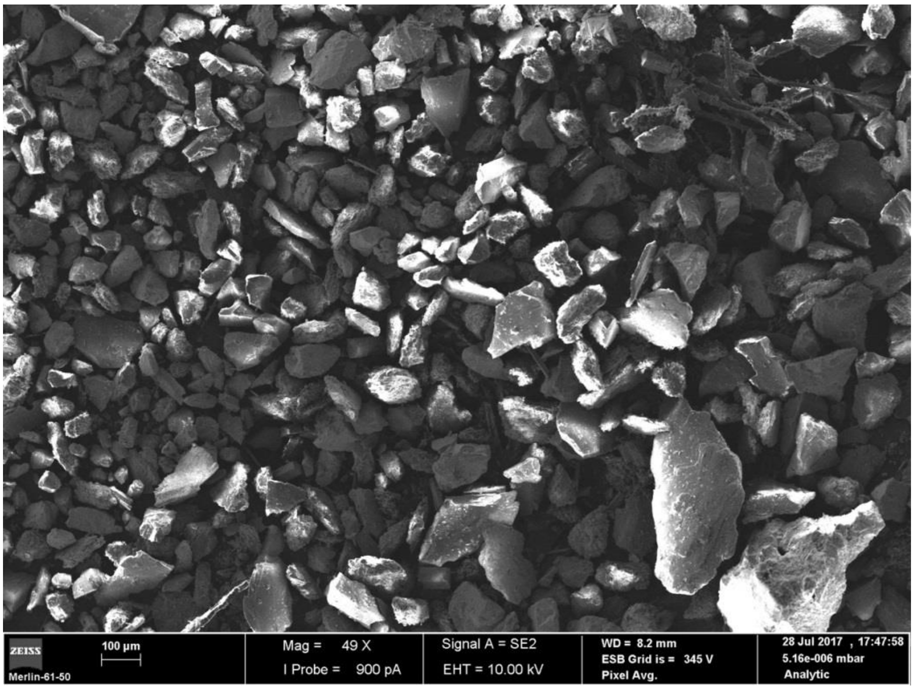

Figure 55 - SEM image of a selected region from the borehole sample B1.S5.4.2.

After we selected the grains we wanted to map, based on the morphological differences between them, we were able to obtain the spectrum charts of each point, where we can see the peak intensities, characteristic of each chemical element (APPENDIX X). Following this, assuming the chemistry of the 8 points selected, we were able to produce an EDS layered image of the selected region and understand more about this sample's mineralogy, which is represented in Figure 56.

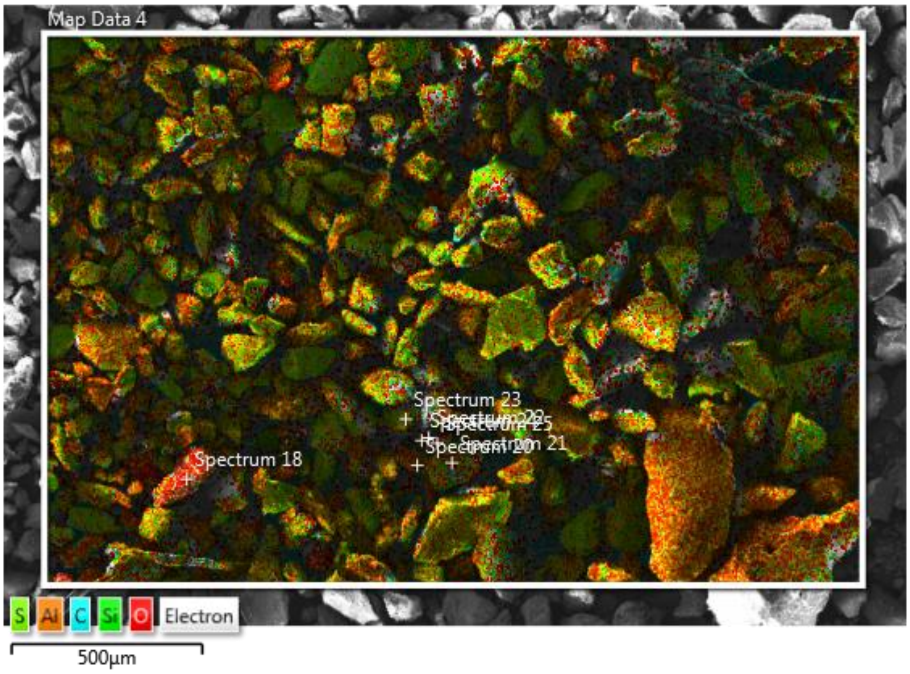

Figure 56 - EDS layered image of a selected region from the borehole sample B1.S5.4.2.

Composed mainly of the silicates quartz and muscovite, arsenopyrite (FeAsS) is also present, especially in Spectrum 21, and wolframite in Spectrum 25 (Figure 56). Looking to the layered image of each selected element, we can identify a reasonable content of critical metals such as Ga, Nb, and especially Ge. (APPENDIX X)

B) FTD 2A

The selected sample B2.S2.3.2 from this fine tailings dam appears, in the selected area, to have some coarser grains, which also possess a more slaty cleavage (Figure 57).

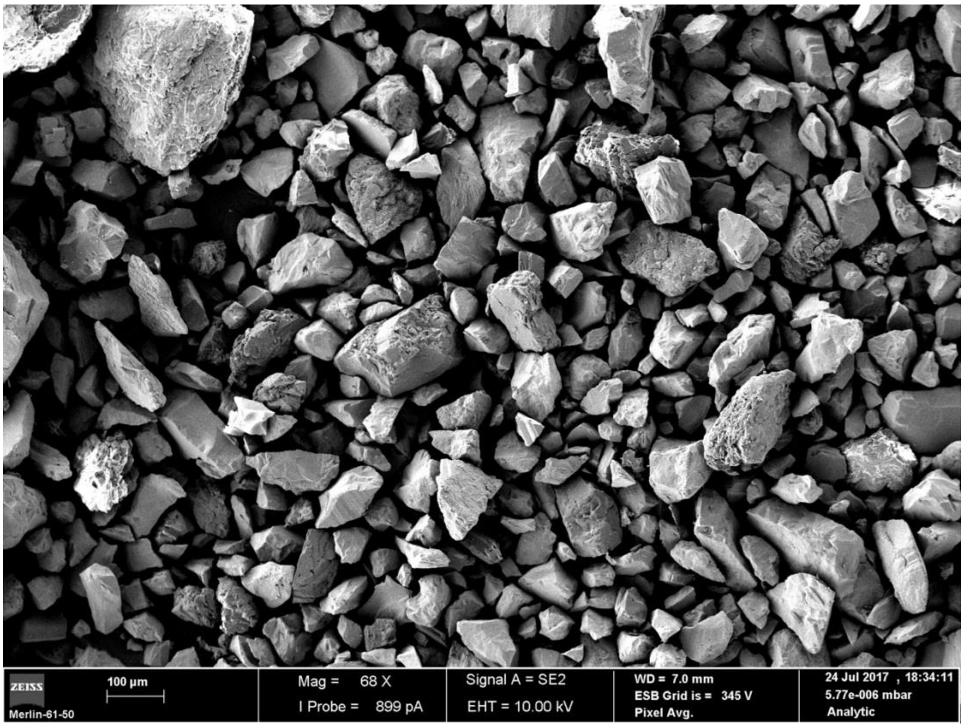

Figure 57 - SEM image of a selected region from the borehole sample B2.S2.3.2.

After we selected the grains we wanted to map, based on the morphological differences between them, we were able to obtain the spectrum charts of each point, where we can see the peak intensities, characteristic of each chemical element (APPENDIX XI). Following this, assuming the chemistry of the 4 points selected, we were able to produce an EDS layered image of the selected region and understand more about this sample's mineralogy, which is represented in Figure 58.

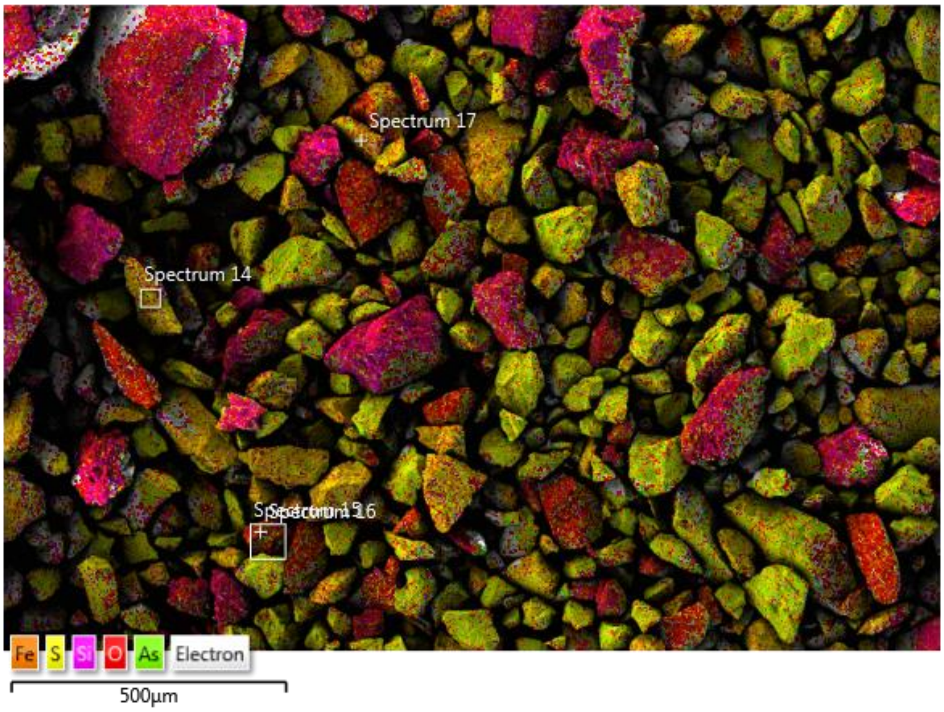

Figure 58 - EDS layered image of a selected region from the borehole sample B2.S2.3.2.

Although it has some quartz minerals (SiO_2) it is mainly composed of Fe, As and S, meaning it is rich in arsenopyrite (FeAsS). Tungsten is evident in Spectrum 15 and 16 (Figure 58), while sphalerite is represented in Spectrum 14 and 17 (Figure 58). Regarding the layered image of each selected element, we can identify a small content in the critical metal Ga. (APPENDIX XI)

7.3. CHEMICAL DATA

7.3.1. X-RAY FLUORESCENCE ANALYSIS

THERMO FISHER

The same samples collected superficially, and all of the borehole samples collected in the fine tailings dams FTD 1 and FTD 2A, were analysed by XRF using a portable spectrometer: Thermo Fisher Scientific Niton^{TM} XL3t GOLDD+, in the operation mode Mining Cu/Zn. As a portable piece of equipment, with lower analytical capacity, compared to the benchtop equipment that was also used, it was intended for use in evaluating the capacity of this portable piece of equipment in identifying and differentiating critical elements and their related base metals, which was the aim of this study. The results for the base metals, and critical metals and semi-metals, are presented in Table 17. The major element magnesium (which is also a critical metal for the EU) was identified with this equipment, and is expressed as a percentage with values under its upper continental crust abundance, which in is oxide form (MgO) is of 2.48ppm, according to the study of Rudnick & Gao, 2014. The sample S11 was omitted from the results as it was considered an outlier[76].

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[76] Data point which is not representative of the case we are studying and it may influence the overall results. In this case the sample S11 wasn't considered in the elaboration of the results; however it can be conferred in APPENDIX V.

Table 17 - Results from XRF Thermo Fisher analysis (Mining Cu/Zn) for critical metals and semi-metals (red) and base metals (yellow).

METHODOLOGY	TYPE OF SAMPLING	FTD	SAMPLE	DEPTH	CHEMICAL ELEMENT										
					Mg	Cr	Co	Ni	Cu	Zn	Nb	Sn	Sb	W	Pb
				m	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
XRF THERMOFISHER (MINING Cu/Zn)	SURFACE SAMPLING	FTD 2A	S1	0.00-0.30	1.91	148.46	<LOD	95.00	829.23	1365.38	<LOD	293.08	<LOD	512.31	71.54
			S2	0.00-0.30	1.60	107.69	<LOD	115.83	2062.31	2723.85	<LOD	312.31	<LOD	866.92	113.08
			S3	0.00-0.30	1.15	124.43	<LOD	93.33	1931.43	1845.71	<LOD	530.71	<LOD	1594.29	114.29
			S4	0.00-0.30	0.93	124.17	<LOD	95.00	2550.00	5867.50	<LOD	580.00	<LOD	1356.67	103.33
			S5	0.00-0.30	0.90	114.55	<LOD	88.89	2431.82	4250.91	<LOD	576.36	<LOD	1457.27	107.27
			S6	0.00-0.30	1.11	120.91	<LOD	120.00	2420.91	5943.64	<LOD	475.45	20.00	1397.27	100.91
			S7	0.00-0.30	1.21	118.18	<LOD	106.00	2578.18	6400.91	<LOD	477.27	<LOD	1109.09	86.36
			S8	0.00-0.30	0.75	128.46	<LOD	90.00	1854.62	4255.38	<LOD	343.08	<LOD	953.85	99.23
			S9	0.00-0.30	0.87	130.00	<LOD	90.00	3637.27	6294.55	<LOD	703.64	<LOD	2500.00	163.64
			S10	0.00-0.30	1.80	146.43	<LOD	104.62	1838.57	8143.57	<LOD	636.43	<LOD	1855.00	102.86
			S12	0.00-0.30	1.61	134.62	<LOD	133.33	1509.23	3883.08	<LOD	316.15	<LOD	1204.62	133.08
			Mean		**1.26**	**127.08**	-	**102.91**	**2149.42**	**4634.04**	-	**476.77**	**20.00**	**1346.12**	**108.69**
			Median		**1.15**	**124.43**	-	**95.00**	**2062.31**	**4255.38**	-	**477.27**	**20.00**	**1356.67**	**103.33**
			SD		**0.40**	**12.51**	-	**14.64**	**714.34**	**2106.99**	-	**143.15**	-	**531.23**	**24.00**
			CV (%)		**32.04**	**9.84**	-	**14.23**	**33.23**	**45.47**	-	**30.02**	-	**39.46**	**22.08**
			Min		**0.75**	**107.69**	-	**88.89**	**829.23**	**1365.38**	-	**293.08**	**20.00**	**512.31**	**71.54**
				Max	**1.91**	**148.46**	-	**133.33**	**3637.27**	**8143.57**	-	**703.64**	**20.00**	**2500.00**	**163.64**
	BOREHOLE LOGGING	FTD 1	B1.S4.2.2	1.58-2.00	1.35	140.00	<LOD	90.00	2080.00	5390.00	20.00	310.00	-	2030.00	-
			B1.S4.3.2	2.63-3.00	1.12	120.00	250.00	90.00	2680.00	7360.00	<LOD	460.00	-	2720.00	-
			B1.S4.4.2	3.33-3.67	1.04	130.00	<LOD	70.00	3170.00	7740.00	20.00	510.00	-	1950.00	-
			Mean		**1.17**	**130.00**	**250.00**	**83.33**	**2643.33**	**6830.00**	**20.00**	**426.67**	-	**2233.33**	-
			Median		**1.12**	**130.00**	**250.00**	**90.00**	**2680.00**	**7360.00**	**20.00**	**460.00**	-	**2030.00**	-
			SD		**0.16**	**10.00**	-	**11.55**	**545.92**	**1261.47**	-	**104.08**	-	**423.36**	-
			CV (%)		**13.80**	**7.69**	-	**13.86**	**20.65**	**18.47**	-	**24.39**	-	**18.96**	-
			Min		**1.04**	**120.00**	**250.00**	**70.00**	**2080.00**	**5390.00**	**20.00**	**310.00**	-	**1950.00**	-
			Max		**1.35**	**140.00**	**250.00**	**90.00**	**3170.00**	**7740.00**	**20.00**	**510.00**	-	**2720.00**	-
			B1.S5.2.2	1.59-2.00	0.96	120.00	<LOD	100.00	2130.00	5060.00	20.00	300.00	-	2080.00	-
			B1.S5.3.2	2.33-2.66	0.93	130.00	<LOD	60.00	1270.00	4450.00	20.00	260.00	-	1880.00	-
			B1.S5.4.2	3.63-4.00	0.77	140.00	<LOD	50.00	1520.00	4750.00	<LOD	290.00	-	1840.00	-
			Mean		**0.88**	**130.00**	-	**70.00**	**1640.00**	**4753.33**	**20.00**	**283.33**	-	**1933.33**	-
			Median		**0.93**	**130.00**	-	**60.00**	**1520.00**	**4750.00**	**20.00**	**290.00**	-	**1880.00**	-
			SD		**0.10**	**10.00**	-	**26.46**	**442.38**	**305.01**	-	**20.82**	-	**128.58**	-
			CV (%)		**11.45**	**7.69**	-	**37.80**	**26.97**	**6.42**	-	**7.35**	-	**6.65**	-
			Min		**0.77**	**120.00**	-	**50.00**	**1270.00**	**4450.00**	**20.00**	**260.00**	-	**1840.00**	-
			Max		**0.96**	**140.00**	-	**100.00**	**2130.00**	**5060.00**	**20.00**	**300.00**	-	**2080.00**	-
		FTD 2A	B2.S2.2.2	1.50-2.00	1.86	130.00	250.00	110.00	1580.00	5680.00	<LOD	420.00	-	1240.00	-
			B2.S2.3.2	2.50-3.00	2.22	140.00	290.00	110.00	2190.00	7060.00	20.00	550.00	-	1550.00	-
			B2.S2.4.2	3.50-4.00	1.61	120.00	310.00	100.00	1700.00	4320.00	20.00	300.00	-	1720.00	-
			Mean		**1.90**	**130.00**	**283.33**	**106.67**	**1823.33**	**5686.67**	**20.00**	**423.33**	-	**1503.33**	-
			Median		**1.86**	**130.00**	**290.00**	**110.00**	**1700.00**	**5680.00**	**20.00**	**420.00**	-	**1550.00**	-
			SD		**0.31**	**10.00**	**30.55**	**5.77**	**323.16**	**1370.01**	-	**125.03**	-	**243.38**	-
			CV (%)		**16.14**	**7.69**	**10.78**	**5.41**	**17.72**	**24.09**	-	**29.54**	-	**16.19**	-
			Min		**1.61**	**120.00**	**250.00**	**100.00**	**1580.00**	**4320.00**	**20.00**	**300.00**	-	**1240.00**	-
			Max		**2.22**	**140.00**	**310.00**	**110.00**	**2190.00**	**7060.00**	**20.00**	**550.00**	-	**1720.00**	-
			B2.S3.2.2	1.50-2.00	1.186	130.00	280.00	130.00	1630.00	3710.00	20.00	310.00	-	1600.00	-
			B2.S3.3.2	2.50-3.00	1.442	120.00	300.00	80.00	1450.00	4270.00	20.00	340.00	-	1440.00	-
			B2.S3.4.2	3.50-4.00	1.058	130.00	270.00	80.00	1660.00	3950.00	20.00	300.00	-	1970.00	-
			Mean		**1.23**	**126.67**	**283.33**	**96.67**	**1580.00**	**3976.67**	**20.00**	**316.67**	-	**1670.00**	-
			Median		**1.19**	**130.00**	**280.00**	**80.00**	**1630.00**	**3950.00**	**20.00**	**310.00**	-	**1600.00**	-
			SD		**0.20**	**5.77**	**15.28**	**28.87**	**113.58**	**280.95**	-	**20.82**	-	**271.85**	-
			CV (%)		**15.91**	**4.56**	**5.39**	**29.86**	**7.19**	**7.06**	-	**6.57**	-	**16.28**	-
			Min		**1.06**	**120.00**	**270.00**	**80.00**	**1450.00**	**3710.00**	**20.00**	**300.00**	-	**1440.00**	-
			Max		**1.44**	**130.00**	**300.00**	**130.00**	**1660.00**	**4270.00**	**20.00**	**340.00**	-	**1970.00**	-

As can be seen in Table 17, with this portable piece of equipment, it was possible to detect, almost always, all of the base metals, namely Ni, Cu, Zn, Sn, and Pb. Only Pb proved to be more difficult to determine from the borehole samples, collected at a depth between 1 and 4 metres. It can be further verified that the results obtained are, mainly, of the same order of magnitude as those obtained with the benchtop equipment.

Regarding critical metals and semi-metals, it was not possible to detect the following elements: Ga, Ge, Y, La, and Ce. Also Co, Nb, and Sb proved to be difficult to determine and were only detected in some samples. The critical metal Mg was not considered to produce the charts, as it appeared in a different unit to the others. Once again, it was possible to verify that the results obtained for the detected elements were, mainly, of the same order of magnitude as those obtained with the benchtop equipment, with Co being an exception. This means that the inactive FTD 1 has, primarily, more content in Cu, Zn, and W than the active FTD 2A (Chart 17 and Chart 18), which means the mine has, possibly, improved its recovery methods in recent years.

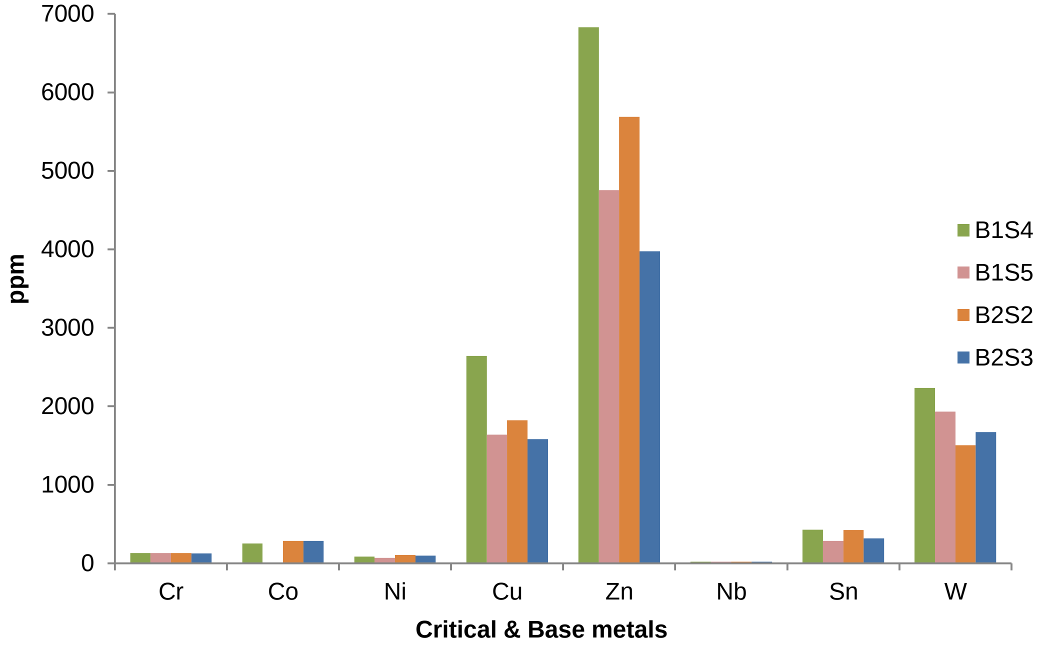

Chart 17 - Results from the borehole logging samples by Thermo Fisher (Mining Cu/Zn) at FTD 1 and FTD 2A.

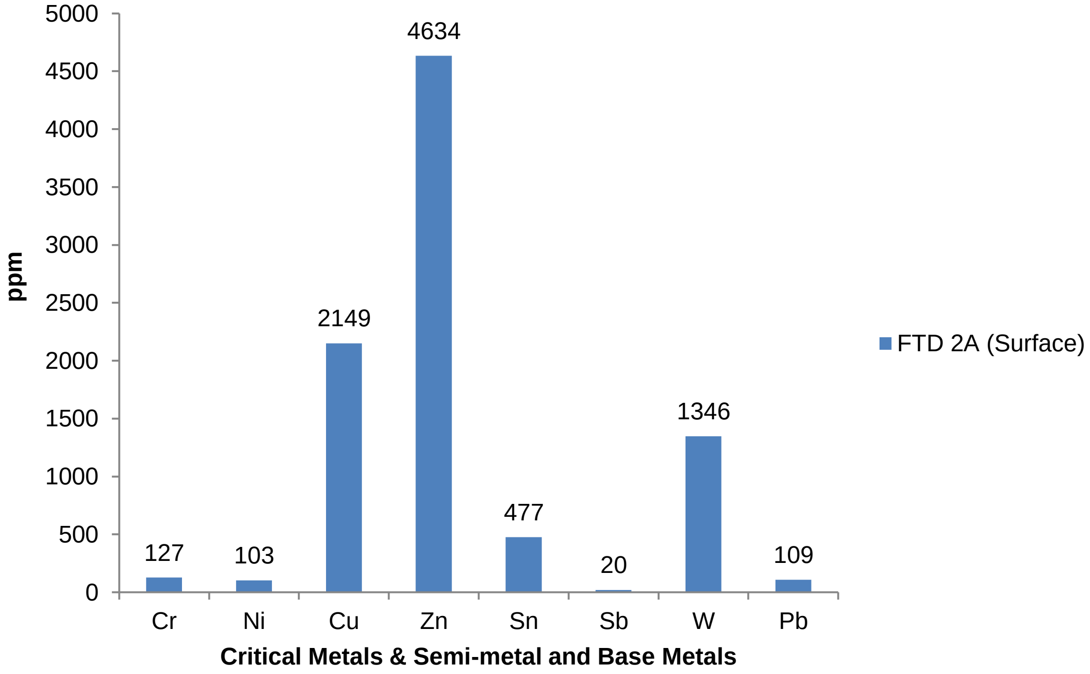

Chart 18 - Results from the surface samples by Thermo Fisher (Mining Cu/Zn) at FTD 2A.

PANALYTICAL

The surface (S1 to S12) and borehole (B1S5 and B2S2) samples collected from the two fine tailings dams (FTD 1 and FTD 2A) were analysed through the PANalytical Axios^{mAX} spectrometer, in the operation mode Pro-Trace, and their results and statistics are shown in Table 18, ordered by the increasing atomic number of the selected elements. It is important to note that the sample S11 was omitted from the results, as it was considered an outlier[77].

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[77] Data point which is not representative of the case we are studying and may influence the overall results. In this case the sample S11 wasn't considered in the elaboration of the results; however it can be consulted in APPENDIX VII.

Table 18 - Results from XRF analysis (Pro-Trace) for critical metals and semi-metals (red), and base metals (yellow).

METHODOLOGY	TYPE OF SAMPLING	FTD	SAMPLE	DEPTH	CHEMICAL ELEMENTS														
					Cr	Co	Ni	Cu	Zn	Ga	Ge	Y	Nb	Sn	Sb	La	Ce	W	Pb
				m	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
XRF PANALYTICAL (PRO-TRACE)	SURFACE SAMPLING	FTD 2A	S1	0.00-0.30	86.30	10.70	24.30	1206.50	1224.30	16.60	2.50	18.00	8.60	249.20	6.60	25.60	268.50	482.30	69.60
			S2	0.00-0.30	88.90	12.90	30.20	2260.20	2728.50	18.00	4.10	19.60	9.80	326.20	7.80	18.80	331.70	738.50	110.80
			S3	0.00-0.30	93.60	11.50	23.70	1934.90	1677.80	18.60	10.80	19.60	9.60	497.10	4.40	26.30	328.10	1256.10	120.40
			S4	0.00-0.30	106.30	18.00	48.00	3430.40	7913.50	22.70	10.10	19.70	9.50	622.60	9.30	22.90	373.70	1354.10	123.50
			S5	0.00-0.30	96.80	12.30	28.00	3042.50	5013.70	20.30	12.00	18.40	9.30	618.20	7.00	19.30	360.60	1517.50	140.40
			S6	0.00-0.30	86.10	12.00	25.90	2439.50	4839.80	17.30	10.80	16.40	8.10	509.10	6.40	22.20	338.60	969.20	101.80
			S7	0.00-0.30	78.10	11.90	26.70	2760.20	5390.20	16.70	11.00	15.90	7.60	540.70	7.20	19.90	326.10	864.20	93.60
			S8	0.00-0.30	105.50	11.00	23.40	1775.90	3496.30	19.20	11.00	19.00	8.80	381.60	4.70	18.90	223.50	599.90	93.40
			S9	0.00-0.30	102.00	14.10	28.90	4143.50	6930.20	19.30	20.10	18.50	9.40	745.60	6.30	19.60	310.70	2089.20	171.00
			S10	0.00-0.30	89.90	13.80	32.30	2995.80	9833.70	17.60	11.80	17.20	8.90	721.50	12.30	21.30	447.40	1788.30	121.30
			S12	0.00-0.30	83.60	12.30	25.40	2305.90	4088.20	17.40	4.70	18.10	9.80	418.30	8.20	22.50	362.20	1043.50	136.40
			Mean		92.46	12.77	28.80	2572.30	4830.56	18.52	9.90	18.22	9.04	511.83	7.29	21.57	333.74	1154.80	116.56
			Median		89.90	12.30	26.70	2439.50	4839.80	18.00	10.80	18.40	9.30	509.10	7.00	21.30	331.70	1043.50	120.40
			SD		9.25	2.03	6.95	820.53	2626.52	1.80	4.81	1.29	0.71	158.87	2.18	2.61	57.54	502.07	27.44
			CV (%)		10.00	15.86	24.14	31.90	54.37	9.75	48.61	7.05	7.91	31.04	29.93	12.12	17.24	43.48	23.54
			Min		78.10	10.70	23.40	1206.50	1224.30	16.60	2.50	15.90	7.60	249.20	4.40	18.80	223.50	482.30	69.60
			Max		106.30	18.00	48.00	4143.50	9833.70	22.70	20.10	19.70	9.80	745.60	12.30	26.30	447.40	2089.20	171.00
	BOREHOLE LOGGING	FTD 1	B1.S5.2.2	1.59-2.00	110.10	17.20	63.70	2434.80	4279.80	28.50	15.10	30.80	12.80	317.50	1.90	29.00	122.10	1563.30	130.70
			B1.S5.3.2	2.33-2.66	117.50	18.70	62.40	1475.20	3908.40	29.60	13.70	25.00	14.30	268.40	4.50	31.90	103.50	1370.20	105.50
			B1.S5.4.2	3.63-4.00	111.20	17.70	59.20	1971.90	5106.20	29.70	14.90	26.00	14.40	344.60	3.50	32.00	107.00	1449.80	89.30
			Mean		112.93	17.87	61.77	1960.63	4431.47	29.27	14.57	27.27	13.83	310.17	3.30	30.97	110.87	1461.10	108.50
			Median		111.20	17.70	62.40	1971.90	4279.80	29.60	14.90	26.00	14.30	317.50	3.50	31.90	107.00	1449.80	105.50
			SD		3.99	0.76	2.32	479.90	613.13	0.67	0.76	3.10	0.90	38.63	1.31	1.70	9.88	97.04	20.86
			CV (%)		3.54	4.27	3.75	24.48	13.84	2.28	5.20	11.37	6.48	12.45	39.74	5.50	8.92	6.64	19.23
			Min		110.10	17.20	59.20	1475.20	3908.40	28.50	13.70	25.00	12.80	268.40	1.90	29.00	103.50	1370.20	89.30
			Max		117.50	18.70	63.70	2434.80	5106.20	29.70	15.10	30.80	14.40	344.60	4.50	32.00	122.10	1563.30	130.70
		FTD 2A	B2.S2.2.2	1.50-2.00	88.50	20.40	60.50	2569.90	8771.10	22.00	7.40	19.90	9.50	425.70	8.00	20.50	303.70	942.10	90.30
			B2.S2.3.2	2.50-3.00	87.80	22.10	67.10	3582.10	11091.30	23.20	9.40	18.80	9.60	509.90	9.20	20.00	303.70	1195.60	121.30
			B2.S2.4.2	3.50-4.00	93.30	23.10	72.00	2524.40	5960.40	21.40	6.90	19.80	11.40	289.80	11.10	22.60	315.50	1329.60	130.40
			Mean		89.87	21.87	66.53	2892.13	8607.60	22.20	7.90	19.50	10.17	408.47	9.43	21.03	307.63	1155.77	114.00
			Median		88.50	22.10	67.10	2569.90	8771.10	22.00	7.40	19.80	9.60	425.70	9.20	20.50	303.70	1195.60	121.30
			SD		2.99	1.37	5.77	597.96	2569.35	0.92	1.32	0.61	1.07	111.06	1.56	1.38	6.81	196.80	21.02
			CV (%)		3.33	6.24	8.67	20.68	29.85	4.13	16.75	3.12	10.52	27.19	16.57	6.56	2.21	17.03	18.44
			Min		87.80	20.40	60.50	2524.40	5960.40	21.40	6.90	18.80	9.50	289.80	8.00	20.00	303.70	942.10	90.30
			Max		93.30	23.10	72.00	3582.10	11091.30	23.20	9.40	19.90	11.40	509.90	11.10	22.60	315.50	1329.60	130.40

After analysing all the XRF Pro-Trace results, it was possible to identify, in the fine tailings, ten critical elements (critical metals and semi-metals) of the twenty previously described and identified as critical for the EU by the EC in 2014, and five other elements (base metals). The base metals include Ni, Cu, Zn, Sn, and Pb, the critical metals include Cr, Co, Ga, Y, Nb, La, Ce, and W, and the critical semi-metals include Ge and Sb.

In order to understand the potential of these fine tailings, the content obtained for each of these elements was compared systematically with their own continental crust abundance, only considering the upper continental crust, reported in the study of Rudnick & Gao (2014) – Table 19.

Table 19 - Upper continental crust abundance vs. tailings abundance (higher values (grey); lower values (white); most significant higher values (red)).

Type of metal	Element	Upper continental crust abundance (ppm)[78]	FTD 1 Borehole abundance (ppm)	FTD 2A Borehole abundance (ppm)	FTD 2A Surface abundance (ppm)
Critical metals & semi-metals	**Cr**	92	112.93	89.87	92.46
	Co	17.3	17.98	21.87	12.77
	Ga	17.5	29.27	22.20	18.52
	Ge	1.4	**14.57**	**7.90**	**9.90**
	Y	21	27.27	19.50	18.22
	Nb	12	13.83	10.17	9.04
	Sb	0.4	**3.30**	**9.43**	**7.29**
	La	31	30.97	21.03	21.57
	Ce	63	**110.87**	**307.63**	**333.74**
	W	1.9	**1461.10**	**1155.77**	**1154.80**
Base metals	**Ni**	47	61.77	66.53	28.80
	Cu	28	1960.63	2892.13	2572.30
	Zn	67	4431.47	8607.60	4830.56
	Sn	2.1	310.17	408.47	511.83
	Pb	17	108.50	114.00	116.56

Apart from the high concentration of the critical element W, and some of the base metals, which can be expected due to the type of mineral deposit occurring here (W-Sn-(Cu) deposit), we can verify that, in general, the contents of the several critical elements identified, especially the elements Ge, Sb, and Ce, are superior to their upper continental crustal

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[78] Data from the study of Rudnick & Gao, 2014.

abundances. This indicates that there is potential of an eventual recovery of these critical elements in the fine tailings studied.

According to some authors, it is possible to make an association between the base metals and the critical metals (Hagelüken & Meskers, 2010). These authors defend that many of the critical elements are related with “atractor” or “carrier” base metals, such as Fe, Al, Ni, Cu, Zn, Sn, and Pb, and therefore can be by-products of those base metals – Figure 59.

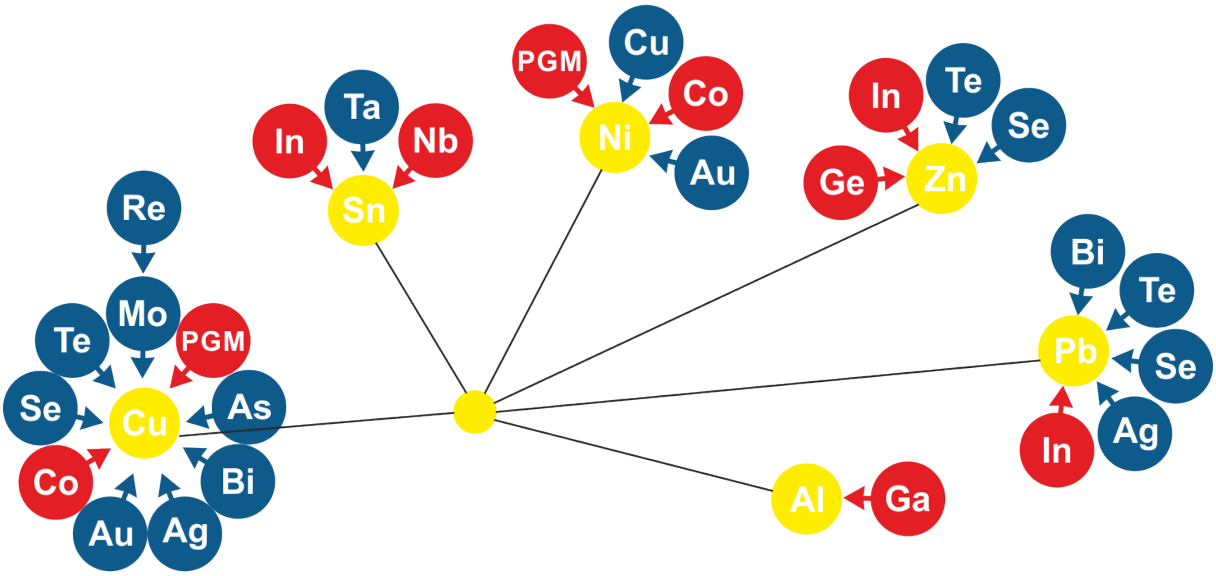


Figure 59 - Metals (blue), critical metals (red) and their associated base metal (yellow) (modified from EASAC, 2016).

These geological “hitch-hikers” (critical metals and semi-metals) are not found in mineralised deposits, where they could be mined as such, but are often found together with a major metal, usually one of the base metals (Ayres & Peiró, 2013). The ore has been formed under certain geological conditions, which determines the mineral accumulations or combinations, as well as the amounts. For example, the occurrence of Nb is sometimes associated with Sn, the occurrence of Co appears to be associated with Ni and Cu, the occurrence of Ge is associated with Zn, and the occurrence of Ga is associated with Al.

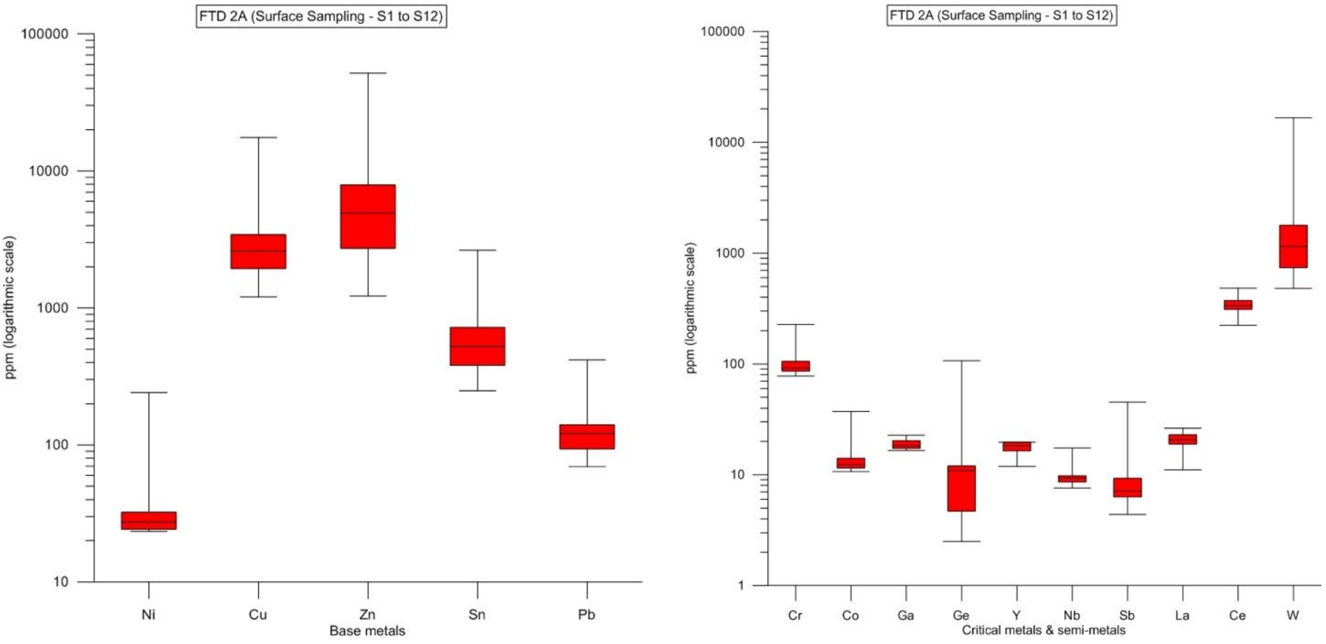
Standard “by-product” metals (Ge, Ga, Co, In, etc.) are detected in the ores of major (carrier) metals at the ppm level. The economic driving force behind the decision to mine here is, undeniably, the major metal, determined by its share in the total intrinsic value. If they can be extracted cost-effectively, by-product metals may create further revenue; in certain circumstances, however, they are considered as impurities that cause an increase in production costs. Other minor metals occur as “coupled elements” without a real carrier metal, and are often found in the same group, meaning they must be mined and processed together. Regarding this content, we can mention PGMs, REEs, and tantalum-niobium

(Hagelüken & Meskers, 2010). These relationships are vital to the design of processes for recycling metals from EoL products (EASAC, 2016).

From this perspective, Ayres & Peiró (2013) point to several strategies to increase production of critical metals from their "carrier" base metals, focusing the study on iron (REEs), aluminium (Ga), copper (Co), zinc (Ge, and In), nickel (Co, and PGMs), and tin (Nb).

A) SURFACE SAMPLING (HORIZONTAL ANALYSIS)

Concerning the samples collected at different points of the surface in FTD 2A, at a depth of between 0 to 30cm, the variation between the concentrations of the elements is significant. See, for example, the cases of Zn, Ge, and W which have a coefficient of variation (CV) of 54.37%, 48.61% and 43.48%, respectively (Table 22). The average values in these samples are visible in the box-whisker plots (Chart 19), which were produced by the software Grapher version 8.2.460 (Golden Software, Inc.), and show us the median, which divided the data into two halves and also calculated the "sub-medians" of those two halves, and the minimum and maximum values.

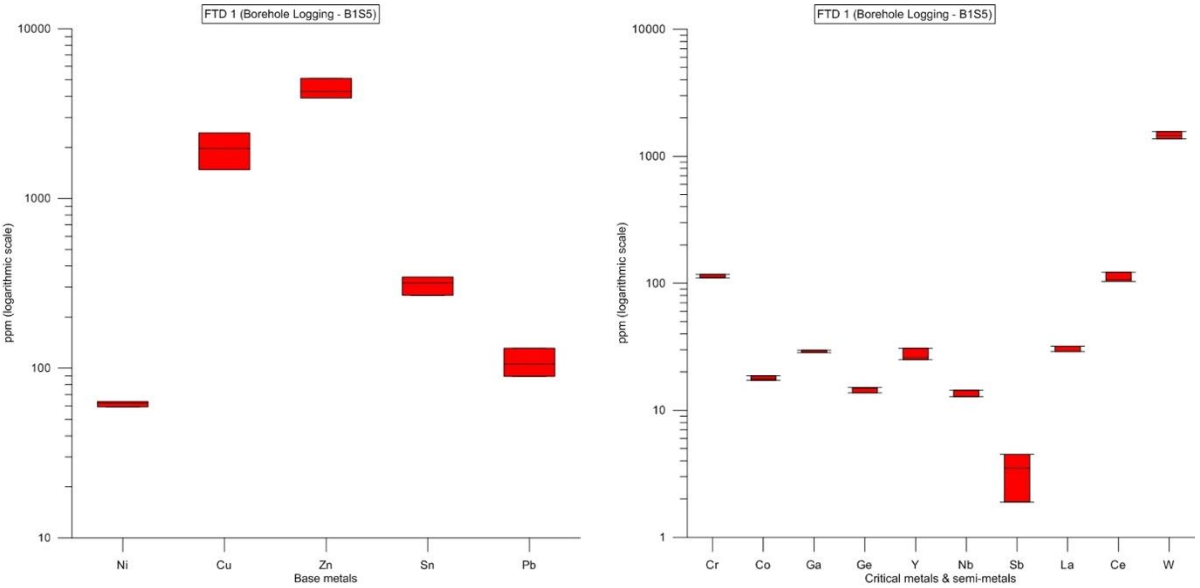


(a) (b)

Chart 19 - (a) Representative box-whisker plot of the base metals (b) Representative box-whisker plot of the critical metals and semi-metals. Both from the surface samples (not including the outlier sample S11).

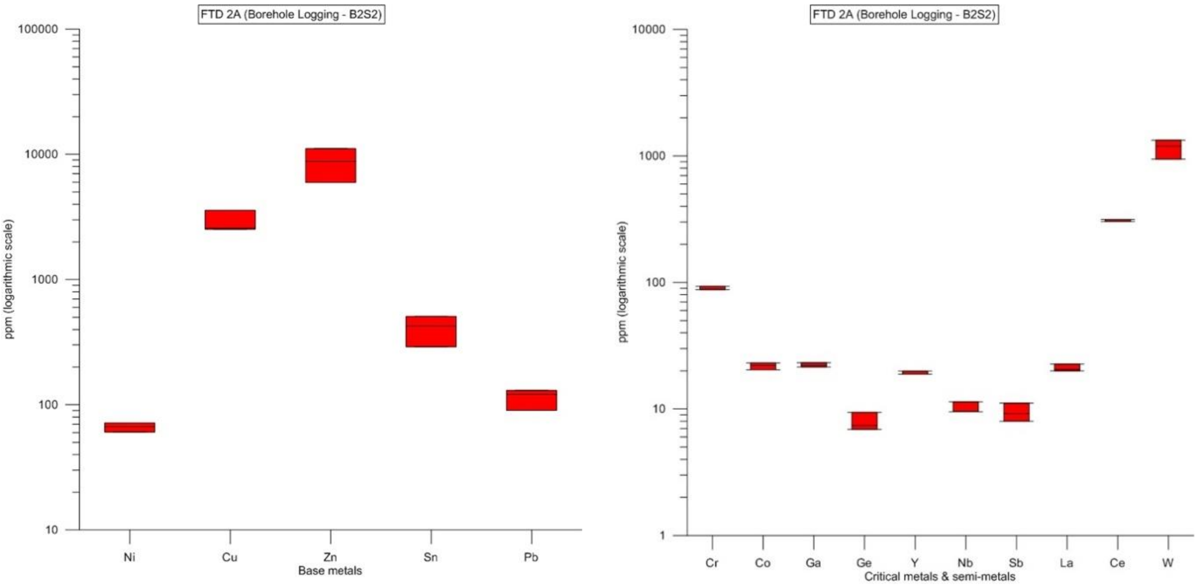
B) BOREHOLE LOGGING (VERTICAL ANALYSIS)

Generally, there are no significant variations in the content of the elements, collected at a depth of between 1 to 4m at both of the fine tailings dams, as shown by the calculated coefficients of variation (CV) of less than 20%. In some cases, however, this variation is more significant, for example in the case of Cu and Sb in FTD 1, and in the case of Cu, Zn, and Sn in FTD 2A (Table 23). The average values were also represented in box-whisker plots; however, the variations of each element are shorter, as they only consider three sample averages per borehole, compared to the eleven surface samples (Chart 20 and Chart 21).



(a) (b)

Chart 20 - (a) Representative box-whisker plot of the base metals (b) Representative box-whisker plot of the critical metals and semi-metals. Both of 3 samples from the borehole B1S5.



(a) (b)

Chart 21 - (a) Representative box-whisker plot of the base metals (b) Representative box-whisker plot of the critical metals and semi-metals. Both of 3 samples from the borehole B2S2.

With regard to the composition of the samples, it is possible to verify that the two fine tailings dams have very similar profiles, obtaining a correlation coefficient of 98% or greater. In Chart 22, the element W was truncated for scale purposes, as it is the critical metal most likely to be found due to the deposit type. W content in FTD 1 is 1461.10ppm, and in FTD 2A it is 1155.77ppm (borehole sample) and 1154.80ppm (surface sample), which demonstrates the higher W contents in the older fine tailings dam (FTD 1) compared to the more recent one (FTD 2A). This may indicate that the recovery process of the tungsten concentrate in the mine processing plant has been more effective in recent years. This trend is also found for most of the critical elements identified, with the exception of Co, Sb, and Ce (Chart 22).

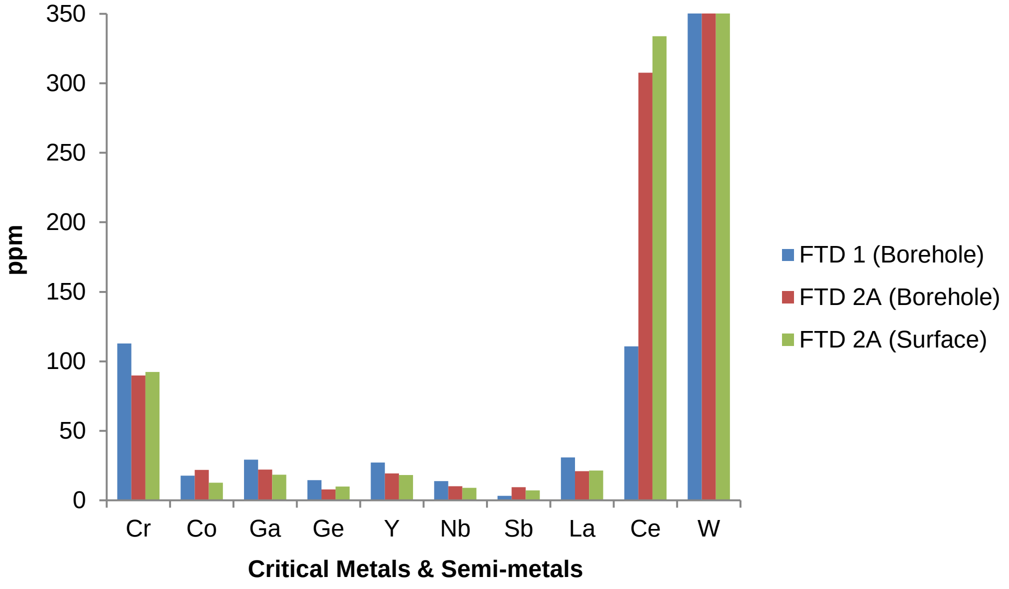


Chart 22 - Critical metals and semi-metals abundance in the two fine tailings dams at Barroca Grande (critical element W was truncated for scale).

Regarding base metals, the most abundant is Zn, especially in fine tailings dam 2A, followed by Cu and Sn (Chart 23) with, obviously, higher values than the rarer critical elements.

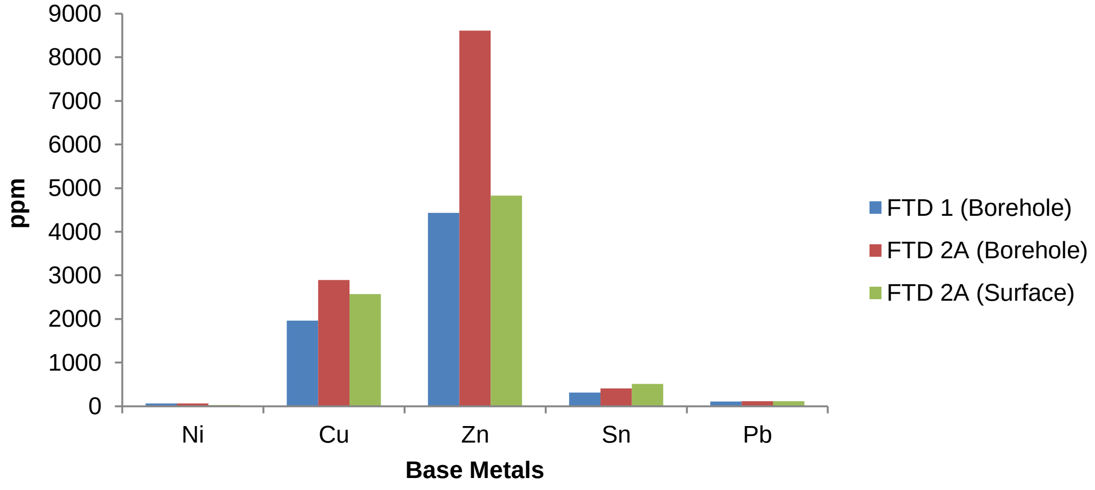


Chart 23 - Base metals abundance in the two fine tailings dams at Barroca Grande.

C) COMPARISON WITH OTHER STUDIES

In 2008, Ávila *et al.* completed a study about the geochemistry and mineralogy of the waste dumps and fine tailings dams at Barroca Grande. Regarding the fine tailings dams, it was only possible to compare the most similar type of sampling, which was also done by surface sampling nine samples (2kg per sample) at about a 40cm depth in the same fine tailings dam as we did (FTD 2A). Although the methodologies they used were slightly different, as they used conductive plasma emission spectrometry (ICP) for almost all of the elements, apart from Sn and W, for which the same method (XRF) was used, it is possible to compare all the base metals, and some of the critical metals and semi-metals, from our more precise results (Pro-Trace) – Table 20.

Table 20 - Comparison of the results from surface sampling at FTD 2A.

Study	**Co (ppm)**	**Cu (ppm)**	**Ni (ppm)**	**Pb (ppm)**	**Sb (ppm)**	**Sn (ppm)**	**W (ppm)**	**Y (ppm)**	**Zn (ppm)**
Ávila study (2008)	25	3662	61	109	29	413	3182	430	4024
This study (2016[79])	13	2572	29	117	7	512	1155	18	4841

As we can see, the present results are very similar to those obtained by Avila *et al*. (2008), with the exception of yttrium (Y). It should be noted that, although samples were collected at similar depths, around 8 years passed between the sampling. The tendency of the concentration of the elements Cu and W to decrease from 2008 to 2016 may be related to slight optimisation in the recovery process at the treatment plant of Barroca Grande.

D) PRINCIPAL COMPONENT ANALYSIS (PCA)

Using the software MATLAB R2016a (MathWorks®), and taking into consideration the XRF Panalytical results (Pro-Trace) for both of the fine tailings dams, we were able to carry out a principal component analysis (PCA). This is a multivariate analysis, which can analyse all the variables simultaneously. It is also known as a linear transformation of the variables into a lower dimensional space, which retains the maximum amount of information possible about the variables.

This PCA was performed on the normalised data. Standardisation served to remove the significance of elements with more expressive concentrations, in order for the PCA to take into account elements that have a less significant concentration.

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[79] Reference to the time the surface sampling was done (May 2016).

We can verify that: with one principal component, it is possible to recover 37% of the original variance; with two principal components, it is possible to recover 70% of the original variance; and with three principal components, it is possible to recover 90% of the original variance.

In order to represent the data graphically, we present them taking into account three different aspects: loadings, scores, and biplot. The loadings are related to the variables, and the more significant the coefficient, in absolute value, the greater the relevance of the variable in the principal component. The scores are related to the observations, and they are a representation of the observations in the new space of principal components. As for the biplot, it is only a representation that summarises loadings and scores for two principal components.

Regarding the analysis of the loadings, we can conclude that the principal components recovered are associated with several elements. Thus, in PC1, we have a more significant coefficient for Zn, as well as for Cu, Sn, Sb, and W. In PC2, we have a more significant coefficient for Ni, as well as for Ce, Ge, and Ga. In PC3, we have a more significant coefficient for Ge, as well as for Ni, Sb, and Sn. (Chart 24)

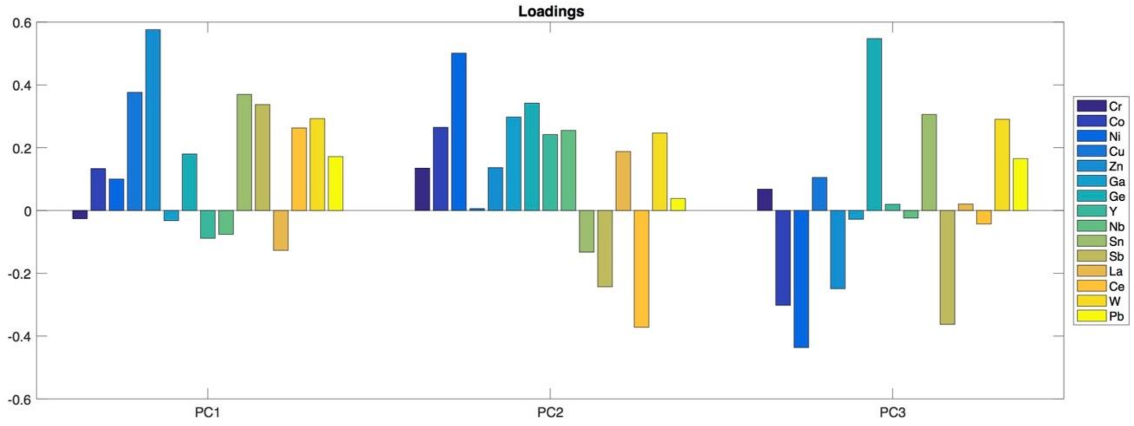

Chart 24 - Representation of the loadings of the three principal components.

Regarding the analysis of the scores, we can conclude that there is a perceptible separation between the two fine tailings dams (FTD 1 and 2A), based on the borehole samples B1S5 (circled in blue on Chart 25) and B2S2 (circled in yellow on Chart 25). Despite the greater variability, it is possible to verify that the surface samples (not including the outlier S11), collected in FTD 2A, have more similar characteristics to the borehole samples collected in the same fine tailings dam (circled in green on Chart 25).

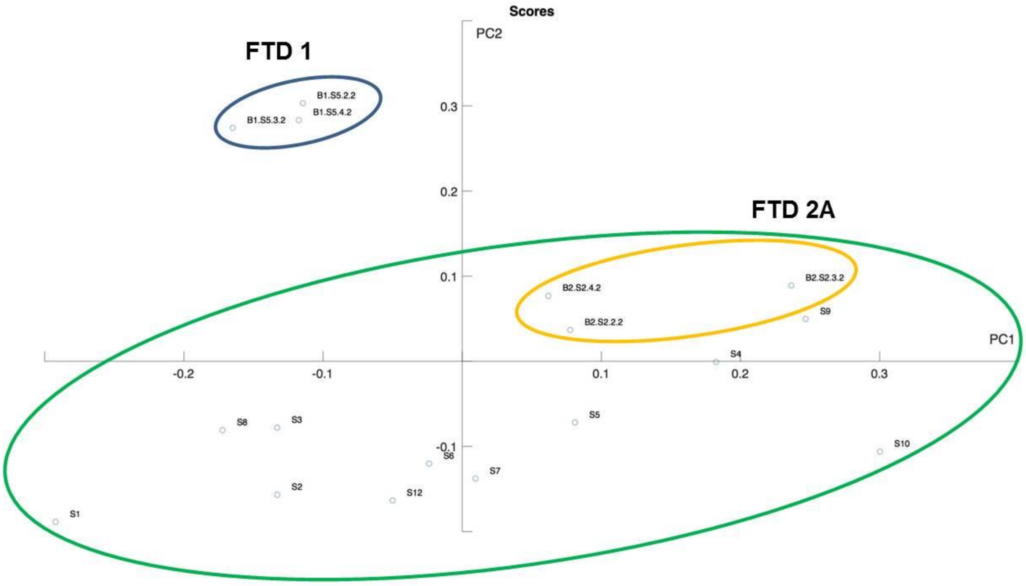

Chart 25 - Representation of the scores on two principal components.

As previously mentioned, a summary of this PCA is presented in a biplot of the first two principal components: PC1 (x-axis) and PC2 (y-axis). Here it is once again visible that Zn is the most dominant element, regarding PC1, followed by Cu, Sn, Sb, and W. Regarding PC2, Ni is the most dominant element, followed by Ce, Ge, and Ga. (Chart 26)

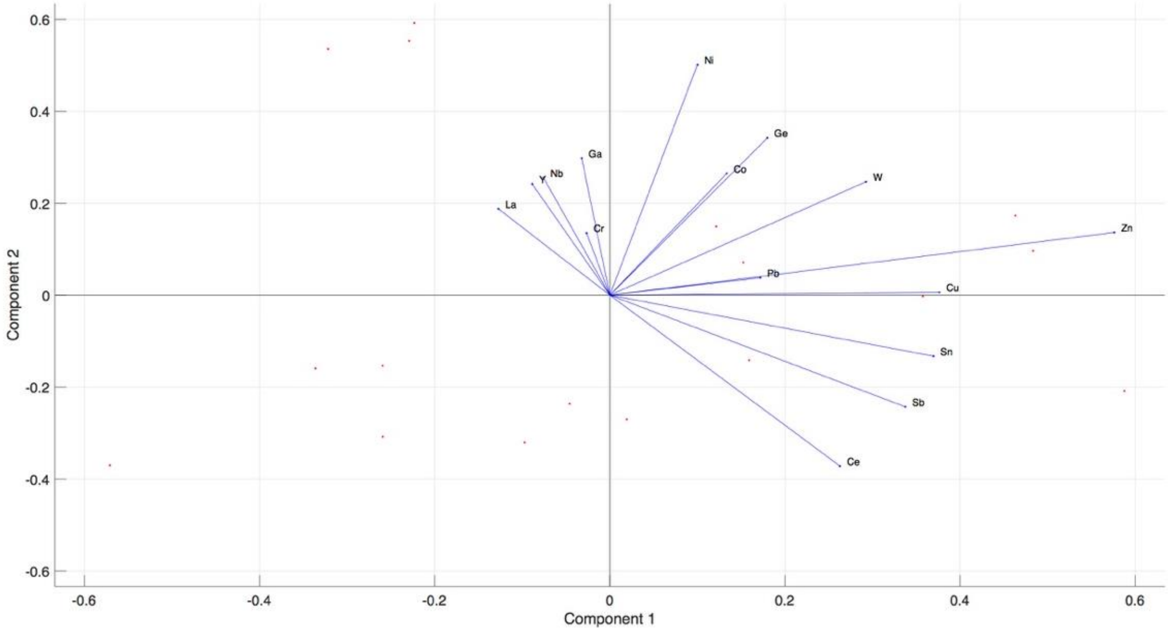

Chart 26 - Representation of the biplot of the first two principal components.

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CHAPTER 8.

FINAL REMARKS

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8.1. CONCLUSION

Regarding physical composition, the inactive fine tailings dam (FTD 1) has a grain-size ranging from medium to coarse silt, and the currently active fine tailings dam (FTD 2A) has a grain-size ranging from fine sand to medium sand, meaning that FTD 1 has finer grains than FTD 2A. Both of the fine tailings dams are mainly mineralogically composed by the silicates quartz (Qtz), muscovite (Ms), and albite (Ab), with the occasional occurrence of the sulphides pyrite (Py), arsenopyrite (Apy), and chalcopyrite (Ccp).

Apart from tungsten (W), which is expected to be the most abundant critical element in the studied fine tailings dams, due to the type of deposit (W-Sn-(Cu)) that is exploited there, with the chemical results (XRF in Pro-Trace operation mode) we can verify that, in comparison to their natural continental crustal abundance, the critical metal and semi-metals concentration is anomalous, the most anomalous being germanium (Ge), antimony (Sb), and cerium (Ce).

Regarding germanium (Ge), its abundance in FTD 1 is 10 times higher than its natural upper continental crust abundance, while in FTD 2A, Ge abundance is approximately 6 to 7 times higher than its natural continental crust abundance, depending on which type of sampling we are considering. It is a critical semi-metal used in wide-angle camera lenses, in fluorescent lamps, in infrared (IR) spectroscopes, in optical fibres and in satellite solar cells and panels.

Regarding antimony (Sb) its abundance in FTD 1 is 8 times higher than its natural upper continental crust abundance, while in FTD 2A, Sb abundance is approximately 18 to 24 times higher than its natural upper continental crust abundance, depending on which type of sampling we are considering. It is a critical semi-metal used in different applications: semiconductor devices (used in iPhones), batteries, cable sheathing, textiles, and PET containers.

Regarding cerium (Ce), its abundance in FTD 1 is approximately 2 times higher than its natural upper continental crust abundance, while in FTD 2A, Ce abundance is approximately 5 times higher than its natural upper continental crust abundance. This critical metal, which belongs to the metallic group of LREEs, is the main component of mischmetal alloys, used in flints for cigarette lighters and in the manufacturing of flat-screen TVs, low-energy light bulbs, and floodlights.

These fine tailings, located at the Barroca Grande site, have the potential to be a "waste-resource" deposit in critical metals, and, according to Martins & Viegas, 2011, they have several advantages: ‘they have already been extracted, fragmented and/or milled, and have a considerably high degree of concentration with respect to the ore at the mine entry. (…) It is important to note that this is a distinct paradigm of the environmental recovery of former mining areas, in which the approach should not only be limited to the environmental component, but also integrate the economic and valorisation component, avoiding interventions that will not provide access to these potential resources'.

In fact, with this dissertation, we are able to conclude that there is a potential in critical metals and semi-metals in the fine tailings dams, especially regarding Ge, Sb, and Ce, which are part of the twenty critical raw materials identified in 2014, by the EU, and are vital for the competitiveness of the European industry in a globalised world, where China is ahead in the race for resources.

8.2. FUTURE WORKS

Considering the methodologies used, and the results obtained in this dissertation, it is important that, in future works, we:

- Extend the sampling plane to a higher number of borehole sampling points, in a regularly spaced grid, and to higher depths which cover the entire depth of each fine tailings dam;
- Create full 3D or 4D models of the fine tailings dams' morphology from the base to the top;
- Correlate the anomalous concentration of the critical metals and semi-metals with their "carrier" base metal.

With the higher number of borehole sampling points, we will be able to optimise and standardise the results, and with higher depths (up to 50 and 70 metres, at FTD 1 and FTD 2A respectively), we will be able to gather more information about the variation in the tailings treatment process over time, which may justify significant variations in the content of critical metals and semi-metals, depending on the depth.

Creating full 3D or 4D models for both of the fine tailings dams is vital in order to know the terrain morphology of these dams, and to precisely calculate the potential mineral reserve, which can be found in these fine tailings dams, maximising the efficiency of a potential economic recovery of critical metals and semi-metals.

Although we know the anomalous concentration of critical metals and semi-metals in the fine tailings dams, it is important to understand that economic deposits of critical metals and semi-metals are difficult to locate, due to, in most cases, them being associated with "carrier" base metals, such as Al, Ni, Cu, Zn, and Sn, and not in their pure form, in nature. Therefore, further research regarding the correlations and relationships between critical metals and base metals should be a priority, in order to trace and discover economic deposits of these critical metals and semi-metals.

Only studies of this nature can measure the actual reserve in critical metals and semi-metals in these fine tailings dams, as well as their economic feasibility.

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UNIVERSITY OF COIMBRA
FACULTY OF SCIENCES AND TECHNOLOGY
Department of Earth Sciences

APPENDICES

APPENDICES

APPENDIX I - SUPPLY RISK OF THE METALLIC AND SEMI-METALLIC CRMs FOR THE EU

Not including industrial minerals and groups of metals (REEs and PGMs). Data from RSC, n.d.

SUPPLY RISK										
PARAMETERS	**CRMs**									
	Be	**Mg**	**Cr**	**Co**	**Ga**	**Ge**	**Nb**	**In**	**Sb**	**W**
Relative supply risk[80]	8.1	7.1	6.2	7.6	7.6	8.1	7.6	7.6	9	9.5
Crustal abundance (ppm)[81]	1.8	24731[82]	129	25.1	17.7	1.4	9.6	0.053	0.3	1
Recycling rate (%)[83]	<10	10-30	>30	>30	<10	<10	>30	<10	<10	10-30
Substitutability[84]	High	High	High	Medium	Medium	Medium	Medium	Low	Medium	High
Production concentration (%)[85]	85	64	37	67	54	67	98	53	88	84
Reserve distribution (%)[86]	-	26	46	45	-	-	97	-	53	61
Top three producers	USA, China, Mozambique	China, Russia, Turkey	South Africa, Kazakhstan, India	DRC, China, Zambia	China, Germany, Kazakhstan	China, Russia, Germany	Brazil, Canada	China, Republic of Korea, Japan	China, Bolivia, Tajikistan	China, Russia, Bolivia
Top three reserve holders	-	Russia, China, North Korea	Kazakhstan, South Africa, India	DRC, Australia, Cuba	-	-	Brazil, Canada	-	China, Russia, Bolivia	China, Russia, USA
Political stability of top producer[87]	56.6	24.1	44.3	2.8	24.1	24.1	48.1	24.1	24.1	24.1
Political stability of top reserve holder[88]	-	18.4	61.8	2.8	-	-	48.1	-	24.1	24.1

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[80] This parameter is calculated by the combination of the scores for crustal abundance, recycling rate, substitutability, production concentration, reserve distribution, and political stability. Supply risk index goes from 1 (very low risk) to 10 (very high risk).

[81] Number of atoms of the chemical element per 1 million atoms of the Earth's crust. The values are an average of the last studies of continental crust (upper, middle, and lower crust) abundance according to Rudnick & Gao (2014).

[82] Value after conversion from weight percent oxide to ppm.

[83] Percentage of a commodity that is recycled. A higher recycling rate can reduce risk of supply.

[84] It measures the availability of suitable substitutes for a given commodity. The substitutability index is Low (substitution is possible with little or no economic and/or performance impact), Medium (substitution is possible but there may be an economic and/or performance impact), and High (substitution not possible or very difficult).

[85] Percentage of a chemical element produced in the top producing country. The higher the value, the larger risk there is to supply.

[86] Percentage of the world reserves located in the country with the largest reserves. The higher the value, the larger the risk is to supply.

[87] Percentile rank for the political stability of the top producing country, derived from the WGI.

[88] Percentile rank for the political stability of the country with the largest reserves, derived from the WGI.

APPENDIX II - CRMs IN PORTUGAL

Not including industrial minerals. Data from DGEG web service, accessed in July 2017.

Mineral Type	**Critical Raw Material (CRM)**	**Mining concessions**	**Experimental exploitation period**	**Prospecting and research**	
Metallic minerals	Beryllium (Be)	Gralheira Mine (C12)	Tabuaço Mine (CE 137)	Sabugal (PP421)	
	Chromium (Cr)	-	-	Vinhais (PP445)	
	Cobalt (Co)	Neves Corvo Mine (C41)	Tabuaço Mine (CE137)	Vinhais (PP445)	
	Gallium (Ga)	-	-	Moura-Ficalho (PP616)	
	Indium (In)	-	-	Moura-Ficalho (PP616)	
	Magnesium (Mg)	-	-	Moura-Ficalho (PP616)	
	Niobium (Nb)	Argemela Mine (C1011)	Tabuaço Mine (CE137)	Ferronha (PP402) Boavista 2 (PP393B) Segura (PP424) Malhão (PP431) Fafia (PP407) Boavista (PP393) Arga Este (PP275) Arga Central (PP396) Tâmega (PP395) Gaia (PP420) Fonte Santa - Bruçó (PP381)	Marão (PP352) Vieiros (PP426) Ferronha (PP402) Picões (PP394B) Murça (PP382) Massueime (PP427) Picões (PP394) Vaqueiro (PP430) Penedo Gordo (PP429) Sabugal (PP421) Arga Oeste (PP274)
	Tungsten (W)	Panasqueira Mine (C18), Teixogueiras Mine (C55), Argemela Mine (C1011)	Covas Mine (CE139), Numão Mine (CE149), Ervedosa Mine (CE1507), Tabuaço Mine (CE137), Vila Seca – Sto Adrião Mine (CE142); Sto António Mine (CE138);	Sepeda (PP4612) Ferronha (PP402) Boavista 2 (PP393B) Marrancos (PP4712) Segura (PP424) Malhão (PP431) Trás-os-Montes (PP216) Fafia (PP407) Marão Oeste (PP376) Borralha (PP3312) Boavista (PP393) Freixeda (PP916) Arga Este (PP275) Lagares – Rebentão (PP443) Arga Central (PP396) Tâmega (PP395) Valongo (PP1513) Fonte Santa – Bruçó (PP381) Marão (PP352) Banjas (PP2912) Vieiros (PP426) Monforte – Tinoca (PP416)	Trevões (PP413) Picões (PP394B) Murça (PP382) Massueime (PP427) Nisa – Monte Claro (PP54) Mata da Rainha (PP1115) Picões (PP394) Argozelo (PP438) Vaqueiro (PP430) Pomar (PP116) Tarouca (PP712) Alcoutim (PP814) Tuela-Agrochão (PP369) Escadia Grande (PP914) Bejanca (PP3412) Ester (PP816) Stª Barbara (PP294) Arga Oeste (PP274) Vila Verde (PP1413) Sabugal (PP421) Lagares (PP713) Adoria (PP444)
Groups of metallic minerals	PGMs	-	-	-	-
	HREEs	Argemela Mine (C1011)	-	Crato-Assumar-Arronches (PP612) Vila Pouca (PP415) Monforte – Tinoca (PP416)	Barroso 2 (PP417) Penedo Gordo (PP429) Évora ESE (PP388) Tuela-Agrochão (PP369)
	LREEs				

Mineral Type	**Critical Raw Material (CRM)**	**Mining concessions**	**Experimental exploitation period**	**Prospecting and research**	
Metalloid minerals	Antimony (Sb)	-	Numão Mine (CE149), Sto António Mine (CE138)	Ferronha (PP402) Moura-Ficalho (PP616) Grijó (PP379) Valongo (PP1513) Fonte Santa – Bruçó (PP381) Banjas (PP2912) Argozelo (PP438)	Vimioso (PP377) Pomar (PP116) Évora-ESE (PP388) Alcoutim (PP814) Escádia Grande (PP914) Alvito (PP412) Lagares (PP713)
	Germanium (Ge)	-	-	Moura-Ficalho (PP616)	-

APPENDIX III - PROFILE OF THE BOREHOLE LOGGING SAMPLES

B1S4 and B1S5 collected from FTD 1, and B2S2 and B2S3 collected from FTD 2A (M= Mud; MS= Mudstone; S= Sand). Created in CorelDRAW X6.

APPENDIX IV – RESULTS XRF THERMO FISHER (TESTALLGEO OPERATION MODE)

METHODOLOGY	TYPE OF SAMPLING	FTD	SAMPLES	DEPTH	CHEMICAL ELEMENT																																				
					Mg	Al	Si	P	S	Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Se	Rb	Sr	Zr	Nb	Mo	Ag	Cd	Sn	Sb	Te	Cs	Ba	W	Au	Hg	Pb	Bi	Th
				m	%	%	%	%	ppm	ppm	%	%	ppm	%	ppm	ppm	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
XRF THERMOFISHER (TestAllGeo)	SURFACE SAMPLING	FTD 2A	S1	0.00-0.30	0.66	2.09	13.30	0.08	244.52	577.76	1.96	0.21	<LOD	0.36	102.38	165.65	0.06	6.56	90.33	1393.42	1007.69	13424.06	12.98	144.92	58.60	130.87	8.03	5.20	13.21	30.55	144.09	21.06	59.69	58.33	484.77	614.51	27.86	<LOD	61.93	41.96	35.76
			S2	0.00-0.30	0.70	2.56	14.31	0.07	259.53	161.43	2.18	0.17	<LOD	0.35	148.75	195.23	0.06	7.16	94.42	1948.50	2329.24	19643.49	12.76	149.44	46.01	112.08	10.36	5.76	15.47	45.71	238.49	24.73	55.37	53.99	452.57	938.39	<LOD	<LOD	94.46	52.50	45.95
			S3	0.00-0.30	0.71	2.65	14.50	0.11	226.06	75.42	2.24	0.20	<LOD	0.41	151.45	209.90	0.05	7.40	92.92	2016.03	1477.55	19204.60	20.24	155.87	45.72	132.13	9.87	7.50	20.41	29.02	370.35	25.49	79.44	56.70	419.63	1901.04	40.15	37.88	110.83	67.36	56.79
			S4	0.00-0.30	0.73	3.93	16.40	0.09	328.29	225.34	2.46	0.32	<LOD	0.38	184.06	243.52	0.05	8.66	77.34	2741.13	6259.74	27740.57	<LOD	162.34	58.39	128.11	10.90	4.90	22.91	111.96	592.00	<LOD	63.83	48.31	422.37	2045.74	<LOD	<LOD	100.94	78.44	<LOD
			S5	0.00-0.30	0.86	3.15	15.54	0.11	244.50	132.35	2.27	0.24	30.92	0.35	165.98	201.11	0.05	7.65	<LOD	2187.18	3266.11	22421.99	<LOD	152.31	48.35	113.71	9.82	4.42	17.89	50.12	478.85	<LOD	107.02	62.48	363.99	1910.96	<LOD	<LOD	122.37	55.91	41.81
			S6	0.00-0.30	0.61	2.16	13.48	0.13	297.53	236.28	1.92	0.21	<LOD	0.31	124.32	190.15	0.07	7.14	90.08	1806.22	3744.44	20096.15	16.49	145.20	56.77	102.09	7.98	7.50	19.15	68.30	325.87	<LOD	70.54	48.46	383.78	926.44	<LOD	44.01	88.11	57.62	52.57
			S7	0.00-0.30	0.82	1.82	12.33	0.11	318.95	364.70	1.76	0.20	<LOD	0.31	106.74	179.34	0.07	6.99	78.84	2098.29	4686.31	18269.70	21.11	133.59	52.10	99.87	7.41	<LOD	18.36	69.82	352.41	<LOD	76.50	49.42	360.33	1125.43	<LOD	40.29	74.13	44.85	40.67
			S8	0.00-0.30	0.72	3.10	16.16	0.10	196.50	185.81	2.46	0.22	<LOD	0.41	121.42	208.48	0.06	6.22	104.16	1596.67	3158.49	11333.23	14.56	156.38	64.87	124.53	8.34	<LOD	22.86	53.42	211.17	21.36	61.40	51.54	448.31	861.33	<LOD	28.96	85.00	42.31	37.68
			S9	0.00-0.30	0.73	2.48	14.02	0.13	324.71	189.67	1.86	0.28	<LOD	0.35	173.22	238.29	0.06	8.34	<LOD	3354.86	5513.84	21710.25	<LOD	131.28	50.92	129.82	9.62	5.83	30.66	82.95	742.31	<LOD	69.55	57.70	353.12	3243.89	<LOD	<LOD	161.87	70.91	<LOD
			S10	0.00-0.30	1.76	3.68	15.95	0.15	410.23	<LOD	1.99	0.23	<LOD	0.31	150.82	248.57	0.05	9.26	87.40	1947.54	6516.73	36011.82	<LOD	132.10	41.62	100.14	8.51	<LOD	21.70	116.21	648.43	<LOD	92.99	59.02	330.74	2826.91	<LOD	<LOD	99.96	94.26	<LOD
			S11	0.00-0.30	1.16	3.99	10.89	0.22	805.27	363.28	2.06	0.67	<LOD	0.29	180.70	526.33	0.21	17.11	252.59	7080.63	26140.07	73559.94	<LOD	102.04	62.32	84.48	17.47	29.85	74.64	326.64	2215.88	<LOD	<LOD	<LOD	247.31	16847.62	156.48	<LOD	416.13	360.18	<LOD
			S12	0.00-0.30	0.76	2.50	13.69	0.11	281.63	369.31	2.02	0.23	29.52	0.33	159.16	198.29	0.05	7.85	64.27	1604.64	2502.82	24160.11	<LOD	142.92	39.11	112.00	9.73	<LOD	12.67	45.80	355.72	<LOD	59.55	61.12	392.83	2121.97	<LOD	<LOD	127.25	72.69	55.70
			Mean		**0.85**	**2.84**	**14.21**	**0.12**	**328.14**	**261.94**	**2.10**	**0.27**	**30.22**	**0.35**	**147.42**	**233.74**	**0.07**	**8.36**	**103.23**	**2481.26**	**5550.25**	**25631.33**	**16.36**	**142.37**	**52.07**	**114.15**	**9.84**	**8.87**	**24.16**	**85.88**	**556.30**	**23.16**	**72.35**	**55.19**	**388.31**	**2947.02**	**74.83**	**37.78**	**128.58**	**86.58**	**45.87**
			Median		**0.73**	**2.61**	**14.16**	**0.11**	**289.58**	**225.34**	**2.04**	**0.22**	**30.22**	**0.35**	**151.14**	**204.80**	**0.06**	**7.53**	**90.20**	**1982.26**	**3505.28**	**20903.20**	**15.53**	**145.06**	**51.51**	**112.90**	**9.68**	**5.80**	**19.78**	**60.86**	**363.04**	**23.04**	**69.55**	**56.70**	**388.31**	**1906.00**	**40.15**	**39.09**	**100.45**	**62.49**	**43.88**
			SD		**0.32**	**0.73**	**1.64**	**0.04**	**160.69**	**143.81**	**0.22**	**0.13**	**0.99**	**0.04**	**27.83**	**95.56**	**0.04**	**2.89**	**53.61**	**1543.12**	**6723.15**	**16383.57**	**3.61**	**16.16**	**8.22**	**15.33**	**2.63**	**8.55**	**16.62**	**80.90**	**553.02**	**2.28**	**15.85**	**5.12**	**63.98**	**4453.97**	**70.98**	**6.40**	**94.31**	**87.61**	**8.22**
			CV (%)		**37.30**	**25.54**	**11.56**	**33.72**	**48.97**	**54.90**	**10.69**	**49.91**	**3.28**	**11.22**	**18.88**	**40.88**	**63.89**	**34.55**	**51.93**	**62.19**	**121.13**	**63.92**	**22.08**	**11.35**	**15.79**	**13.43**	**26.78**	**96.41**	**68.80**	**94.20**	**99.41**	**9.83**	**21.90**	**9.28**	**16.48**	**151.13**	**94.86**	**16.95**	**73.35**	**101.18**	**17.93**
			Min		**0.61**	**1.82**	**10.89**	**0.07**	**196.50**	**75.42**	**1.76**	**0.17**	**29.52**	**0.29**	**102.38**	**165.65**	**0.05**	**6.22**	**64.27**	**1393.42**	**1007.69**	**11333.23**	**12.76**	**102.04**	**39.11**	**84.48**	**7.41**	**4.42**	**12.67**	**29.02**	**144.09**	**21.06**	**55.37**	**48.31**	**247.31**	**614.51**	**27.86**	**28.96**	**61.93**	**41.96**	**35.76**
			Max		**1.76**	**3.99**	**16.40**	**0.22**	**805.27**	**577.76**	**2.46**	**0.67**	**30.92**	**0.41**	**184.06**	**526.33**	**0.21**	**17.11**	**252.59**	**7080.63**	**26140.07**	**73559.94**	**21.11**	**162.34**	**64.87**	**132.13**	**17.47**	**29.85**	**74.64**	**326.64**	**2215.88**	**25.49**	**107.02**	**62.48**	**484.77**	**16847.62**	**156.48**	**44.01**	**416.13**	**360.18**	**56.79**

APPENDIX V – RESULTS XRF THERMO FISHER (MINING Cu/Zn OPERATION MODE)

METHODOLOGY	TYPE OF SAMPLING	FTD	SAMPLES	DEPTH	CHEMICAL ELEMENT																																	
					Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Rb	Sr	Zr	Nb	Mo	Pd	Ag	Cd	Sn	Sb	Ba	W	Au	Pb	Bi	Cr2O3
				m	%	%	%	%	ppm	ppm	%	%	%	ppm	ppm	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
XRF THERMOFISHER (Mining Cu/Zn)	SURFACE SAMPLING	FTD 2A	S1	0.00-0.30	1.91	3.47	16.01	0.09	40073.08	<LOD	1.59	0.13	0.24	113.08	148.46	0.07	6.74	<LOD	95.00	829.23	1365.38	12191.54	150.00	38.46	118.46	<LOD	30.00	<LOD	<LOD	20.00	293.08	<LOD	546.92	512.31	<LOD	71.54	43.08	-
			S2	0.00-0.30	1.60	2.65	14.06	0.08	41282.31	<LOD	1.29	0.16	0.20	93.85	107.69	0.06	6.48	<LOD	115.83	2062.31	2723.85	15544.62	144.62	34.62	105.38	<LOD	<LOD	<LOD	20.00	46.15	312.31	<LOD	526.15	866.92	50.00	113.08	60.77	-
			S3	0.00-0.30	1.15	2.56	13.31	0.13	40042.14	<LOD	1.44	0.20	0.23	109.29	121.43	0.05	6.90	<LOD	93.33	1931.43	1845.71	17536.43	136.43	41.43	114.29	<LOD	<LOD	<LOD	21.00	27.14	530.71	<LOD	513.57	1594.29	<LOD	114.29	68.57	-
			S4	0.00-0.30	0.93	2.00	10.80	0.10	49178.33	110.00	1.23	0.25	0.21	99.17	124.17	0.05	7.10	<LOD	95.00	2550.00	5867.50	21865.00	119.17	38.33	92.50	<LOD	<LOD	<LOD	26.67	94.17	580.00	<LOD	498.33	1356.67	<LOD	103.33	65.00	-
			S5	0.00-0.30	0.90	2.35	13.88	0.12	37246.36	80.00	1.36	0.19	0.21	106.36	114.55	0.05	6.86	<LOD	88.89	2431.82	4250.91	19352.73	132.73	37.27	94.55	<LOD	<LOD	<LOD	22.73	66.36	576.36	<LOD	503.64	1457.27	<LOD	107.27	61.82	-
			S6	0.00-0.30	1.11	2.15	12.41	0.10	33944.55	<LOD	1.25	0.17	0.20	98.18	120.91	0.07	7.65	<LOD	120.00	2420.91	5943.64	20656.36	133.64	40.91	96.36	<LOD	<LOD	<LOD	23.33	70.00	475.45	20.00	530.00	1397.27	<LOD	100.91	58.18	-
			S7	0.00-0.30	1.21	2.01	11.83	0.10	35470.00	<LOD	1.27	0.14	0.20	102.73	118.18	0.07	7.60	<LOD	106.00	2578.18	6400.91	20795.45	129.09	33.64	90.91	<LOD	20.00	<LOD	20.00	78.18	477.27	<LOD	486.36	1109.09	<LOD	86.36	63.64	-
			S8	0.00-0.30	0.75	2.96	15.90	0.11	24705.38	<LOD	1.65	0.21	0.26	126.92	128.46	0.05	6.03	<LOD	90.00	1854.62	4255.38	10103.08	151.54	43.08	115.38	<LOD	<LOD	<LOD	20.00	52.31	343.08	<LOD	467.69	953.85	<LOD	99.23	40.00	-
			S9	0.00-0.30	0.87	2.53	14.07	0.10	30280.91	<LOD	1.22	0.19	0.24	105.45	130.00	0.06	7.57	<LOD	90.00	3637.27	6294.55	18473.64	125.45	42.73	120.91	<LOD	<LOD	<LOD	31.82	92.73	703.64	<LOD	400.00	2500.00	<LOD	163.64	80.00	-
			S10	0.00-0.30	1.80	2.37	10.88	0.09	33952.86	<LOD	1.43	0.14	0.22	117.14	146.43	0.05	8.92	<LOD	104.62	1838.57	8143.57	34805.00	135.00	36.43	88.57	<LOD	<LOD	<LOD	25.00	121.43	636.43	<LOD	477.14	1855.00	<LOD	102.86	100.71	-
			S11	0.00-0.30	3.18	7.40	15.02	0.31	84308.33	<LOD	1.86	0.58	0.28	150.00	375.00	0.21	16.99	430.00	278.33	7551.67	28292.50	72452.50	111.67	70.00	78.33	20.00	<LOD	20.00	85.83	367.50	2805.00	<LOD	337.50	15759.17	150.00	445.00	369.17	-
			S12	0.00-0.30	1.61	3.03	14.61	0.10	27141.54	<LOD	1.59	0.19	0.25	116.92	134.62	0.05	7.27	<LOD	133.33	1509.23	3883.08	21266.92	151.54	44.62	103.08	<LOD	<LOD	<LOD	<LOD	53.33	316.15	<LOD	556.92	1204.62	<LOD	133.08	52.31	-
			Mean		**1.42**	**2.96**	**13.57**	**0.12**	**39802.15**	**95.00**	**1.43**	**0.21**	**0.23**	**111.59**	**147.49**	**0.07**	**8.01**	-	**117.53**	**2599.60**	**6605.58**	**23753.61**	**135.07**	**41.79**	**101.56**	-	**25.00**	-	**29.64**	**90.78**	**670.79**	-	**487.02**	**2547.20**	**100.00**	**136.72**	**88.60**	-
			Median		**1.18**	**2.55**	**13.97**	**0.10**	**36358.18**	**95.00**	**1.40**	**0.19**	**0.22**	**107.82**	**126.31**	**0.05**	**7.19**	-	**99.81**	**2241.61**	**5061.44**	**20004.55**	**134.32**	**39.69**	**99.72**	-	**25.00**	-	**23.03**	**68.18**	**503.99**	-	**500.98**	**1376.97**	**100.00**	**105.30**	**62.73**	-
			SD		**0.67**	**1.46**	**1.77**	**0.06**	**15502.84**	**21.21**	**0.20**	**0.12**	**0.03**	**15.28**	**72.65**	**0.04**	**2.92**	-	**52.53**	**1701.74**	**7118.95**	**16501.00**	**12.77**	**9.52**	**13.52**	-	**7.07**	-	**20.09**	**91.77**	**685.82**	-	**62.79**	**4191.41**	**70.71**	**99.74**	**89.79**	-
			CV (%)		**47.57**	**49.53**	**13.05**	**51.09**	**38.95**	**22.33**	**14.17**	**56.14**	**11.28**	**13.70**	**49.26**	**63.50**	**36.45**	-	**44.70**	**65.46**	**107.77**	**69.47**	**9.46**	**22.78**	**13.31**	-	**28.28**	-	**67.80**	**101.10**	**102.24**	-	**12.89**	**164.55**	**70.71**	**72.96**	**101.34**	-
			Min		**0.75**	**2.00**	**10.80**	**0.08**	**24705.38**	**80.00**	**1.22**	**0.13**	**0.20**	**93.85**	**107.69**	**0.05**	**6.03**	-	**88.89**	**829.23**	**1365.38**	**10103.08**	**111.67**	**33.64**	**78.33**	-	**20.00**	-	**20.00**	**20.00**	**293.08**	-	**337.50**	**512.31**	**50.00**	**71.54**	**40.00**	-
			Max		**3.18**	**7.40**	**16.01**	**0.31**	**84308.33**	**110.00**	**1.86**	**0.58**	**0.28**	**150.00**	**375.00**	**0.21**	**16.99**	-	**278.33**	**7551.67**	**28292.50**	**72452.50**	**151.54**	**70.00**	**120.91**	-	**30.00**	-	**85.83**	**367.50**	**2805.00**	-	**556.92**	**15759.17**	**150.00**	**445.00**	**369.17**	-
	BOREHOLE LOGGING	FTD 1	B1.S4.2.2		1.35	8.08	27.13	0.16	26502.35	1720.00	2.28	1.00	0.38	162.35	142.35	0.12	6.18	<LOD	86.67	2076.47	5385.29	3613.53	174.71	51.18	165.88	20.00	<LOD	-	20.00	59.41	307.06	-	453.53	2034.71	44.67	119.41	30.67	208.24
			B1.S4.3.2		1.12	6.71	26.47	0.15	28101.43	3035.00	2.09	0.87	0.32	134.29	119.29	0.12	6.16	245.00	87.50	2675.00	7360.00	6097.14	165.71	55.00	160.71	<LOD	<LOD	-	20.00	94.29	459.29	-	458.57	2715.71	52.50	102.14	34.29	174.29
			B1.S4.4.2		1.04	7.59	26.58	0.16	24364.62	<LOD	2.33	0.81	0.37	163.08	130.77	0.10	6.25	<LOD	65.00	3168.46	7743.08	5256.92	175.38	56.15	153.85	20.00	<LOD	-	24.29	99.23	510.77	-	462.31	1949.23	42.86	133.85	31.82	190.00
			Mean		**1.17**	**7.46**	**26.73**	**0.16**	**26322.80**	**2377.50**	**2.23**	**0.90**	**0.36**	**153.24**	**130.80**	**0.11**	**6.19**	-	**79.72**	**2639.98**	**6829.46**	**4989.20**	**171.93**	**54.11**	**160.15**	**20.00**	-	-	**21.43**	**84.31**	**425.70**	-	**458.14**	**2233.22**	**46.67**	**118.47**	**32.26**	**190.84**
			Median		**1.12**	**7.59**	**26.58**	**0.16**	**26502.35**	**2377.50**	**2.28**	**0.87**	**0.37**	**162.35**	**130.77**	**0.12**	**6.18**	-	**86.67**	**2675.00**	**7360.00**	**5256.92**	**174.71**	**55.00**	**160.71**	**20.00**	-	-	**20.00**	**94.29**	**459.29**	-	**458.57**	**2034.71**	**44.67**	**119.41**	**31.82**	**190.00**
			SD		**0.16**	**0.69**	**0.36**	**0.01**	**1874.87**	**929.85**	**0.13**	**0.10**	**0.03**	**16.42**	**11.53**	**0.01**	**0.05**	-	**12.76**	**546.84**	**1265.26**	**1263.27**	**5.40**	**2.61**	**6.04**	**0.00**	-	-	**2.47**	**21.70**	**105.93**	-	**4.41**	**420.03**	**5.13**	**15.87**	**1.85**	**16.99**
			CV (%)		**13.76**	**9.28**	**1.33**	**3.31**	**7.12**	**39.11**	**5.66**	**10.90**	**9.54**	**10.71**	**8.82**	**6.87**	**0.77**	-	**16.00**	**20.71**	**18.53**	**25.32**	**3.14**	**4.81**	**3.77**	**0.00**	-	-	**11.55**	**25.74**	**24.88**	-	**0.96**	**18.81**	**10.98**	**13.40**	**5.73**	**8.90**
			Min		**1.04**	**6.71**	**26.47**	**0.15**	**24364.62**	**1720.00**	**2.09**	**0.81**	**0.32**	**134.29**	**119.29**	**0.10**	**6.16**	-	**65.00**	**2076.47**	**5385.29**	**3613.53**	**165.71**	**51.18**	**153.85**	**20.00**	-	-	**20.00**	**59.41**	**307.06**	-	**453.53**	**1949.23**	**42.86**	**102.14**	**30.67**	**174.29**
			Max		**1.35**	**8.08**	**27.13**	**0.16**	**28101.43**	**3035.00**	**2.33**	**1.00**	**0.38**	**163.08**	**142.35**	**0.12**	**6.25**	-	**87.50**	**3168.46**	**7743.08**	**6097.14**	**175.38**	**56.15**	**165.88**	**20.00**	-	-	**24.29**	**99.23**	**510.77**	-	**462.31**	**2715.71**	**52.50**	**133.85**	**34.29**	**208.24**
			B1.S5.2.2		0.95	6.65	21.51	0.14	30659.33	70.00	2.56	1.40	0.37	160.67	124.67	0.09	5.71	<LOD	104.00	2133.33	5058.67	4589.33	207.33	50.00	152.67	20.00	<LOD	-	20.00	76.36	301.33	-	491.33	2078.67	47.14	152.00	26.15	180.00
			B1.S5.3.2		0.93	6.17	19.25	0.10	28600.77	8236.00	3.05	1.61	0.41	180.77	134.62	0.12	5.35	<LOD	60.00	1273.85	4450.77	2541.54	229.23	49.23	160.00	20.00	<LOD	-	<LOD	26.67	261.54	-	520.00	1877.69	45.38	107.69	33.08	193.08
			B1.S5.4.2		0.77	6.91	21.04	0.11	25618.18	4680.00	3.15	1.33	0.42	204.55	144.55	0.10	5.32	<LOD	50.00	1521.82	4747.27	2981.82	222.73	50.00	156.36	<LOD	<LOD	-	<LOD	30.91	290.91	-	577.27	1840.91	42.73	92.73	30.91	212.73
			Mean		**0.88**	**6.58**	**20.60**	**0.11**	**28292.76**	**4328.67**	**2.92**	**1.45**	**0.40**	**181.99**	**134.61**	**0.10**	**5.46**	-	**71.33**	**1643.00**	**4752.24**	**3370.90**	**219.76**	**49.74**	**156.34**	**20.00**	-	-	-	**44.65**	**284.59**	-	**529.54**	**1932.42**	**45.08**	**117.47**	**30.05**	**195.27**
			Median		**0.93**	**6.65**	**21.04**	**0.11**	**28600.77**	**4680.00**	**3.05**	**1.40**	**0.41**	**180.77**	**134.62**	**0.10**	**5.35**	-	**60.00**	**1521.82**	**4747.27**	**2981.82**	**222.73**	**50.00**	**156.36**	**20.00**	-	-	-	**30.91**	**290.91**	-	**520.00**	**1877.69**	**45.38**	**107.69**	**30.91**	**193.08**
			SD		**0.10**	**0.38**	**1.19**	**0.02**	**2534.65**	**4094.32**	**0.32**	**0.15**	**0.02**	**21.97**	**9.94**	**0.02**	**0.22**	-	**28.73**	**442.37**	**303.98**	**1077.92**	**11.25**	**0.44**	**3.67**	**0.00**	-	-	-	**27.55**	**20.64**	-	**43.76**	**127.98**	**2.22**	**30.82**	**3.54**	**16.47**
			CV (%)		**11.48**	**5.75**	**5.80**	**16.95**	**8.96**	**94.59**	**10.84**	**10.22**	**5.89**	**12.07**	**7.38**	**16.19**	**4.05**	-	**40.27**	**26.92**	**6.40**	**31.98**	**5.12**	**0.89**	**2.35**	**0.00**	-	-	-	**61.71**	**7.25**	-	**8.26**	**6.62**	**4.93**	**26.24**	**11.79**	**8.44**
			Min		**0.77**	**6.17**	**19.25**	**0.10**	**25618.18**	**70.00**	**2.56**	**1.33**	**0.37**	**160.67**	**124.67**	**0.09**	**5.32**	-	**50.00**	**1273.85**	**4450.77**	**2541.54**	**207.33**	**49.23**	**152.67**	**20.00**	-	-	-	**26.67**	**261.54**	-	**491.33**	**1840.91**	**42.73**	**92.73**	**26.15**	**180.00**
			Max		**0.95**	**6.91**	**21.51**	**0.14**	**30659.33**	**8236.00**	**3.15**	**1.61**	**0.42**	**204.55**	**144.55**	**0.12**	**5.71**	-	**104.00**	**2133.33**	**5058.67**	**4589.33**	**229.23**	**50.00**	**160.00**	**20.00**	-	-	-	**76.36**	**301.33**	-	**577.27**	**2078.67**	**47.14**	**152.00**	**33.08**	**212.73**
		FTD 2A	B2.S2.2.2		1.86	9.00	26.02	0.18	47607.27	2136.67	2.33	1.55	0.34	149.09	134.09	0.09	7.27	253.33	110.00	1576.36	5682.73	17545.00	171.36	49.09	136.82	<LOD	<LOD	-	21.11	90.00	417.73	-	523.18	1243.18	<LOD	75.91	49.47	195.00
			B2.S2.3.2		2.22	10.19	28.23	0.20	44810.48	1330.00	2.33	0.88	0.35	150.00	143.81	0.12	8.66	285.00	113.57	2193.33	7056.19	20575.24	163.81	51.90	140.00	20.00	<LOD	-	25.00	117.62	552.38	-	523.33	1548.10	50.00	110.95	63.50	211.43
			B2.S2.4.2		1.61	7.14	22.05	0.12	55220.00	3006.67	2.24	1.99	0.33	147.27	124.55	0.10	7.88	306.67	102.31	1704.55	4324.09	21178.18	167.27	45.00	130.45	20.00	<LOD	-	20.00	53.64	301.36	-	495.00	1723.64	35.00	123.18	70.00	182.73
			Mean		**1.90**	**8.77**	**25.43**	**0.17**	**49212.58**	**2157.78**	**2.30**	**1.47**	**0.34**	**148.79**	**134.15**	**0.10**	**7.93**	**281.67**	**108.63**	**1824.75**	**5687.67**	**19766.14**	**167.48**	**48.67**	**135.76**	**20.00**	-	-	-	**87.09**	**423.82**	-	**513.84**	**1504.97**	**42.50**	**103.35**	**60.99**	**196.39**
			Median		**1.86**	**9.00**	**26.02**	**0.18**	**47607.27**	**2136.67**	**2.33**	**1.55**	**0.34**	**149.09**	**134.09**	**0.10**	**7.88**	**285.00**	**110.00**	**1704.55**	**5682.73**	**20575.24**	**167.27**	**49.09**	**136.82**	**20.00**	-	-	-	**90.00**	**417.73**	-	**523.18**	**1548.10**	**42.50**	**110.95**	**63.50**	**195.00**
			SD		**0.31**	**1.54**	**3.13**	**0.04**	**5387.24**	**838.53**	**0.05**	**0.56**	**0.01**	**1.39**	**9.63**	**0.01**	**0.70**	**26.82**	**5.76**	**325.58**	**1366.06**	**1947.04**	**3.78**	**3.47**	**4.86**	**0.00**	-	-	-	**32.09**	**125.62**	-	**16.31**	**243.11**	**10.61**	**24.54**	**10.49**	**14.40**
			CV (%)		**16.15**	**17.52**	**12.30**	**22.70**	**10.95**	**38.86**	**2.30**	**37.79**	**3.85**	**0.93**	**7.18**	**12.65**	**8.80**	**9.52**	**5.30**	**17.84**	**24.02**	**9.85**	**2.26**	**7.13**	**3.58**	**0.00**	-	-	-	**36.85**	**29.64**	-	**3.18**	**16.15**	**24.96**	**23.74**	**17.20**	**7.33**
			Min		**1.61**	**7.14**	**22.05**	**0.12**	**44810.48**	**1330.00**	**2.24**	**0.88**	**0.33**	**147.27**	**124.55**	**0.09**	**7.27**	**253.33**	**102.31**	**1576.36**	**4324.09**	**17545.00**	**163.81**	**45.00**	**130.45**	**20.00**	-	-	-	**53.64**	**301.36**	-	**495.00**	**1243.18**	**35.00**	**75.91**	**49.47**	**182.73**
			Max		**2.22**	**10.19**	**28.23**	**0.20**	**55220.00**	**3006.67**	**2.33**	**1.99**	**0.35**	**150.00**	**143.81**	**0.12**	**8.66**	**306.67**	**113.57**	**2193.33**	**7056.19**	**21178.18**	**171.36**	**51.90**	**140.00**	**20.00**	-	-	-	**117.62**	**552.38**	-	**523.33**	**1723.64**	**50.00**	**123.18**	**70.00**	**211.43**
			B2.S3.2.2		1.19	5.37	17.80	0.10	46565.42	1100.00	2.22	1.52	0.33	146.67	126.25	0.10	7.35	280.00	131.82	1628.33	3709.17	16095.83	164.17	46.25	133.75	20.00	<LOD	-	20.00	55.26	306.25	-	462.50	1598.75	<LOD	108.75	62.50	184.17
			B2.S3.3.2		1.44	7.92	24.72	0.13	32793.00	<LOD	2.37	0.85	0.33	134.50	119.50	0.10	7.06	295.00	79.23	1454.50	4271.50	14396.50	164.50	43.50	138.50	20.00	20.00	-	20.00	57.00	339.50	-	496.00	1437.50	40.00	67.50	51.05	174.50
			B2.S3.4.2		1.06	6.55	20.20	0.13	45508.26	950.00	2.31	1.90	0.35	156.96	130.87	0.11	7.86	270.00	84.62	1664.78	3946.96	19576.09	166.96	43.48	136.09	20.00	<LOD	-	20.00	47.83	303.04	-	496.96	1973.91	40.00	106.09	61.30	191.74
			Mean		**1.23**	**6.62**	**20.91**	**0.12**	**41622.23**	**1025.00**	**2.30**	**1.42**	**0.34**	**146.04**	**125.54**	**0.10**	**7.42**	**281.67**	**98.55**	**1582.54**	**3975.87**	**16689.47**	**165.21**	**44.41**	**136.11**	**20.00**	-	-	-	**53.36**	**316.26**	-	**485.15**	**1670.05**	**40.00**	**94.11**	**58.29**	**183.47**
			Median		**1.19**	**6.55**	**20.20**	**0.13**	**45508.26**	**1025.00**	**2.31**	**1.52**	**0.33**	**146.67**	**126.25**	**0.10**	**7.35**	**280.00**	**84.62**	**1628.33**	**3946.96**	**16095.83**	**164.50**	**43.50**	**136.09**	**20.00**	-	-	-	**55.26**	**306.25**	-	**496.00**	**1598.75**	**40.00**	**106.09**	**61.30**	**184.17**
			SD		**0.20**	**1.28**	**3.52**	**0.02**	**7664.58**	**106.07**	**0.07**	**0.53**	**0.01**	**11.24**	**5.72**	**0.00**	**0.41**	**12.58**	**28.93**	**112.37**	**282.28**	**2640.33**	**1.52**	**1.59**	**2.38**	**0.00**	-	-	-	**4.87**	**20.19**	-	**19.62**	**275.22**	**0.00**	**23.09**	**6.29**	**8.64**
			CV (%)		**15.91**	**19.35**	**16.82**	**15.30**	**18.41**	**10.35**	**3.18**	**37.30**	**3.44**	**7.70**	**4.55**	**4.82**	**5.46**	**4.47**	**29.36**	**7.10**	**7.10**	**15.82**	**0.92**	**3.59**	**1.74**	**0.00**	-	-	-	**9.13**	**6.38**	-	**4.04**	**16.48**	**0.00**	**24.53**	**10.80**	**4.71**
			Min		**1.06**	**5.37**	**17.80**	**0.10**	**32793.00**	**950.00**	**2.22**	**0.85**	**0.33**	**134.50**	**119.50**	**0.10**	**7.06**	**270.00**	**79.23**	**1454.50**	**3709.17**	**14396.50**	**164.17**	**43.48**	**133.75**	**20.00**	-	-	-	**47.83**	**303.04**	-	**462.50**	**1437.50**	**40.00**	**67.50**	**51.05**	**174.50**
			Max		**1.44**	**7.92**	**24.72**	**0.13**	**46565.42**	**1100.00**	**2.37**	**1.90**	**0.35**	**156.96**	**130.87**	**0.11**	**7.86**	**295.00**	**131.82**	**1664.78**	**4271.50**	**19576.09**	**166.96**	**46.25**	**138.50**	**20.00**	-	-	-	**57.00**	**339.50**	-	**496.96**	**1973.91**	**40.00**	**108.75**	**62.50**	**191.74**

APPENDIX VI – RESULTS XRF PANALYTICAL (OMNIAN OPERATION MODE)

METHODOLOGY	TYPE OF SAMPLING	FTD	SAMPLE	DEPTH	CHEMICAL ELEMENT																										
					F	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	K2O	CaO	Ti	Cr	Mn	Fe2O3	Ni	Cu	Zn	As	Rb	Sr	Zr	Nb	Cd	Ag	Sn	Ba	W	Bi
				m	ppm	%	%	%	%	%	%	%	%	%	ppm	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
XRF PANALYTICAL (Omnian)	SURFACE SAMPLING	FTD 2A	S1	0.00-0.30	4910.00	0.59	1.98	15.05	58.66	0.36	3.72	4.33	0.42	0.75	120.00	0.07	11.01	70.00	1540.00	1450.00	20030.00	660.00	100.00	220.00	<LOD	<LOD	<LOD	270.00	390.00	650.00	80.00
			S2	0.00-0.30	5690.00	0.61	<LOD	15.18	58.26	0.35	4.48	4.20	0.38	0.73	110.00	0.07	11.65	80.00	2540.00	2760.00	27320.00	630.00	90.00	230.00	<LOD	<LOD	70.00	300.00	340.00	790.00	100.00
			S3	0.00-0.30	7600.00	0.56	<LOD	16.09	55.72	0.41	4.74	4.42	0.35	0.80	120.00	0.07	12.56	70.00	2240.00	1670.00	27580.00	720.00	100.00	260.00	<LOD	<LOD	<LOD	530.00	330.00	1480.00	180.00
			S4	0.00-0.30	8410.00	0.62	<LOD	17.12	53.49	0.37	5.96	4.06	0.48	0.72	160.00	0.07	12.04	90.00	2790.00	6190.00	29560.00	790.00	90.00	190.00	<LOD	<LOD	130.00	530.00	280.00	1230.00	110.00
			S5	0.00-0.30	7340.00	0.55	<LOD	15.88	51.38	0.43	5.79	4.30	0.37	0.77	150.00	0.08	14.68	100.00	3350.00	5180.00	37380.00	670.00	100.00	250.00	20.00	<LOD	100.00	690.00	270.00	1920.00	180.00
			S6	0.00-0.30	6400.00	0.51	<LOD	14.42	55.94	0.46	5.28	4.13	0.44	0.69	110.00	0.09	13.07	60.00	2850.00	5170.00	31850.00	580.00	100.00	240.00	<LOD	<LOD	120.00	650.00	300.00	1180.00	110.00
			S7	0.00-0.30	6980.00	0.54	<LOD	13.65	57.13	0.48	5.69	3.78	0.42	0.65	140.00	0.10	12.69	<LOD	3460.00	6140.00	28620.00	680.00	110.00	220.00	<LOD	<LOD	120.00	650.00	270.00	1240.00	170.00
			S8	0.00-0.30	7870.00	0.62	<LOD	16.45	60.15	0.43	3.23	4.59	0.48	0.77	150.00	0.08	10.09	80.00	2140.00	3890.00	14440.00	730.00	100.00	230.00	<LOD	<LOD	50.00	430.00	320.00	750.00	90.00
			S9	0.00-0.30	6550.00	0.56	<LOD	14.11	53.77	0.47	6.61	3.61	0.40	0.73	130.00	0.09	14.18	80.00	4440.00	6630.00	31880.00	630.00	110.00	270.00	<LOD	<LOD	150.00	880.00	230.00	2430.00	160.00
			S10	0.00-0.30	6860.00	0.47	<LOD	13.71	50.46	0.43	7.36	3.85	0.35	0.66	170.00	0.08	15.30	90.00	2830.00	8170.00	51130.00	620.00	100.00	210.00	<LOD	<LOD	220.00	750.00	120.00	1750.00	290.00
			S11	0.00-0.30	4750.00	<LOD	<LOD	11.67	30.63	0.45	19.54	2.53	0.70	0.42	290.00	0.21	21.50	190.00	8690.00	23670.00	73100.00	400.00	80.00	140.00	20.00	140.00	260.00	1580.00	<LOD	9670.00	520.00
			S12	0.00-0.30	5620.00	0.56	<LOD	14.31	55.68	0.44	5.51	4.08	0.43	0.76	120.00	0.07	13.17	70.00	2630.00	4290.00	33820.00	670.00	90.00	240.00	<LOD	<LOD	80.00	520.00	320.00	1320.00	170.00
			Mean		**6581.67**	**0.56**	**-**	**14.80**	**53.44**	**0.42**	**6.49**	**3.99**	**0.43**	**0.70**	**147.50**	**0.09**	**13.50**	**89.09**	**3291.67**	**6267.50**	**33892.50**	**648.33**	**97.50**	**225.00**	**20.00**	**-**	**130.00**	**648.33**	**288.18**	**2034.17**	**180.00**
			Median		**6705.00**	**0.56**	**-**	**14.74**	**55.70**	**0.43**	**5.60**	**4.10**	**0.42**	**0.73**	**135.00**	**0.08**	**12.88**	**80.00**	**2810.00**	**5175.00**	**30705.00**	**665.00**	**100.00**	**230.00**	**20.00**	**-**	**120.00**	**590.00**	**300.00**	**1280.00**	**165.00**
			SD		**1158.14**	**0.05**	**-**	**1.49**	**7.74**	**0.04**	**4.27**	**0.54**	**0.10**	**0.10**	**49.01**	**0.04**	**2.93**	**35.34**	**1850.20**	**5840.44**	**15240.30**	**96.18**	**8.66**	**34.51**	**0.00**	**-**	**65.83**	**342.50**	**70.26**	**2458.63**	**121.58**
			CV (%)		**17.60**	**8.07**	**-**	**10.04**	**14.48**	**10.29**	**65.73**	**13.45**	**22.01**	**14.22**	**33.23**	**44.87**	**21.69**	**39.67**	**56.21**	**93.19**	**44.97**	**14.84**	**8.88**	**15.34**	**0.00**	**-**	**50.64**	**52.83**	**24.38**	**120.87**	**67.54**
			Min		**4750.00**	**0.47**	**-**	**11.67**	**30.63**	**0.35**	**3.23**	**2.53**	**0.35**	**0.42**	**110.00**	**0.07**	**10.09**	**60.00**	**1540.00**	**1450.00**	**14440.00**	**400.00**	**80.00**	**140.00**	**20.00**	**-**	**50.00**	**270.00**	**120.00**	**650.00**	**80.00**
			Max		**8410.00**	**0.62**	**-**	**17.12**	**60.15**	**0.48**	**19.54**	**4.59**	**0.70**	**0.80**	**290.00**	**0.21**	**21.50**	**190.00**	**8690.00**	**23670.00**	**73100.00**	**790.00**	**110.00**	**270.00**	**20.00**	**-**	**260.00**	**1580.00**	**390.00**	**9670.00**	**520.00**
	BOREHOLE LOGGING	FTD 1	B1.S5.2.2	1.59-2.00	7410.00	0.84	2.18	18.82	60.23	0.33	1.81	4.51	0.47	0.81	120.00	0.10	7.76	120.00	2430.00	3950.00	3970.00	820.00	70.00	210.00	20.00	60.00	-	250.00	360.00	1750.00	<LOD
			B1.S5.3.2	2.33-2.66	8040.00	0.81	2.37	20.44	57.70	0.30	1.53	5.41	0.51	0.86	130.00	0.12	8.01	100.00	1580.00	3780.00	2760.00	840.00	80.00	230.00	10.00	<LOD	-	230.00	450.00	1570.00	<LOD
			B1.S5.4.2	3.63-4.00	8610.00	0.84	2.39	20.34	57.90	0.31	1.72	5.04	0.49	0.84	140.00	0.11	7.79	80.00	2000.00	4630.00	3340.00	770.00	80.00	220.00	20.00	50.00	-	290.00	440.00	1520.00	<LOD
			Mean		**8020.00**	**0.83**	**2.31**	**19.87**	**58.61**	**0.31**	**1.69**	**4.99**	**0.49**	**0.84**	**130.00**	**0.11**	**7.86**	**100.00**	**2003.33**	**4120.00**	**3356.67**	**810.00**	**76.67**	**220.00**	**16.67**	**55.00**	**-**	**256.67**	**416.67**	**1613.33**	**-**
			Median		**8040.00**	**0.84**	**2.37**	**20.34**	**57.90**	**0.31**	**1.72**	**5.04**	**0.49**	**0.84**	**130.00**	**0.08**	**7.79**	**100.00**	**2000.00**	**3950.00**	**3340.00**	**820.00**	**80.00**	**220.00**	**20.00**	**55.00**	**-**	**250.00**	**440.00**	**1570.00**	**-**
			SD		**600.25**	**0.01**	**0.12**	**0.91**	**1.40**	**0.02**	**0.15**	**0.45**	**0.02**	**0.03**	**10.00**	**0.01**	**0.14**	**20.00**	**425.01**	**449.78**	**605.17**	**36.06**	**5.77**	**10.00**	**5.77**	**7.07**	**-**	**30.55**	**49.33**	**120.97**	**-**
			CV (%)		**7.48**	**1.64**	**4.99**	**4.58**	**2.39**	**6.20**	**8.70**	**9.09**	**3.58**	**3.53**	**7.69**	**9.53**	**1.75**	**20.00**	**21.22**	**10.92**	**18.03**	**4.45**	**7.53**	**4.55**	**34.64**	**12.86**	**-**	**11.90**	**11.84**	**7.50**	**-**
			Min		**7410.00**	**0.81**	**2.18**	**18.82**	**57.70**	**0.30**	**1.53**	**4.51**	**0.47**	**0.81**	**120.00**	**0.10**	**7.76**	**80.00**	**1580.00**	**3780.00**	**2760.00**	**770.00**	**70.00**	**210.00**	**10.00**	**50.00**	**-**	**230.00**	**360.00**	**1520.00**	**-**
			Max		**8610.00**	**0.84**	**2.39**	**20.44**	**60.23**	**0.33**	**1.81**	**5.41**	**0.51**	**0.86**	**140.00**	**0.12**	**8.01**	**120.00**	**2430.00**	**4630.00**	**3970.00**	**840.00**	**80.00**	**230.00**	**20.00**	**60.00**	**-**	**290.00**	**450.00**	**1750.00**	**-**
		FTD 2A	B2.S2.2.2	1.50-2.00	8080.00	0.67	2.09	15.47	58.87	0.39	4.31	3.60	0.66	0.67	1300.00	0.10	9.47	80.00	2060.00	6440.00	17760.00	700.00	70.00	190.00	20.00	90.00	-	310.00	180.00	850.00	90.00
			B2.S2.3.2	2.50-3.00	7390.00	0.64	2.12	16.05	55.79	0.39	5.04	3.83	0.79	0.69	1500.00	0.12	10.51	70.00	2730.00	8060.00	19180.00	740.00	80.00	160.00	<LOD	110.00	-	370.00	200.00	1050.00	<LOD
			B2.S2.4.2	3.50-4.00	7910.00	0.69	2.25	15.94	58.02	0.33	4.24	3.68	0.64	0.68	1200.00	0.10	9.82	70.00	1910.00	4220.00	19180.00	730.00	70.00	170.00	<LOD	<LOD	-	240.00	280.00	1110.00	140.00
			Mean		**7793.33**	**0.66**	**2.15**	**15.82**	**57.56**	**0.37**	**4.53**	**3.70**	**0.70**	**0.68**	**1333.33**	**0.11**	**9.93**	**73.33**	**2233.33**	**6240.00**	**18706.67**	**723.33**	**73.33**	**173.33**	**-**	**100.00**	**-**	**306.67**	**220.00**	**1003.33**	**115.00**
			Median		**7910.00**	**0.67**	**2.12**	**15.94**	**58.02**	**0.39**	**4.31**	**3.68**	**0.66**	**0.68**	**1300.00**	**0.10**	**9.82**	**70.00**	**2060.00**	**6440.00**	**19180.00**	**730.00**	**70.00**	**170.00**	**-**	**100.00**	**-**	**310.00**	**200.00**	**1050.00**	**115.00**
			SD		**359.49**	**0.03**	**0.09**	**0.31**	**1.59**	**0.04**	**0.44**	**0.12**	**0.08**	**0.01**	**152.75**	**0.01**	**0.53**	**5.77**	**436.62**	**1927.80**	**819.84**	**20.82**	**5.77**	**15.28**	**-**	**14.14**	**-**	**65.06**	**52.92**	**136.14**	**35.36**
			CV (%)		**4.61**	**3.91**	**4.00**	**1.98**	**2.76**	**10.19**	**9.70**	**3.12**	**11.91**	**2.02**	**11.46**	**10.88**	**5.33**	**7.87**	**19.55**	**30.89**	**4.38**	**2.88**	**7.87**	**8.81**	**-**	**14.14**	**-**	**21.22**	**24.05**	**13.57**	**30.74**
			Min		**7390.00**	**0.64**	**2.09**	**15.47**	**55.79**	**0.33**	**4.24**	**3.60**	**0.64**	**0.67**	**1200.00**	**0.10**	**9.47**	**70.00**	**1910.00**	**4220.00**	**17760.00**	**700.00**	**70.00**	**160.00**	**-**	**90.00**	**-**	**240.00**	**180.00**	**850.00**	**90.00**
			Max		**8080.00**	**0.69**	**2.25**	**16.05**	**58.87**	**0.39**	**5.04**	**3.83**	**0.79**	**0.69**	**1500.00**	**0.12**	**10.51**	**80.00**	**2730.00**	**8060.00**	**19180.00**	**740.00**	**80.00**	**190.00**	**-**	**110.00**	**-**	**370.00**	**280.00**	**1110.00**	**140.00**

APPENDIX VII – RESULTS XRF PANALYTICAL (PRO-TRACE OPERATION MODE)

METHODOLOGY	TYPE OF SAMPLING	FTD	SAMPLE	DEPTH	CHEMICAL ELEMENT																																					
					CaO	Sc	TiO2	V	Cr	Mn	Fe2O3	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	Ag	Cd	Sn	Sb	I	Cs	Ba	La	Ce	Hf	W	Tl	Pb	Bi	Th	U
				m	%	ppm	%	ppm	ppm	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
XRF PANALYTICAL (Pro-Trace)	SURFACE SAMPLING	FTD 2A	S1	0-0.3	0.33	12.00	0.62	107.80	86.30	0.05	9909.00	10.70	24.30	1206.50	1224.30	16.60	2.50	13712.00	<LOD	22.00	362.30	59.60	18.00	147.30	8.60	3.00	11199.00	22.70	249.20	6.60	3.00	45.00	382.30	25.60	268.50	3.90	482.30	1.50	69.60	<LOD	6.10	3.30
			S2	0-0.3	0.29	10.80	0.60	101.20	88.90	0.05	10561.00	12.90	30.20	2260.20	2728.50	18.00	4.10	20990.20	<LOD	34.80	375.00	59.50	19.60	153.10	9.80	3.20	15367.00	51.70	326.20	7.80	6.30	37.30	370.60	18.80	331.70	4.00	738.50	13.80	110.80	<LOD	6.20	3.00
			S3	0-0.3	0.28	12.40	0.66	105.30	93.60	0.04	11097.00	11.50	23.70	1934.90	1677.80	18.60	10.80	20124.40	<LOD	31.70	392.90	69.30	19.60	165.40	9.60	3.00	29593.00	32.90	497.10	4.40	5.50	33.60	365.60	26.30	328.10	3.10	1256.10	11.60	120.40	<LOD	6.80	2.70
			S4	0-0.3	0.40	12.90	0.65	105.60	106.30	0.05	11883.00	18.00	48.00	3430.40	7913.50	22.70	10.10	30360.70	<LOD	54.10	423.60	81.90	19.70	173.00	9.50	2.70	31064.00	138.90	622.60	9.30	8.00	27.40	365.40	22.90	373.70	<LOD	1354.10	27.80	123.50	<LOD	5.90	2.90
			S5	0-0.3	0.27	13.10	0.63	97.90	96.80	0.05	12693.00	12.30	28.00	3042.50	5013.70	20.30	12.00	28380.20	<LOD	43.40	393.20	70.40	18.40	165.70	9.30	3.60	34135.00	76.10	618.20	7.00	6.10	28.40	357.80	19.30	360.60	2.30	1517.50	23.40	140.40	<LOD	5.90	3.10
			S6	0-0.3	0.32	12.20	0.54	88.60	86.10	0.06	11125.00	12.00	25.90	2439.50	4839.80	17.30	10.80	21940.90	<LOD	36.10	351.00	69.30	16.40	150.50	8.10	3.50	31917.00	83.20	509.10	6.40	5.30	34.30	319.10	22.20	338.60	0.10	969.20	14.80	101.80	<LOD	5.20	2.30
			S7	0-0.3	0.30	11.80	0.53	85.10	78.10	0.06	10980.00	11.90	26.70	2760.20	5390.20	16.70	11.00	20719.30	<LOD	33.30	330.40	67.00	15.90	139.30	7.60	2.40	27516.00	87.40	540.70	7.20	4.60	25.40	310.80	19.90	326.10	0.50	864.20	12.90	93.60	<LOD	5.10	3.20
			S8	0-0.3	0.36	13.30	0.62	114.90	105.50	0.05	9133.00	11.00	23.40	1775.90	3496.30	19.20	11.00	10530.30	<LOD	15.00	394.20	70.20	19.00	154.90	8.80	2.60	20200.00	57.20	381.60	4.70	1.50	48.80	396.90	18.90	223.50	0.60	599.90	0.90	93.40	5016.00	6.20	1.40
			S9	0-0.3	0.31	12.60	0.61	90.30	102.00	0.06	12346.00	14.10	28.90	4143.50	6930.20	19.30	20.10	23628.60	<LOD	37.20	337.30	73.50	18.50	178.60	9.40	3.80	37249.00	101.20	745.60	6.30	13.30	23.60	278.80	19.60	310.70	<LOD	2089.20	21.50	171.00	<LOD	5.90	2.00
			S10	0-0.3	0.26	12.70	0.54	79.00	89.90	0.05	13072.00	13.80	32.30	2995.80	9833.70	17.60	11.80	41696.90	<LOD	67.50	342.10	67.80	17.20	153.30	8.90	3.70	32494.00	154.80	721.50	12.30	7.10	7.90	298.80	21.30	447.40	<LOD	1788.30	38.40	121.30	<LOD	5.90	3.00
			S11	0-0.3	0.60	14.60	0.39	41.20	227.40	0.16	19866.00	37.30	241.20	17598.90	51729.00	21.30	106.80	110218.60	<LOD	192.10	248.60	85.60	11.90	161.90	17.40	13.10	88370.00	419.40	2631.50	45.30	35.50	<LOD	242.00	11.10	483.90	<LOD	16649.70	133.70	417.20	254181.00	3.40	<LOD
			S12	0-0.3	0.32	13.30	0.60	94.70	83.60	0.05	11386.00	12.30	25.40	2305.90	4088.20	17.40	4.70	24707.60	<LOD	37.80	359.00	62.30	18.10	149.10	9.80	3.80	20289.00	71.20	418.30	8.20	6.20	18.10	336.90	22.50	362.20	<LOD	1043.50	16.50	136.40	<LOD	6.00	2.30
			Mean		**0.34**	**12.64**	**0.58**	**92.63**	**103.71**	**0.06**	**12004.25**	**14.82**	**46.50**	**3824.52**	**8738.77**	**18.75**	**17.98**	**30584.14**	-	**50.42**	**359.13**	**69.70**	**17.69**	**157.68**	**9.73**	**4.03**	**31616.08**	**108.06**	**688.47**	**10.46**	**8.53**	**29.98**	**335.42**	**20.70**	**346.25**	**2.07**	**2446.04**	**26.40**	**141.62**	**129598.50**	**5.72**	**2.65**
			Median		**0.31**	**12.65**	**0.61**	**96.30**	**91.75**	**0.05**	**11255.50**	**12.30**	**27.35**	**2599.85**	**4926.75**	**18.30**	**10.90**	**22784.75**	-	**36.65**	**360.65**	**69.30**	**18.25**	**154.10**	**9.35**	**3.35**	**30328.50**	**79.65**	**524.90**	**7.10**	**6.15**	**28.40**	**347.35**	**20.60**	**335.15**	**2.30**	**1149.80**	**15.65**	**120.85**	**129598.50**	**5.90**	**2.90**
			SD		**0.09**	**0.94**	**0.08**	**19.23**	**39.94**	**0.03**	**2718.58**	**7.34**	**61.67**	**4407.79**	**13768.08**	**1.90**	**28.35**	**26308.07**	-	**46.63**	**44.54**	**7.91**	**2.20**	**11.41**	**2.51**	**2.90**	**19588.19**	**105.42**	**630.37**	**11.17**	**8.96**	**11.68**	**46.39**	**3.92**	**69.92**	**1.67**	**4498.53**	**35.36**	**90.64**	**176186.26**	**0.85**	**0.59**
			CV (%)		**27.16**	**7.45**	**12.94**	**20.76**	**38.51**	**53.88**	**22.65**	**49.53**	**132.63**	**115.25**	**157.55**	**10.13**	**157.70**	**86.02**	-	**92.49**	**12.40**	**11.35**	**12.42**	**7.24**	**25.77**	**71.79**	**61.96**	**97.56**	**91.56**	**106.78**	**105.04**	**38.96**	**13.83**	**18.93**	**20.19**	**80.53**	**183.91**	**133.95**	**64.01**	**135.95**	**14.93**	**22.18**
			Min		**0.26**	**10.80**	**0.39**	**41.20**	**78.10**	**0.04**	**9133.00**	**10.70**	**23.40**	**1206.50**	**1224.30**	**16.60**	**2.50**	**10530.30**	-	**15.00**	**248.60**	**59.50**	**11.90**	**139.30**	**7.60**	**2.40**	**11199.00**	**22.70**	**249.20**	**4.40**	**1.50**	**7.90**	**242.00**	**11.10**	**223.50**	**0.10**	**482.30**	**0.90**	**69.60**	**5016.00**	**3.40**	**1.40**
			Max		**0.60**	**14.60**	**0.66**	**114.90**	**227.40**	**0.16**	**19866.00**	**37.30**	**241.20**	**17598.90**	**51729.00**	**22.70**	**106.80**	**110218.60**	-	**192.10**	**423.60**	**85.60**	**19.70**	**178.60**	**17.40**	**13.10**	**88370.00**	**419.40**	**2631.50**	**45.30**	**35.50**	**48.80**	**396.90**	**26.30**	**483.90**	**4.00**	**16649.70**	**133.70**	**417.20**	**254181.00**	**6.80**	**3.30**
	BOREHOLE LOGGING	FTD 1	B1.S5.2.2	1.59-2.00	0.43	14.20	0.78	141.10	110.10	0.07	8457.00	17.20	63.70	2434.80	4279.80	28.50	15.10	3667.50	1.10	2.80	531.60	74.40	30.80	193.80	12.80	2.80	13228.00	58.90	317.50	1.90	2.10	76.70	470.20	29.00	122.10	1.20	1563.30	<LOD	130.70	18035.00	7.40	3.80
			B1.S5.3.2	2.33-2.66	0.43	15.70	0.83	161.80	117.50	0.09	8473.00	18.70	62.40	1475.20	3908.40	29.60	13.70	2411.90	1.80	<LOD	611.90	70.10	25.00	195.90	14.30	3.00	14754.00	36.60	268.40	4.50	3.10	91.30	557.00	31.90	103.50	1.90	1370.20	<LOD	105.50	20609.00	7.90	3.20
			B1.S5.4.2.	3.63-4.00	0.46	15.20	0.84	157.00	111.20	0.09	8622.00	17.70	59.20	1971.90	5106.20	29.70	14.90	3158.00	1.70	1.20	591.70	81.40	26.00	201.60	14.40	2.50	17347.00	56.80	344.60	3.50	3.60	83.90	544.00	32.00	107.00	1.10	1449.80	<LOD	89.30	20807.00	9.10	4.20
			Mean		**0.44**	**15.03**	**0.82**	**153.30**	**112.93**	**0.08**	**8517.33**	**17.87**	**61.77**	**1960.63**	**4431.47**	**29.27**	**14.57**	**3079.13**	**1.53**	**2.00**	**578.40**	**75.30**	**27.27**	**197.10**	**13.83**	**2.77**	**15109.67**	**50.77**	**310.17**	**3.30**	**2.93**	**83.97**	**523.73**	**30.97**	**110.87**	**1.40**	**1461.10**	-	**108.50**	**19817.00**	**8.13**	**3.73**
			Median		**0.43**	**15.20**	**0.83**	**157.00**	**111.20**	**0.09**	**8473.00**	**17.70**	**62.40**	**1971.90**	**4279.80**	**29.60**	**14.90**	**3158.00**	**1.70**	**2.00**	**591.70**	**74.40**	**26.00**	**195.90**	**14.30**	**2.80**	**14754.00**	**56.80**	**317.50**	**3.50**	**3.10**	**83.90**	**544.00**	**31.90**	**107.00**	**1.20**	**1449.80**	-	**105.50**	**20609.00**	**7.90**	**3.80**
			SD		**0.01**	**0.76**	**0.03**	**10.83**	**3.99**	**0.01**	**91.00**	**0.76**	**2.32**	**479.90**	**613.13**	**0.67**	**0.76**	**631.50**	**0.38**	**1.13**	**41.77**	**5.70**	**3.10**	**4.04**	**0.90**	**0.25**	**2082.41**	**12.31**	**38.63**	**1.31**	**0.76**	**7.30**	**46.81**	**1.70**	**9.88**	**0.44**	**97.04**	-	**20.86**	**1546.43**	**0.87**	**0.50**
			CV (%)		**3.32**	**5.08**	**3.78**	**7.07**	**3.54**	**13.97**	**1.07**	**4.27**	**3.75**	**24.48**	**13.84**	**2.28**	**5.20**	**20.51**	**24.69**	**56.57**	**7.22**	**7.57**	**11.37**	**2.05**	**6.48**	**9.10**	**13.78**	**24.26**	**12.45**	**39.74**	**26.04**	**8.69**	**8.94**	**5.50**	**8.92**	**31.13**	**6.64**	-	**19.23**	**7.80**	**10.74**	**13.48**
			Min		**0.43**	**14.20**	**0.78**	**141.10**	**110.10**	**0.07**	**8457.00**	**17.20**	**59.20**	**1475.20**	**3908.40**	**28.50**	**13.70**	**2411.90**	**1.10**	**1.20**	**531.60**	**70.10**	**25.00**	**193.80**	**12.80**	**2.50**	**13228.00**	**36.60**	**268.40**	**1.90**	**2.10**	**76.70**	**470.20**	**29.00**	**103.50**	**1.10**	**1370.20**	-	**89.30**	**18035.00**	**7.40**	**3.20**
			Max		**0.46**	**15.70**	**0.84**	**161.80**	**117.50**	**0.09**	**8622.00**	**18.70**	**63.70**	**2434.80**	**5106.20**	**29.70**	**15.10**	**3667.50**	**1.80**	**2.80**	**611.90**	**81.40**	**30.80**	**201.60**	**14.40**	**3.00**	**17347.00**	**58.90**	**344.60**	**4.50**	**3.60**	**91.30**	**557.00**	**32.00**	**122.10**	**1.90**	**1563.30**	-	**130.70**	**20807.00**	**9.10**	**4.20**
		FTD 2A	B2.S2.2.2.	1.5-2.0	0.58	11.10	0.63	104.60	88.50	0.08	10126.00	20.40	60.50	2569.90	8771.10	22.00	7.40	20126.90	<LOD	36.20	397.80	74.80	19.90	180.80	9.50	2.30	19014.00	109.30	425.70	8.00	2.30	40.40	359.80	20.50	303.70	0.70	942.10	16.20	90.30	<LOD	6.80	3.00
			B2.S2.3.2	2.5-3.0	0.69	12.10	0.62	99.90	87.80	0.09	11064.00	22.10	67.10	3582.10	11091.30	23.20	9.40	24136.10	<LOD	43.30	391.20	76.70	18.80	165.20	9.60	2.90	19156.00	134.60	509.90	9.20	4.20	41.70	351.90	20.00	303.70	<LOD	1195.60	24.50	121.30	<LOD	6.60	2.80
			B2.S2.4.2.	3.5-4.0	0.60	12.50	0.65	107.40	93.30	0.08	10771.00	23.10	72.00	2524.40	5960.40	21.40	6.90	22929.90	<LOD	42.20	399.50	67.90	19.80	181.90	11.40	6.70	12008.00	66.30	289.80	11.10	0.60	31.10	374.10	22.60	315.50	0.10	1329.60	20.40	130.40	12930.00	7.10	3.30
			Mean		**0.62**	**11.90**	**0.63**	**103.97**	**89.87**	**0.08**	**10653.67**	**21.87**	**66.53**	**2892.13**	**8607.60**	**22.20**	**7.90**	**22397.63**	-	**40.57**	**396.17**	**73.13**	**19.50**	**175.97**	**10.17**	**3.97**	**16726.00**	**103.40**	**408.47**	**9.43**	**2.37**	**37.73**	**361.93**	**21.03**	**307.63**	**0.40**	**1155.77**	**20.37**	**114.00**	-	**6.83**	**3.03**
			Median		**0.60**	**12.10**	**0.63**	**104.60**	**88.50**	**0.08**	**10771.00**	**22.10**	**67.10**	**2569.90**	**8771.10**	**22.00**	**7.40**	**22929.90**	-	**42.20**	**397.80**	**74.80**	**19.80**	**180.80**	**9.60**	**2.90**	**19014.00**	**109.30**	**425.70**	**9.20**	**2.30**	**40.40**	**359.80**	**20.50**	**303.70**	**0.40**	**1195.60**	**20.40**	**121.30**	-	**6.80**	**3.00**
			SD		**0.06**	**0.72**	**0.02**	**3.79**	**2.99**	**0.01**	**479.88**	**1.37**	**5.77**	**597.96**	**2569.35**	**0.92**	**1.32**	**2056.92**	-	**3.82**	**4.38**	**4.63**	**0.61**	**9.34**	**1.07**	**2.39**	**4086.52**	**34.53**	**111.06**	**1.56**	**1.80**	**5.78**	**11.25**	**1.38**	**6.81**	**0.42**	**196.80**	**4.15**	**21.02**	-	**0.25**	**0.25**
			CV (%)		**9.20**	**6.06**	**2.47**	**3.65**	**3.33**	**9.86**	**4.50**	**6.24**	**8.67**	**20.68**	**29.85**	**4.13**	**16.75**	**9.18**	-	**9.42**	**1.11**	**6.33**	**3.12**	**5.31**	**10.52**	**60.15**	**24.43**	**33.39**	**27.19**	**16.57**	**76.10**	**15.32**	**3.11**	**6.56**	**2.21**	**106.07**	**17.03**	**20.38**	**18.44**	-	**3.68**	**8.30**
			Min		**0.58**	**11.10**	**0.62**	**99.90**	**87.80**	**0.08**	**10126.00**	**20.40**	**60.50**	**2524.40**	**5960.40**	**21.40**	**6.90**	**20126.90**	-	**36.20**	**391.20**	**67.90**	**18.80**	**165.20**	**9.50**	**2.30**	**12008.00**	**66.30**	**289.80**	**8.00**	**0.60**	**31.10**	**351.90**	**20.00**	**303.70**	**0.10**	**942.10**	**16.20**	**90.30**	-	**6.60**	**2.80**
			Max		**0.69**	**12.50**	**0.65**	**107.40**	**93.30**	**0.09**	**11064.00**	**23.10**	**72.00**	**3582.10**	**11091.30**	**23.20**	**9.40**	**24136.10**	-	**43.30**	**399.50**	**76.70**	**19.90**	**181.90**	**11.40**	**6.70**	**19156.00**	**134.60**	**509.90**	**11.10**	**4.20**	**41.70**	**374.10**	**22.60**	**315.50**	**0.70**	**1329.60**	**24.50**	**130.40**	-	**7.10**	**3.30**

APPENDIX VIII – RESULTS XRD ANALYSIS SURFACE AND BOREHOLE SAMPLES

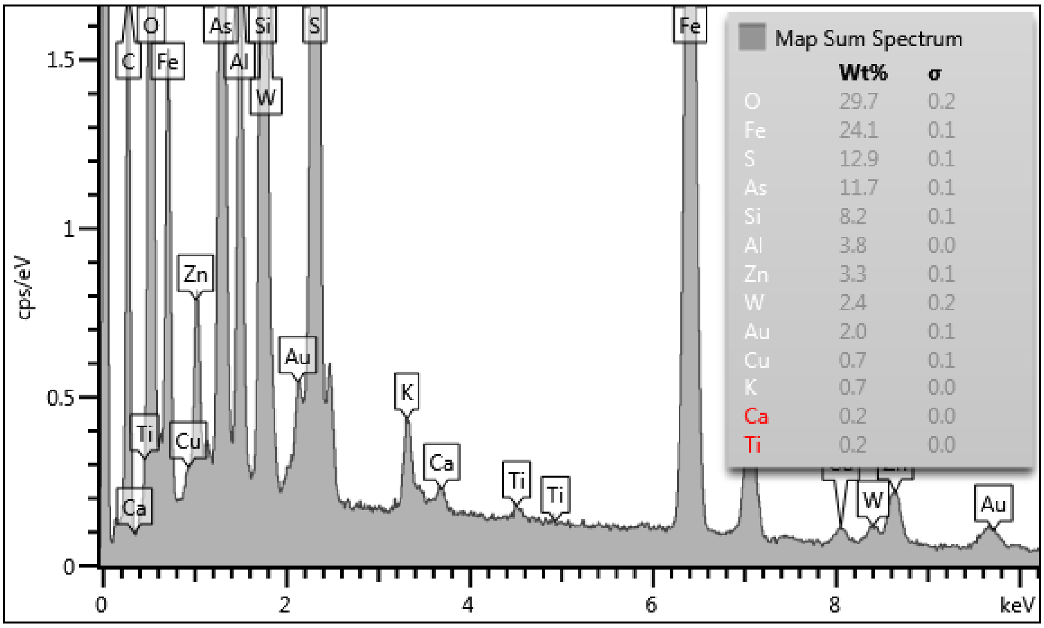
In order to calculate an estimate of the overall content of each mineral for each sample, we first had to multiply the peak width (W) by the relative intensity of the peak (H). Secondly, and after having all the results for each mineral, we added all these results to get the total amount of minerals (T). Finally, we multiplied each result by 100 and divided it by the total amount of minerals, and then we got the estimated overall mineral content for each mineral from the samples, as a percentage.

Estimated overall mineral content (%) = ((W * H) * 100) / T.

METHODOLOGY	TYPE OF SAMPLING	FTD	SAMPLE	DEPTH	ESTIMATED OVERALL MINERAL CONTENT																							
					Qtz	Ms	Ab	Clay min.	Hl	Py	Fo	Usp	Sme	Hem	Prh	Ilm	Arg	Chr	Str	Lrn	Mag	Lct	Ap	Sd	Zeo	Anh	Cal	Aeg
				m	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
XRD Philips PW3710	**SURFACE SAMPLING**	**FTD 2A**	S1	0.00-0.30	72.00	9.26	2.96	4.42	4.01	-	-	-	-	-	-	3.95	2.88	-	-	-	0.51	-	-	-	-	-	-	-
			S2	0.00-0.30	64.34	8.73	2.21	2.76	9.39	-	-	-	-	-	-	5.88	-	-	-	-	-	3.82	-	-	2.87	-	-	-
			S3	0.00-0.30	64.27	16.27	3.34	2.83	6.68	2.96	-	-	-	-	3.64	-	-	-	-	-	-	-	-	-	-	-	-	-
			S4	0.00-0.30	58.28	7.27	4.85	-	-	10.12	-	-	7.83	-	-	-	7.93	-	-	3.73	-	-	-	-	-	-	-	-
			S5	0.00-0.30	72.32	7.38	3.09	5.21	9.16	2.84	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
			S6	0.00-0.30	70.24	5.73	3.48	1.85	-	-	3.37	-	7.08	1.55	-	-	-	-	5.23	-	-	-	-	-	-	1.46	-	-
			S7	0.00-0.30	68.84	6.08	3.58	1.45	7.34	-	3.44	-	3.21	3.44	-	2.62	-	-	-	-	-	-	-	-	-	-	-	-
			S8	0.00-0.30	46.06	12.34	7.88	-	12.90	-	-	-	7.92	-	-	-	-	-	-	-	-	-	-	-	-	-	-	12.90
			S9	0.00-0.30	49.96	7.79	6.13	5.80	7.66	-	-	-	10.49	-	3.40	-	-	-	-	5.08	-	-	3.70	-	-	-	-	-
			S10	0.00-0.30	62.58	6.00	7.09	2.63	5.01	6.18	-	-	-	-	-	-	-	-	-	-	10.51	-	-	-	-	-	-	-
			S11	0.00-0.30	23.32	9.23	11.75	-	-	11.89	-	-	-	6.40	-	-	-	21.55	-	8.69	-	-	-	-	-	-	7.17	-
			S12	0.00-0.30	71.71	5.53	3.69	2.87	-	-	4.43	5.33	-	-	-	-	4.00	-	2.46	-	-	-	-	-	-	-	-	-
	BOREHOLE LOGGING	**FTD 1**	B1.S5.2.2	1.59-2.00	66.06	12.11	3.08	3.11	8.59	1.98	4.40	-	-	-	-	-	-	-	-	-	-	0.66	-	-	-	-	-	-
			B1.S5.3.2	2.33-2.66	51.25	14.94	8.90	5.49	-	-	5.17	-	-	-	3.44	-	-	-	3.38	-	-	-	1.31	6.11	-	-	-	-
			B1.S5.4.2	3.63-4.00	44.95	16.22	4.65	2.70	10.52	2.02	-	9.59	-	-	1.89	-	-	2.79	-	-	-	-	-	4.68	-	-	-	-
		FTD 2A	B2.S2.2.2	1.50-2.00	56.85	10.08	5.12	2.79	6.25	2.62	3.87	6.37	-	-	-	-	-	6.06	-	-	-	-	-	-	-	-	-	-
			B2.S2.3.2	2.50-3.00	65.36	6.32	5.05	-	5.05	6.27	3.53	4.71	-	3.70	-	-	-	-	-	-	-	-	-	-	-	-	-	-
			B2.S2.4.2	3.50-4.00	70.55	7.14	6.17	2.96	3.71	3.02	-	6.45	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

APPENDIX IX – RESULTS SEM ANALYSIS SAMPLE S10

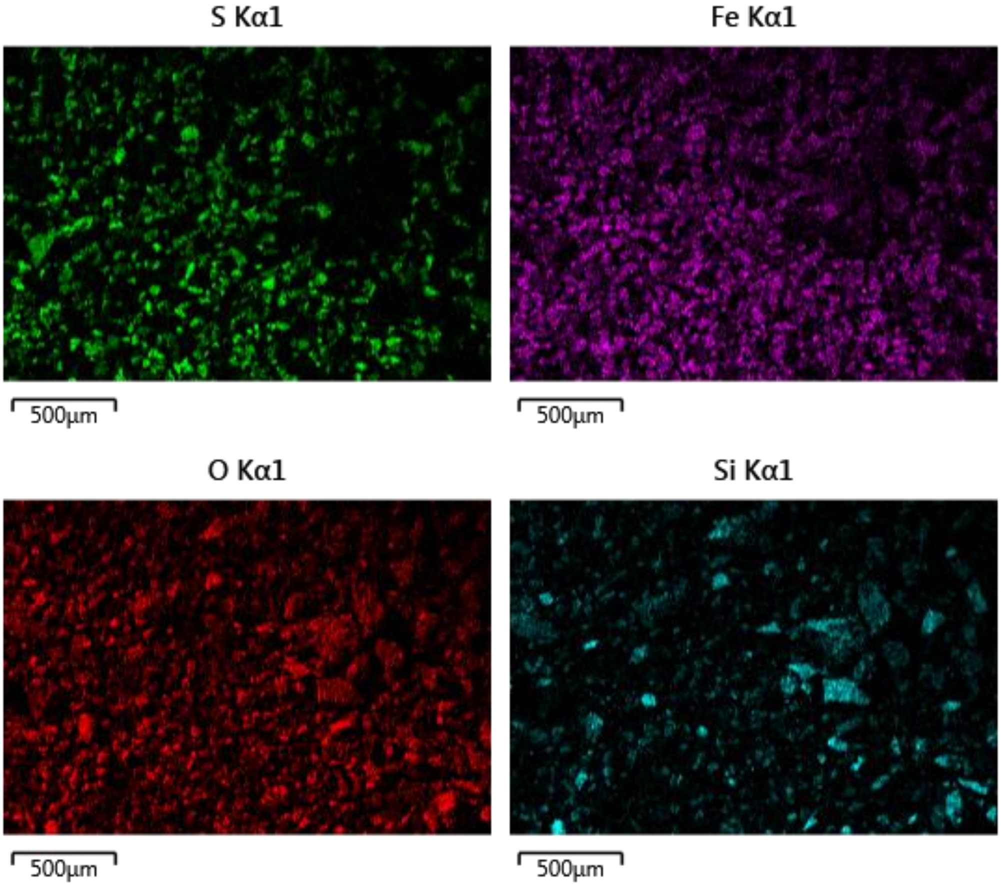
Summary spectrum chart in the selected region from the surface sample S10



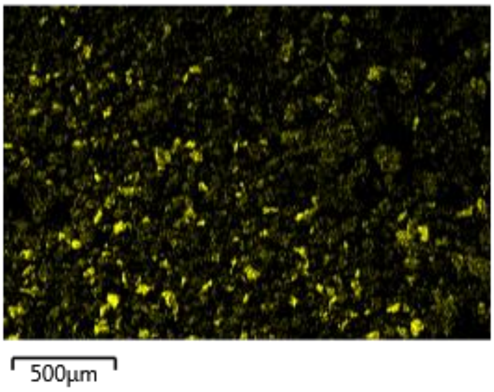
Map Sum Spectrum

	Wt%	σ
O	29.7	0.2
Fe	24.1	0.1
S	12.9	0.1
As	11.7	0.1
Si	8.2	0.1
Al	3.8	0.0
Zn	3.3	0.1
W	2.4	0.2
Au	2.0	0.1
Cu	0.7	0.1
K	0.7	0.0
Ca	0.2	0.0
Ti	0.2	0.0

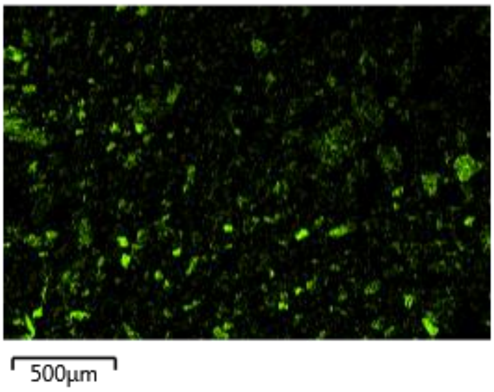
EDS layered image of the main chemical elements in the selected region from the surface sample S10



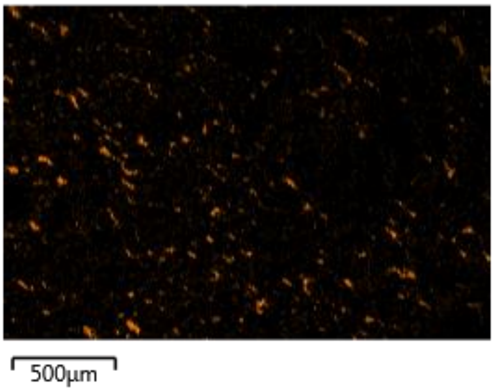
As Lα1_2



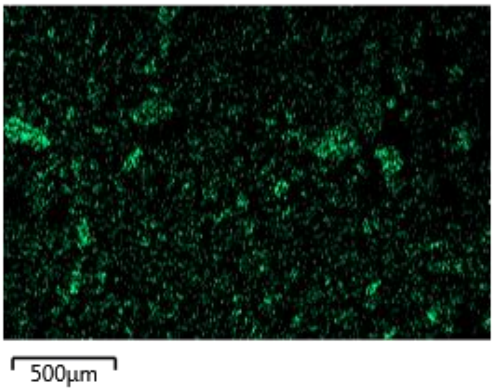
Al Kα1



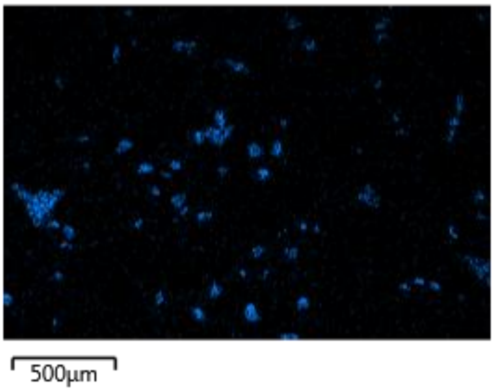
C Kα1_2



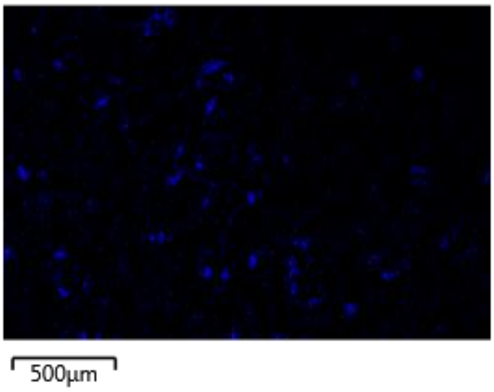
K Kα1



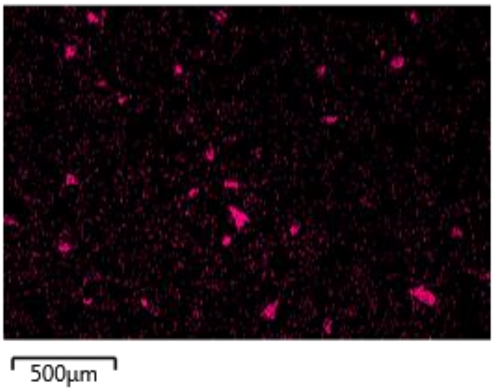
Zn Kα1



W Lα1

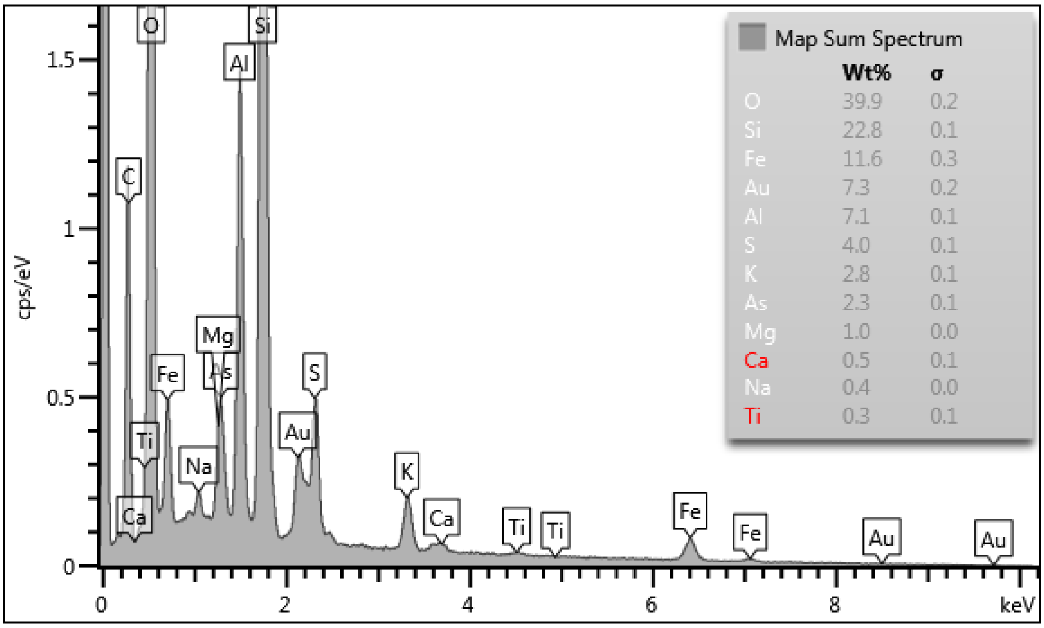


Cu Kα1



APPENDIX X – RESULTS SEM ANALYSIS SAMPLE B1.S5.4.2

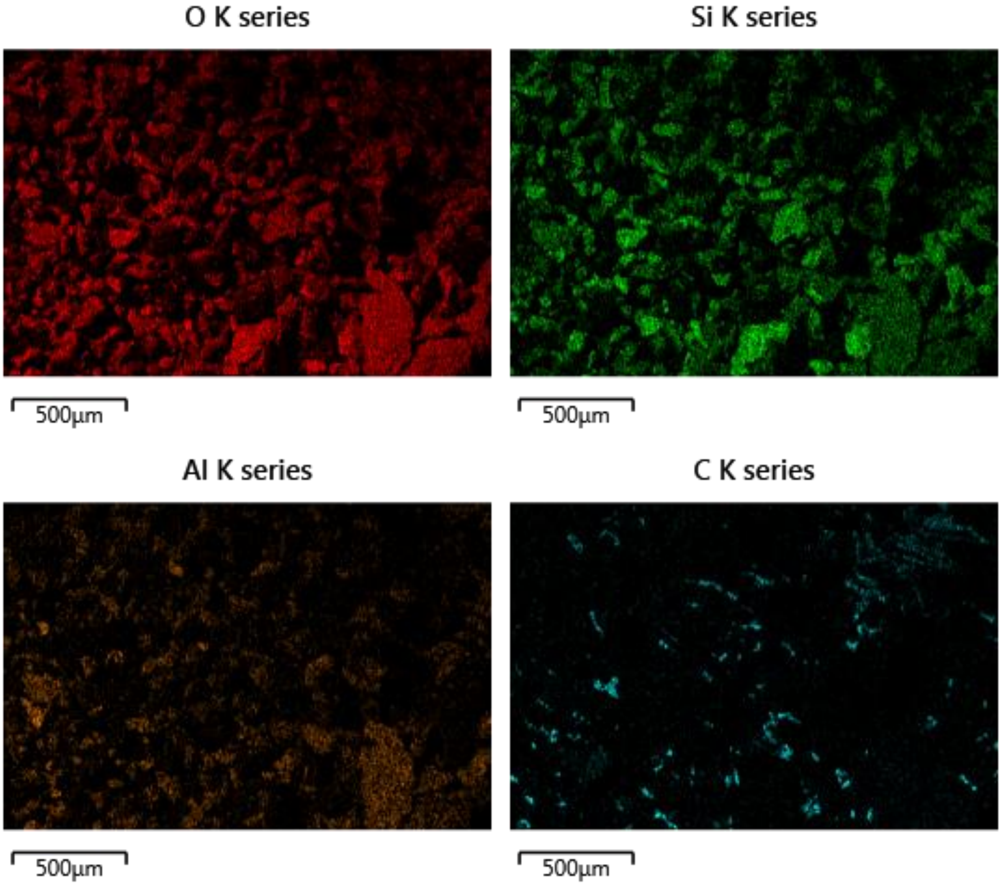
Summary spectrum chart in the selected region from the borehole sample B1.S5.4.2



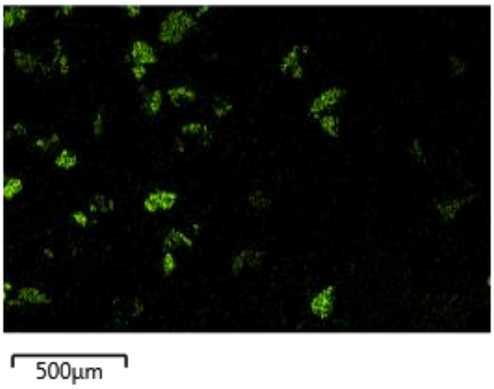
Map Sum Spectrum

	Wt%	σ
O	39.9	0.2
Si	22.8	0.1
Fe	11.6	0.3
Au	7.3	0.2
Al	7.1	0.1
S	4.0	0.1
K	2.8	0.1
As	2.3	0.1
Mg	1.0	0.0
Ca	0.5	0.1
Na	0.4	0.0
Ti	0.3	0.1

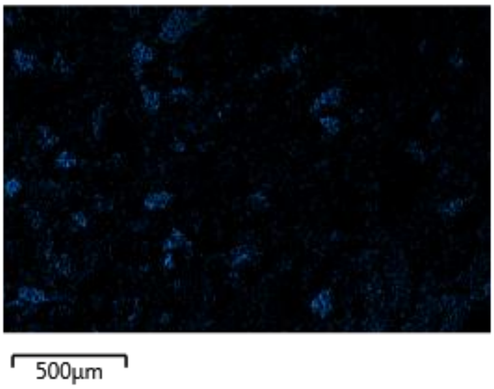
EDS layered image of the main chemical elements in the selected region from the borehole sample B1.S5.4.2



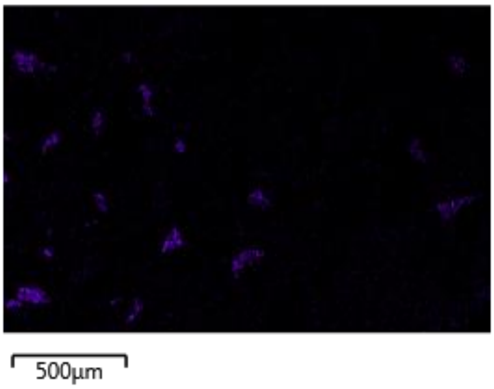
S K series



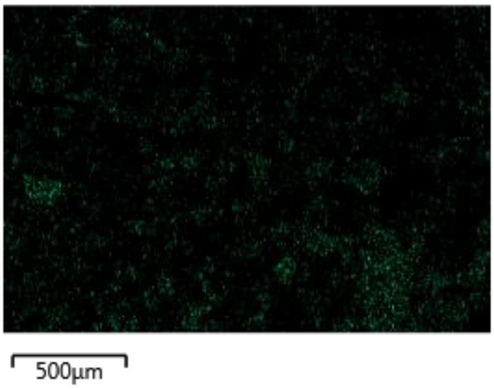
Fe L series



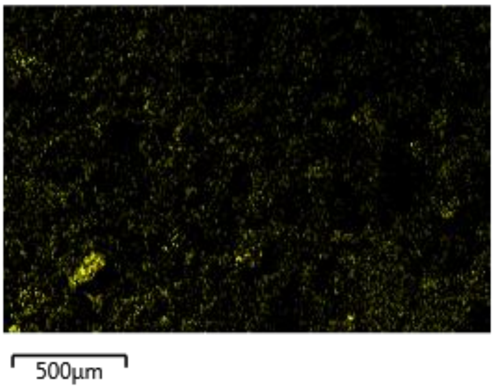
As L series



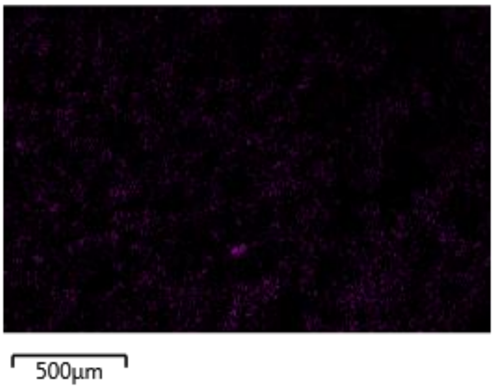
K K series



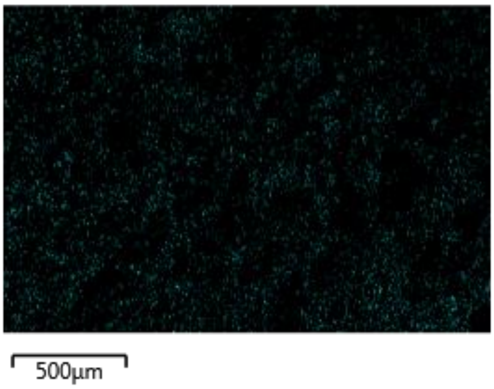
Mg K series



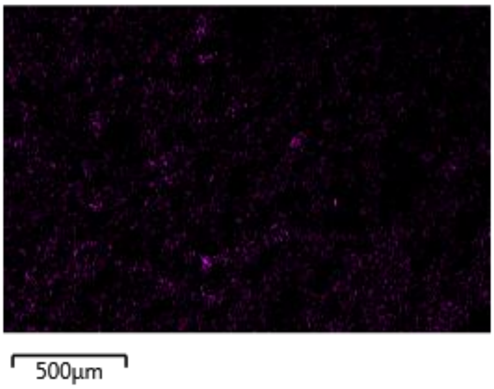
W M series

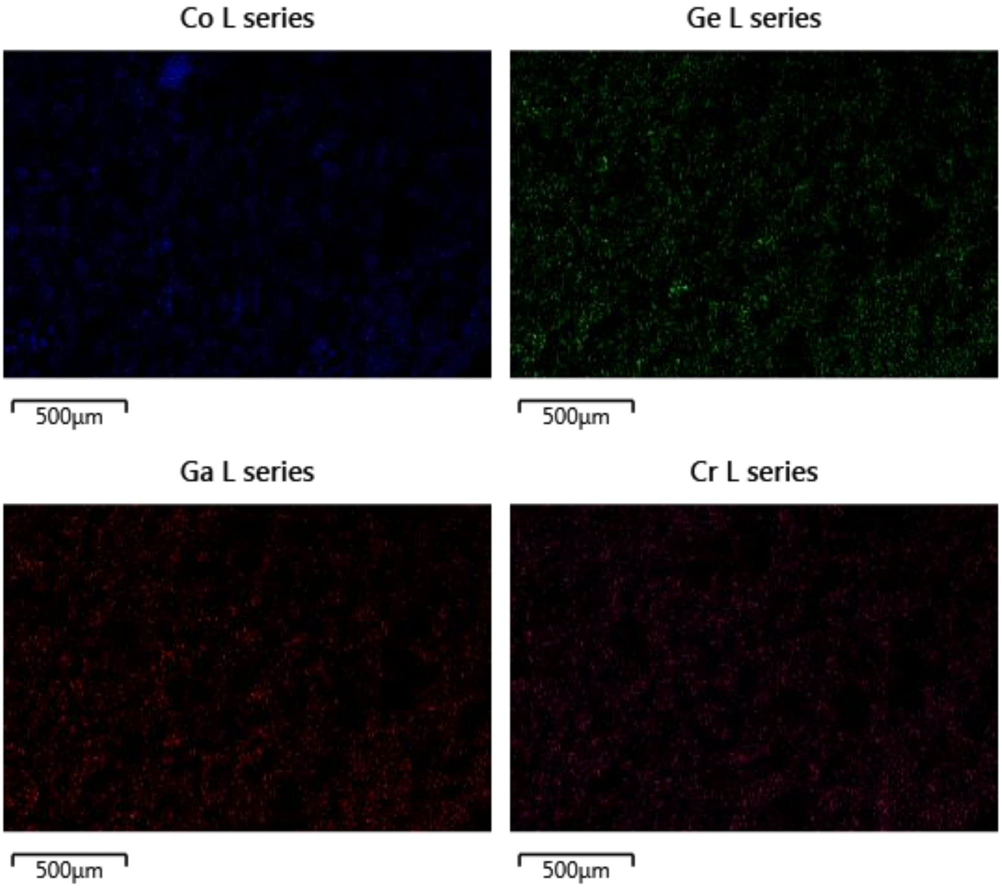


Nb L series



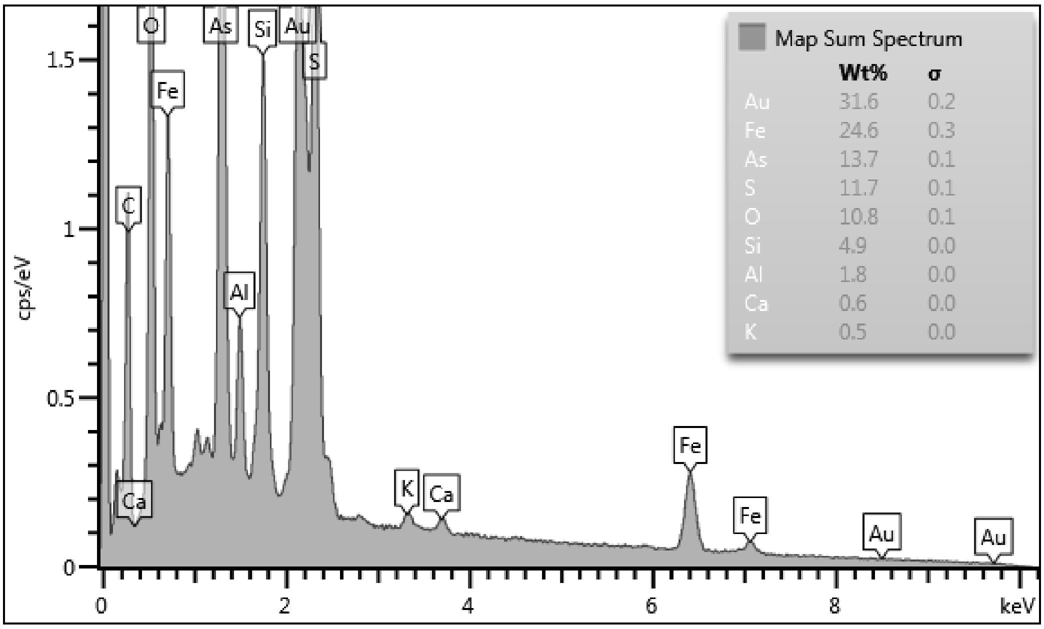
Na K series




Co L series
Ge L series
500µm
500µm
Ga L series
Cr L series
500µm
500µm

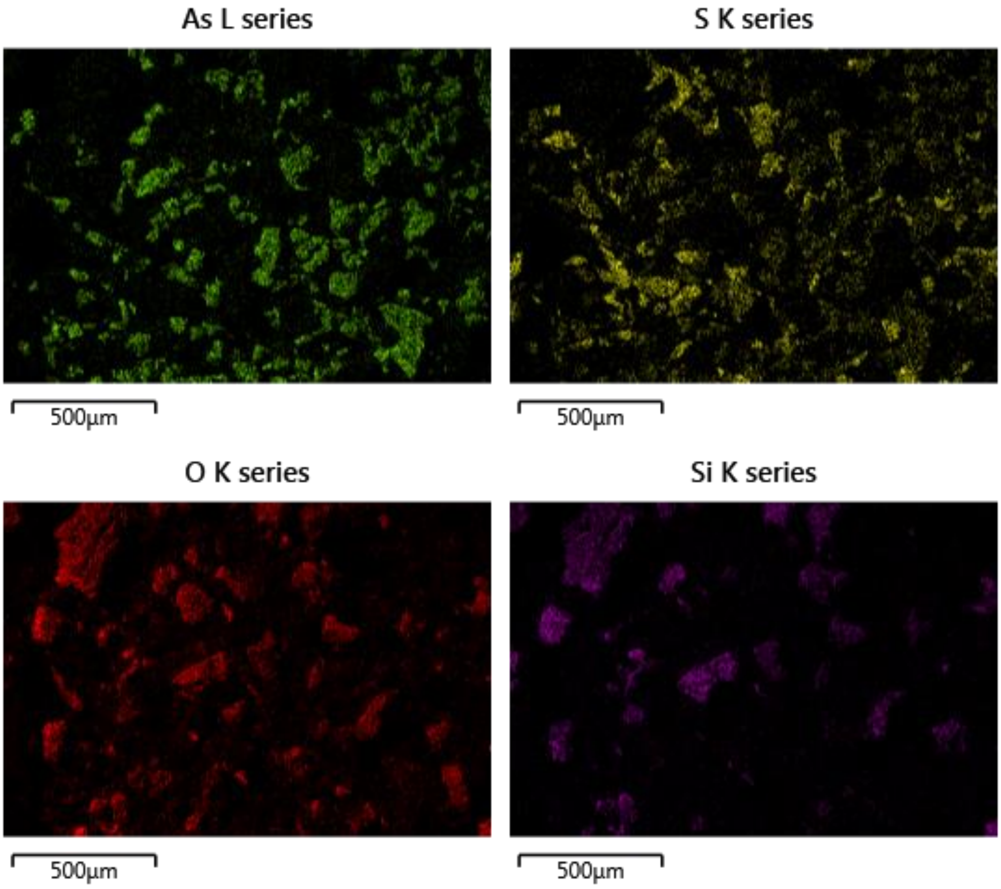
APPENDIX XI – RESULTS SEM ANALYSIS SAMPLE B2.S2.3.2

Summary spectrum chart in the selected region from the borehole sample B2.S2.3.2

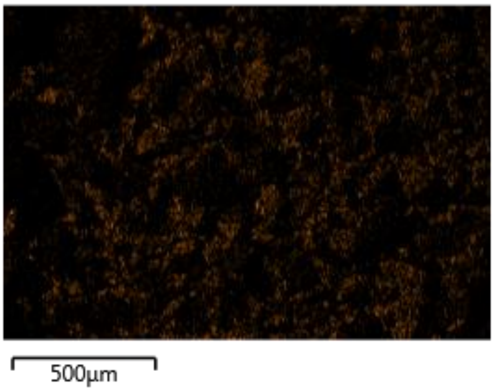


	Wt%	σ
Au	31.6	0.2
Fe	24.6	0.3
As	13.7	0.1
S	11.7	0.1
O	10.8	0.1
Si	4.9	0.0
Al	1.8	0.0
Ca	0.6	0.0
K	0.5	0.0

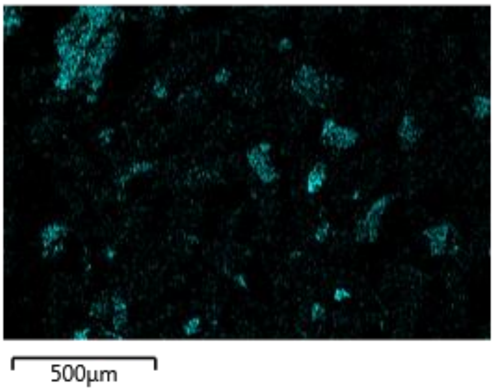
EDS layered image of the main chemical elements in the selected region from the borehole sample B2.S2.3.2



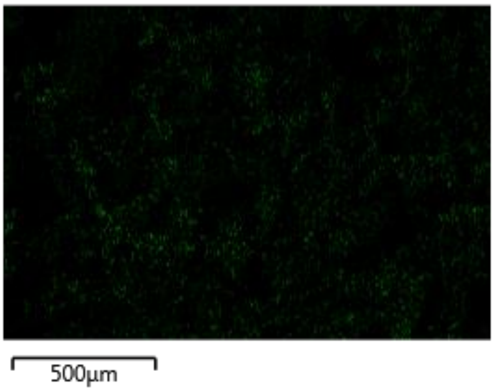
Fe L series



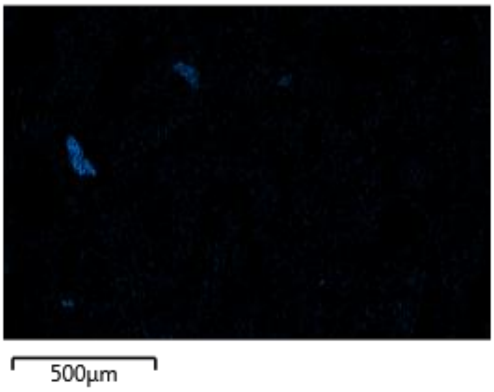
Al K series



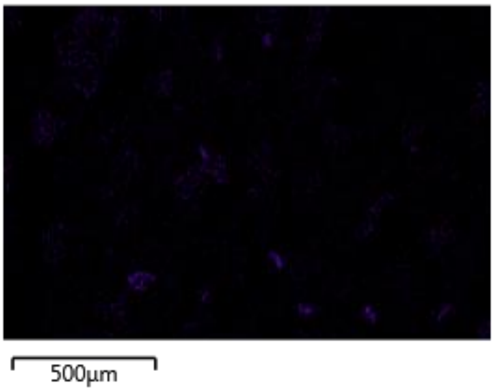
Pb M series



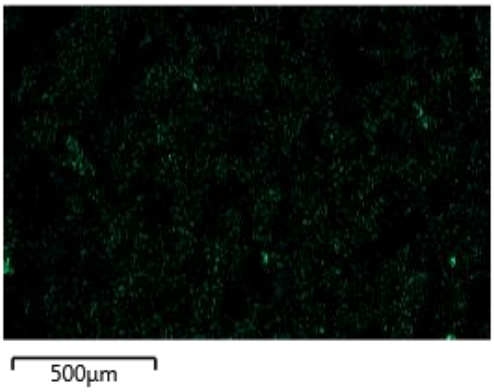
Zn L series



W M series



Cu L series



Ga L series