



EU-Latin America
Partnership
on Raw Materials



Funded by
the European Union

Project START: From WASTE to HIGH-TECH



The Geological Surveys of Europe



www.START-HEproject.com



Project: 101058632
HORIZON-CL4-2021-RESILIENCE-01



Co-funded by
the European Union

START

SUSTAINABLE ENERGY HARVESTING SYSTEMS BASED ON INNOVATIVE MINE WASTE RECYCLING

Horizon Europe Programme

Pillar II – Global Challenges and European Industrial Competitiveness

Cluster 4

Digital, Industry
and Space

Destination

Increased
Autonomy in Key
Strategic Value
Chains for
Resilient Industry

Call HORIZON-CL4-2021-RESILIENCE-01

A digitised, resource-efficient and resilient industry 2021

Topic HORIZON-CL4-2021-RESILIENCE-01-07

Building innovative value chains from raw materials to sustainable products

Innovation Action

Challenge: to develop innovative and sustainable technology and business solutions for new high value added and sustainable products with enhanced functional properties based on the EU produced raw materials.

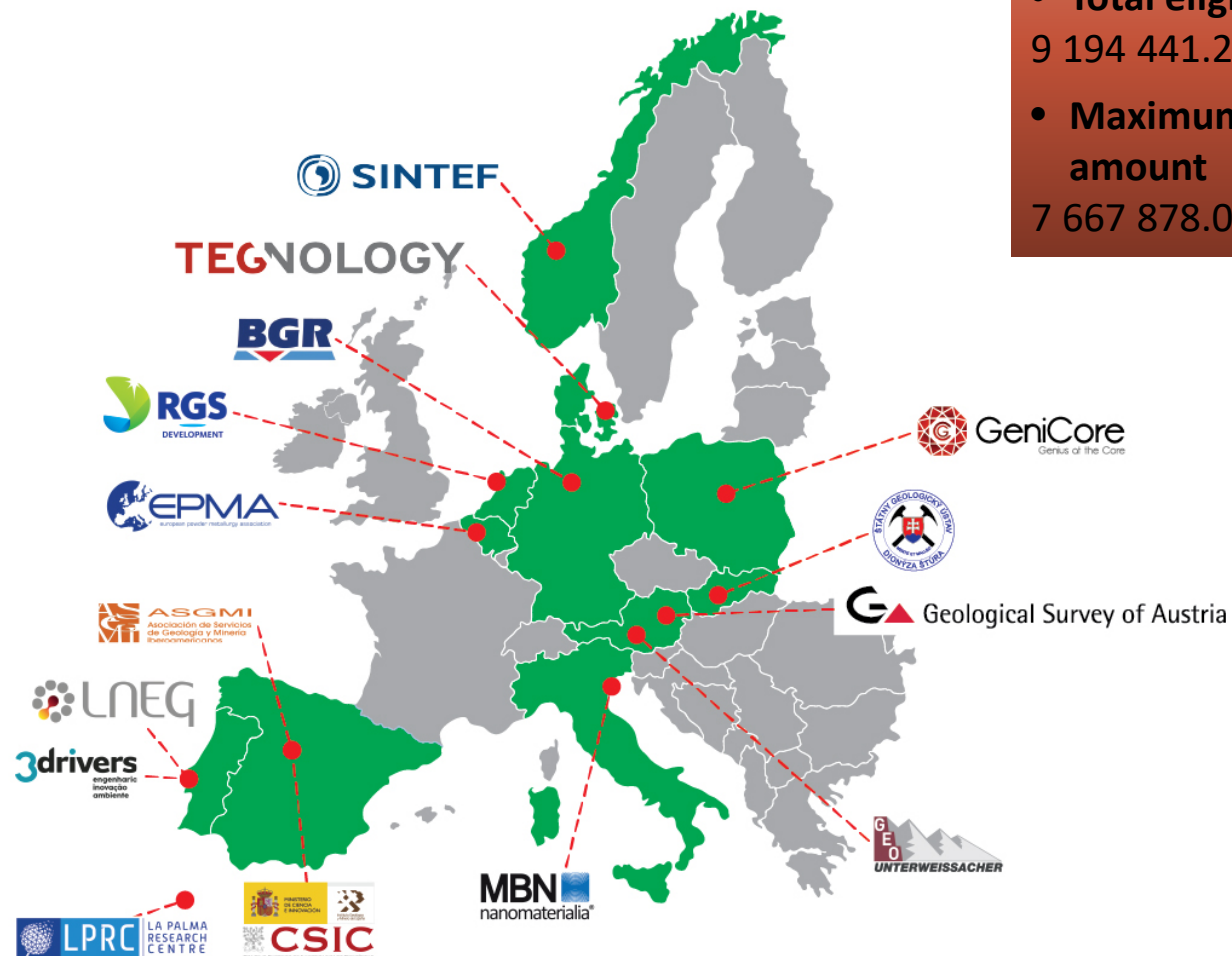
Focus: on raw materials necessary for the renewable energy ecosystems.

Main objective

Build an innovation ecosystem in the EU related to the development of sustainable and economically viable tellurium-free thermoelectric (*TE) waste heat harvesting systems

How to achieve

By producing advanced sulphide p-type thermoelements that incorporates discarded waste secondary sulphides, mainly tetrahedrite to replace the current commercial tellurium-based p-type thermoelements (expensive and rare element, which is predominantly sourced in China).



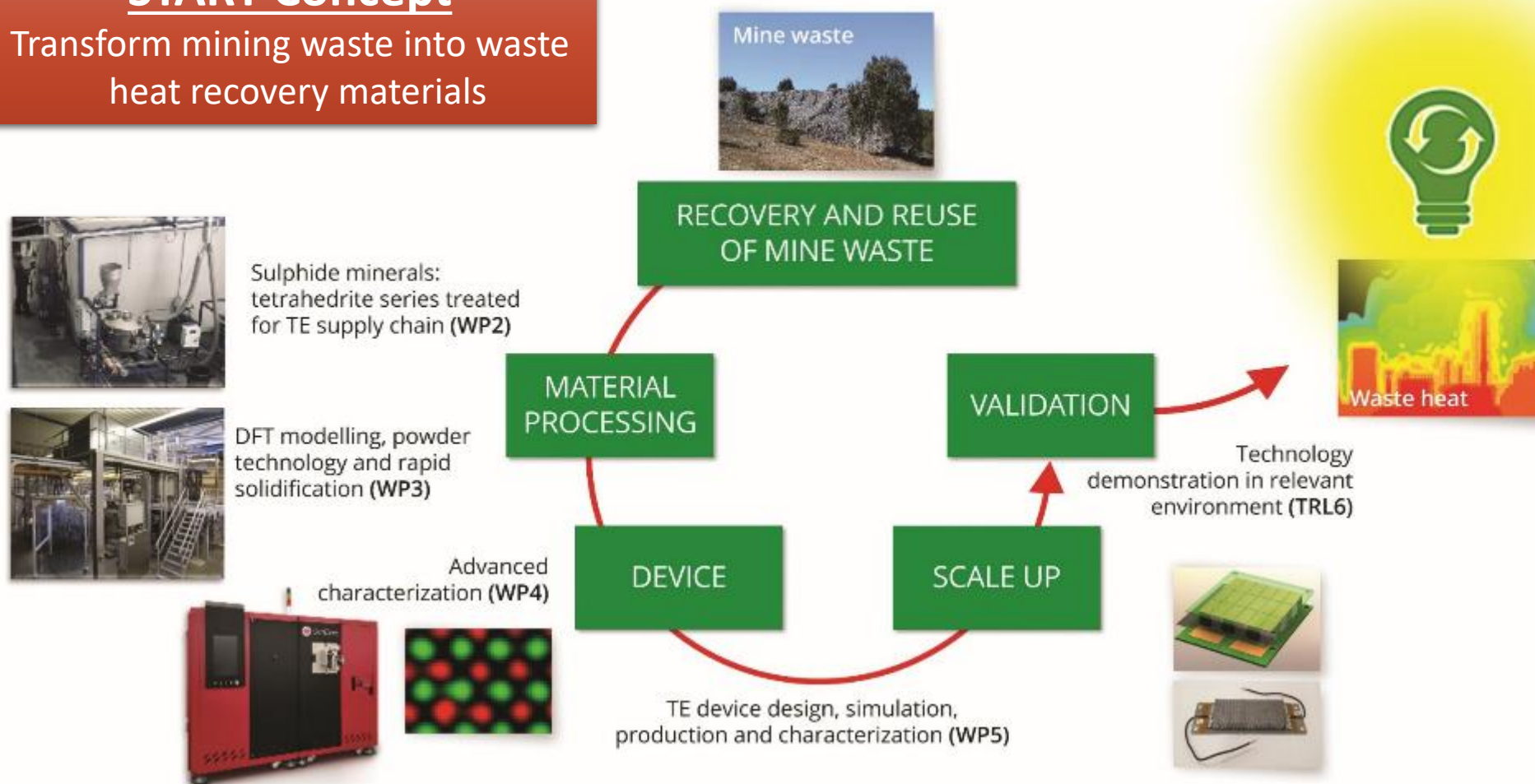
- **Duration**
48 months
(1/6/2022 – 31/5/2022)
- **Total eligible costs**
9 194 441.25 €
- **Maximum grant amount**
7 667 878.00 €

(*) thermoelectric device creates voltage when there is a different temperature on each side

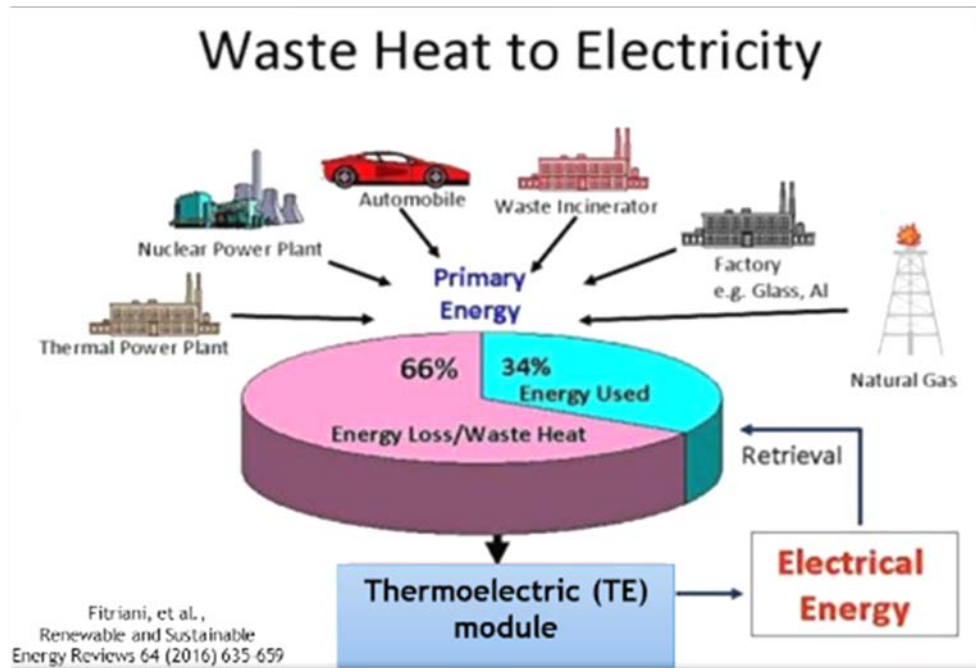


START Concept

Transform mining waste into waste
heat recovery materials

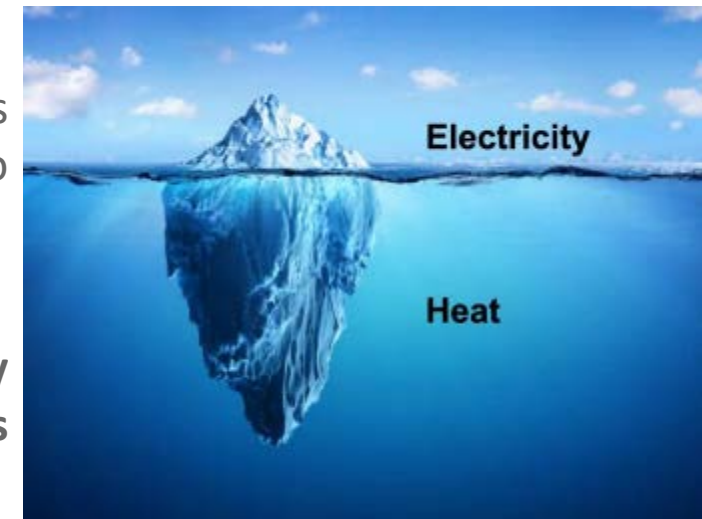


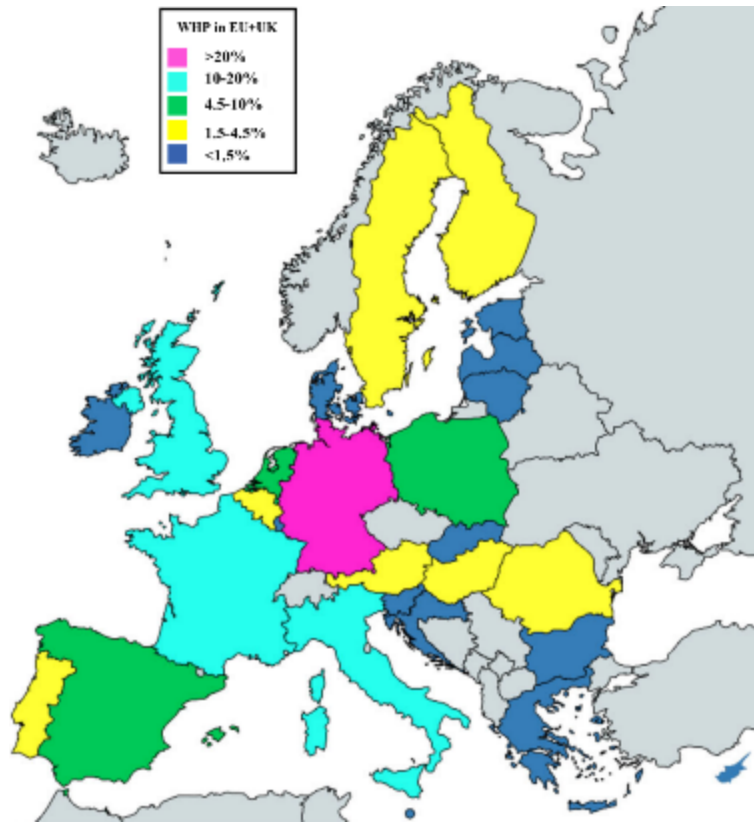
Green energy harvesting aims to supply electricity to electric or electronic systems from an energy source present in the environment [e.g., thermal energy (**thermoelectricity**)] **without grid connection or utilization of batteries.**



Almost all manufacturing processes and machines generate heat, the so called “waste heat”

Around two-thirds of the primary energy produced worldwide is lost as waste heat





Shares of waste heat recover potential in the EU
Industry by member state.

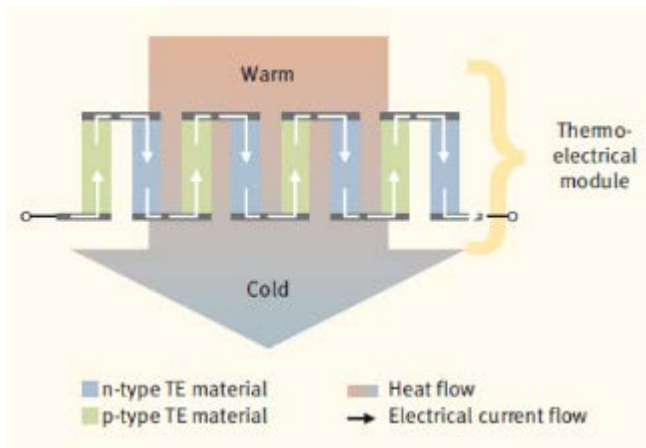
(R. Agathokleous, et al., Energy Procedia 161 (2019) 489–496)

The **waste heat recovery potential in EU** has been estimated to be **300 – 350 TWh/year**

This amount of recoverable heat has the potentiality to avoid tens of millions of tons of CO₂ emissions

The possibility of using a **thermoelectric (TE) device** to **capture and to directly convert the waste heat into electric power** is a very attractive and valuable approach to **improve the overall energy efficiency**.

- **TE energy harvesting** has a unique edge as a sustainable power supply in all scales and, by turning the **waste heat energy released to the environment in to emissions-free electricity**
- it has become an increasingly important contributor to **sustainable renewable energy ecosystems**



Design and operation of a TE device.
The heat flow creates an electric current
(Seebeck effect).

(BINE Themeninfo: Thermoelectrics: power from waste heat
(I/2016).)

The **TE device is a robust and highly reliable solid-state energy converter**, made from several TE junctions electrically connected in series that consist of n- and p-type TE semiconductor materials (thermoelements), with unique features:

- no moving parts
- no maintenance
- quiet operation
- absence of production of environmental harmful waste



Courtesy RGS Development
B.V. (RGS), Netherlands



TEGMAT
Flex-TEG

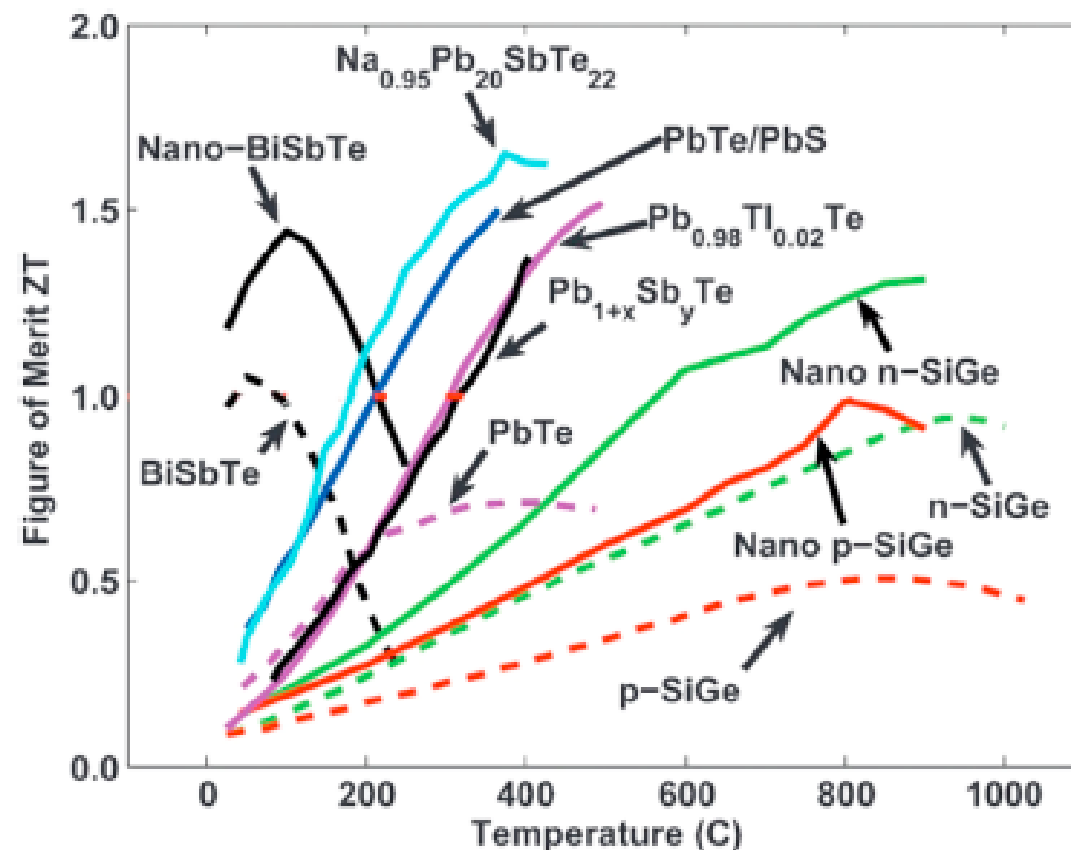
Flexible
ThermoElectric
Generator

Courtesy TEGnology ApS, Denmark



$zT =$
EFFICIENCY

zT as a function of temperature
for state-of-the-art TE materials



Tetrahedrite-based materials have excellent properties for TE applications

p-type
semiconductor
material
behavior



High Seebeck
coefficient

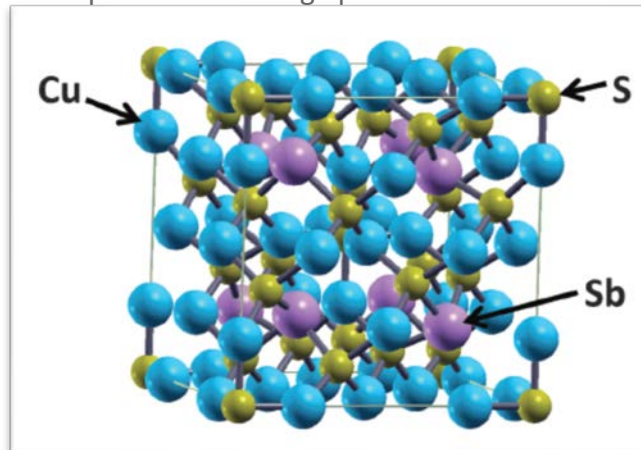


Extremely low
thermal
conductivity



The low thermal conductivity is partially a
consequence of the large primitive unit cell volume

Is characterized by a
body-centred cubic
structure (space
group I-43m) and its
cell parameter is
around 10.3\AA .



Its large unit cell contains 58 atoms
on 5 distinct crystallographic sites.



Characteristics of commercially relevant TE materials and comparison with tetrahedrites

Materials	Bi ₂ Te ₃	PbTe	SiGe	Mg ₂ Si-based materials	Tetrahedrite
Current commercial materials					
Figure of merit (zT)	> 1	> 1	> 1	> 1	> 1
Operational temperature	< 300 °C	< 500 °C	< 900 °C	< 550 °C	< 550 °C
Toxicity	■	■	■	■	■
Environmental aspects	■	■	■	■	■
Raw materials availability	■	■	■	■	■
Large scale manufacture	■	■	■	■	■
Positive assessment ■ Negative assessment ■ Less favourable ■					

(A.V. Powell, J. Appl. Phys. 126, 100901 (2019).; H. Huang, et al., J. Alloys and Compounds 881 (2021) 160546)



Tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) is a copper antimony sulphosalt, and forms a complete solid solution with **Tennantite** in which the antimony (Sb) is replaced by arsenic ($\text{Cu}_{12}(\text{Sb,As})_4\text{S}_{13}$)

The **Tetrahedrite-Tennantite mineral series** is relatively **abundant in some copper (Cu) mine tailings** (are considered as “dirty concentrates” because antimony and arsenic are impurity elements in the copper concentrate – waste material)



Abandoned Barrigão copper mine in southern Portugal

Telluride-based TE technology

- **Global consumption** estimates of **tellurium** by end user are:
 - solar, 40%
 - thermoelectric production, 30%

Abundance and geographic concentration of production:

- *tellurium is a relatively scarce element,*
- terrestrial abundance of ca. 1 ppb, and, simultaneously,
- Europe is **heavily dependent on imports,**
- ***China accounts for more than 60% of its production***

Tetrahedrite is very abundant and can be found all around the world

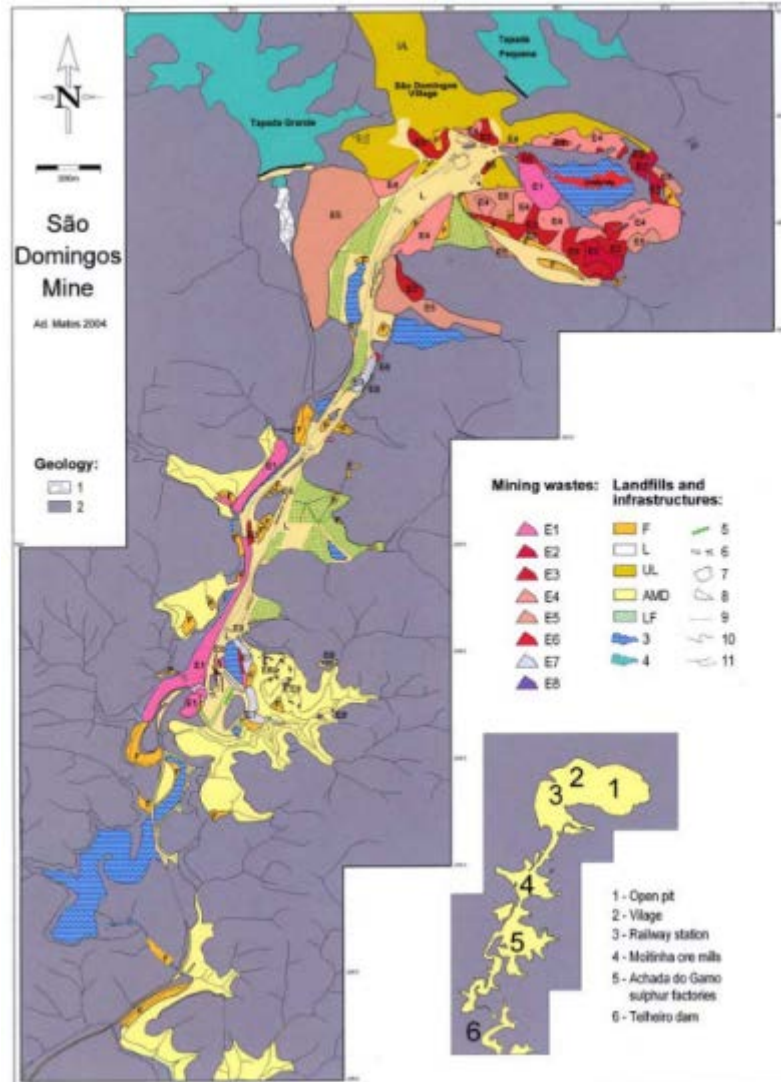




START project proposes a unique technological solution, based on the conversion of mining waste into materials for waste heat recovery, thus contributing to an efficient use of resources while promoting the use of green energy harvesting through thermoelectrics

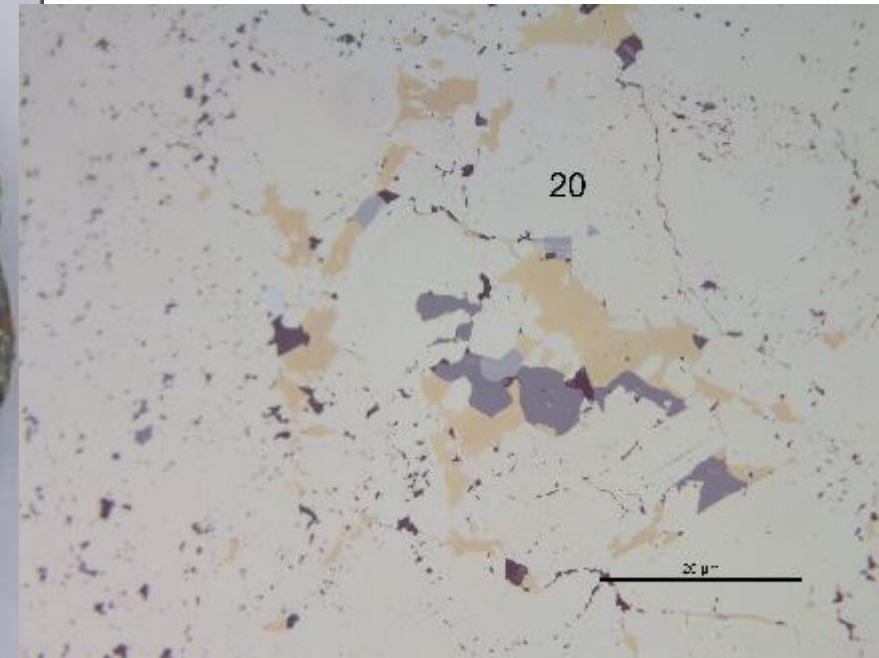
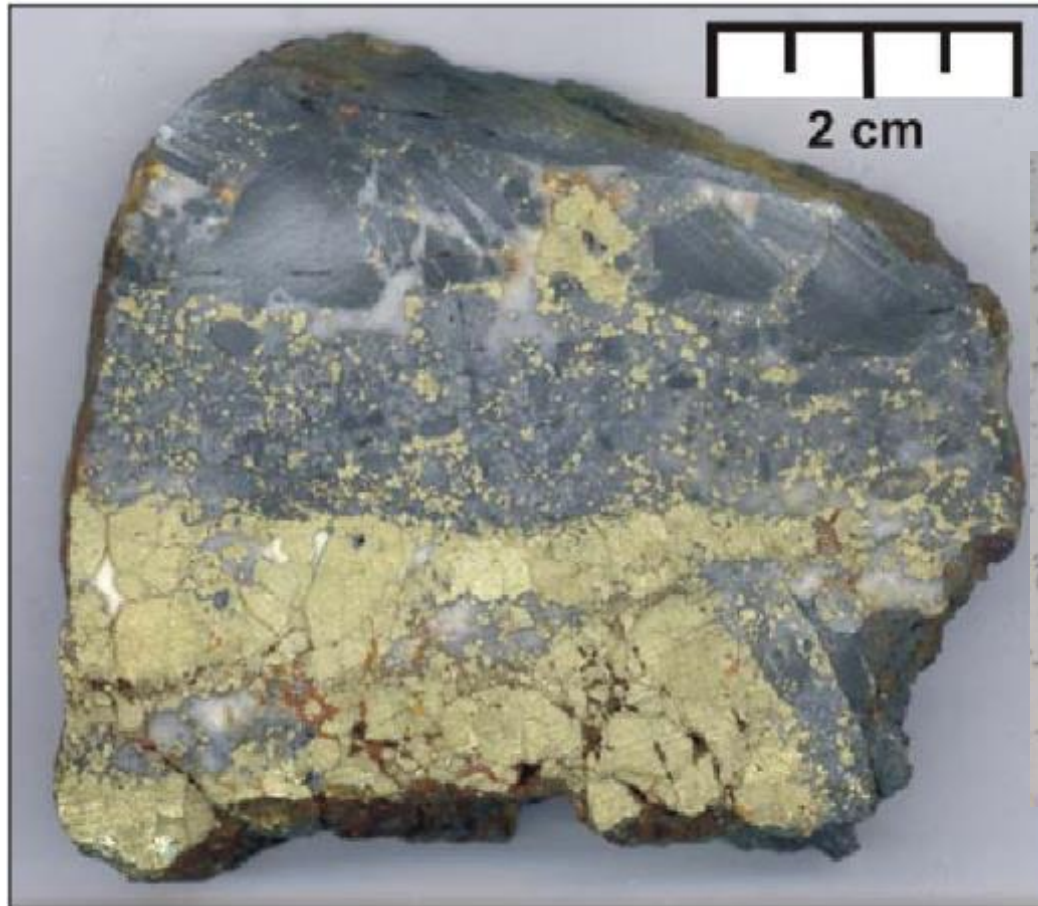
In line with:

- European Green Deal
- EU Action Plan on Critical Raw Materials
- EU Action Plan on Circular Economy



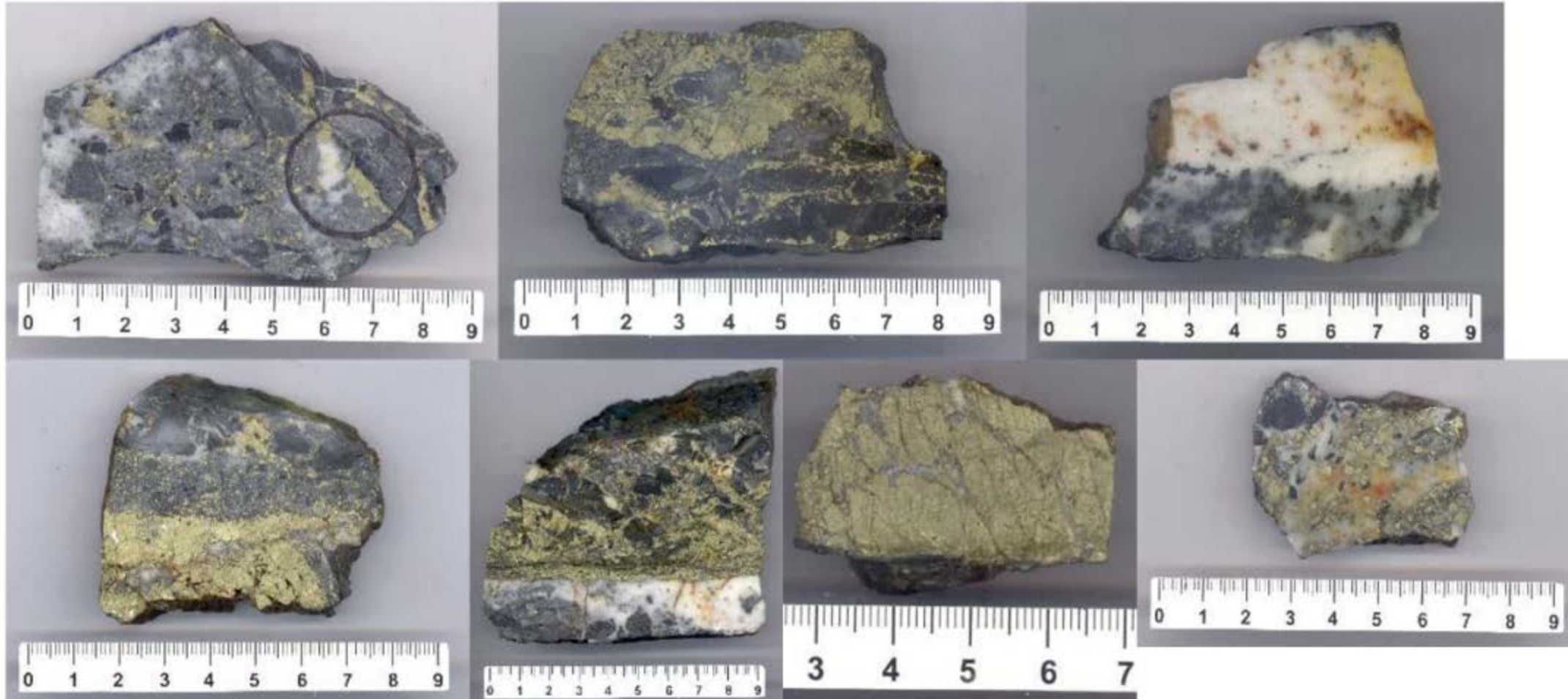
Potential environmental impact at São Domingos mining district (Iberian Pyrite Belt, SW Iberian Peninsula): evidence from a chemical and mineralogical characterization AM Álvarez-Valero, R Pérez-López, J Matos, MA Capitán, JM Nieto, R. Sáez, J. Delgado, M. Caraballo, Environmental Geology 55 (8), 1797-1809

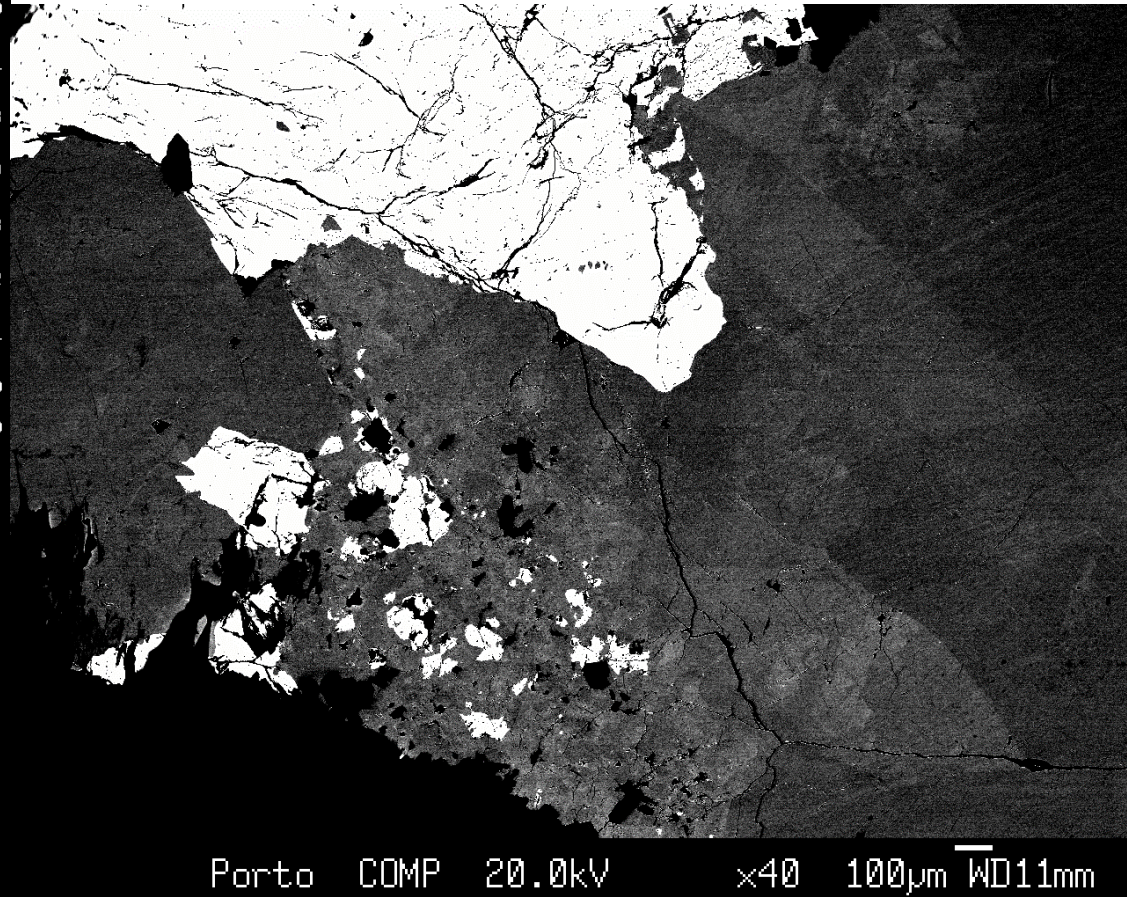
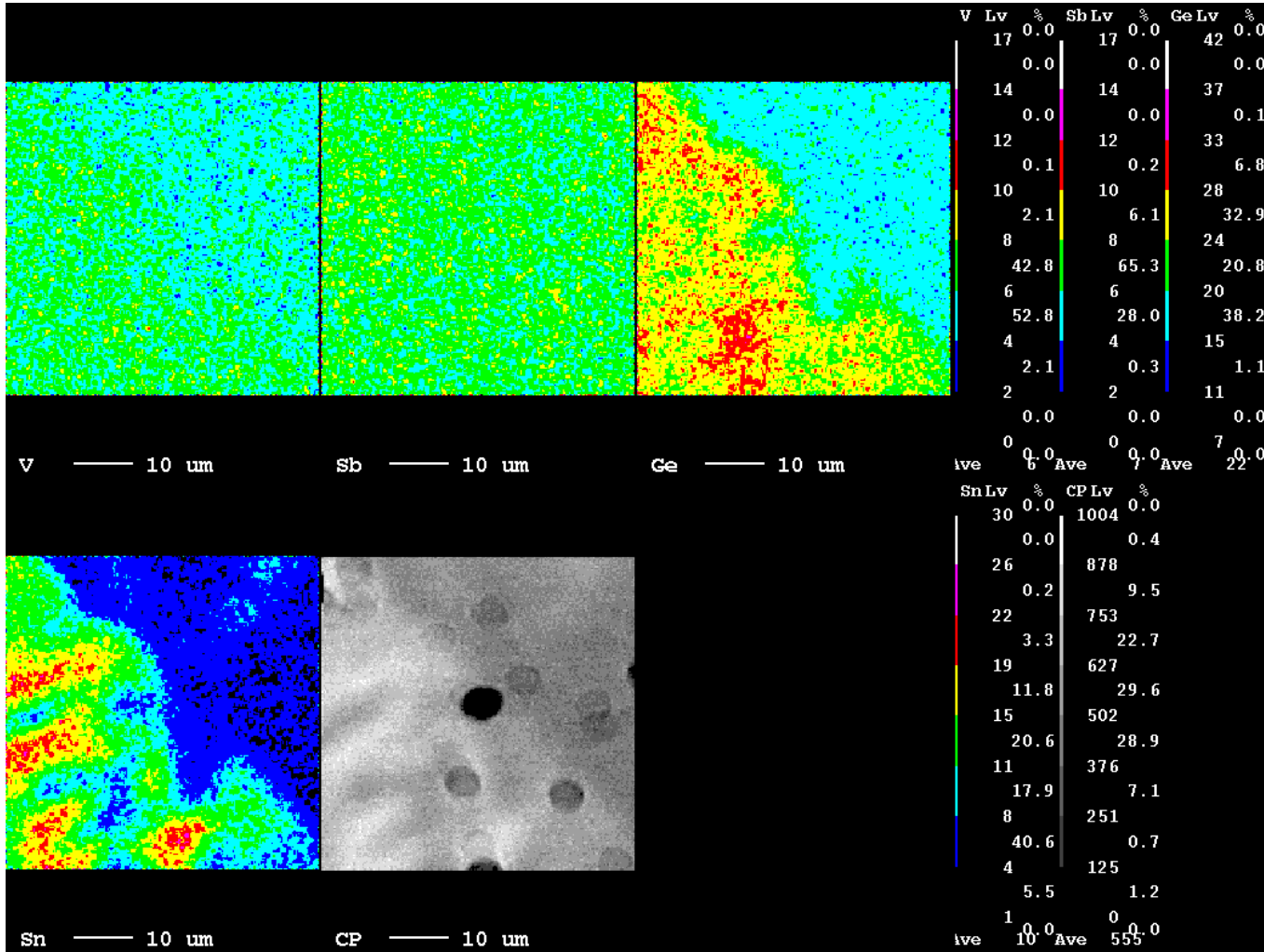






CHALLENGES



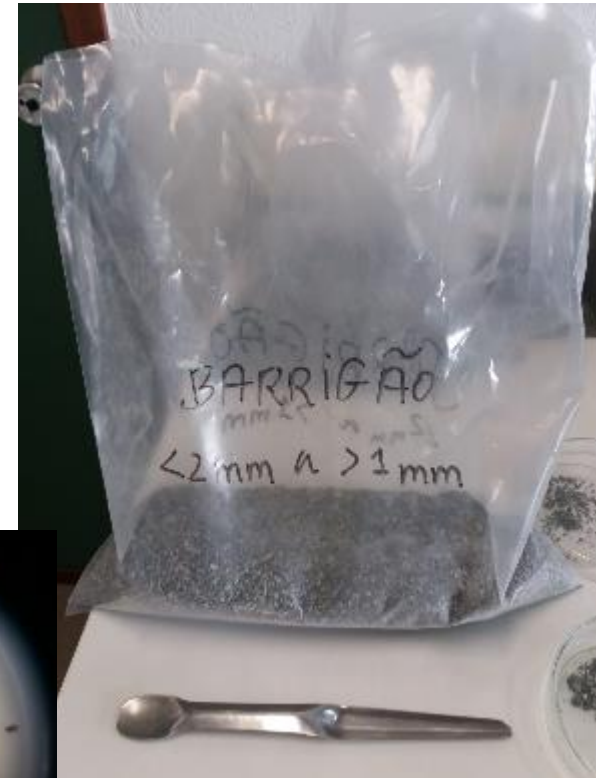
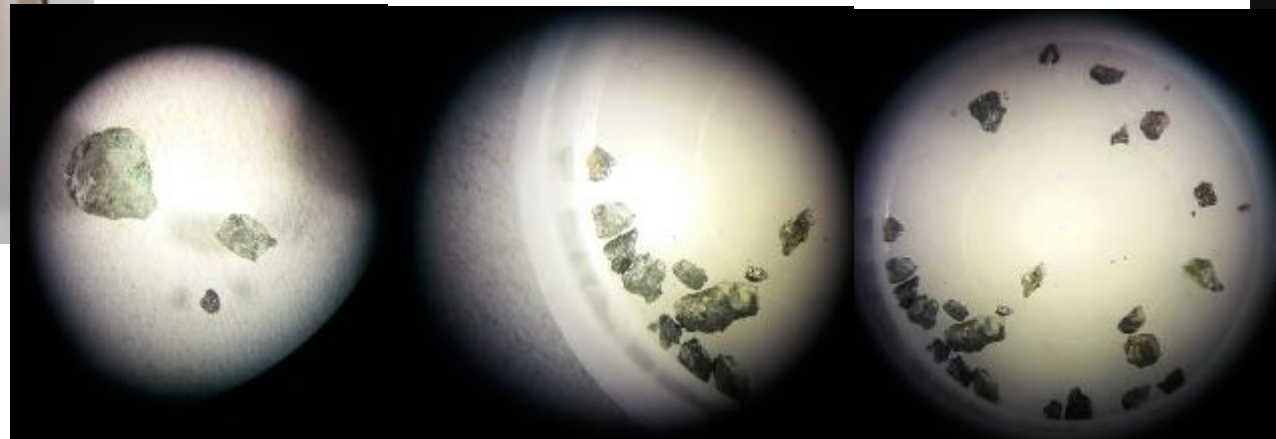
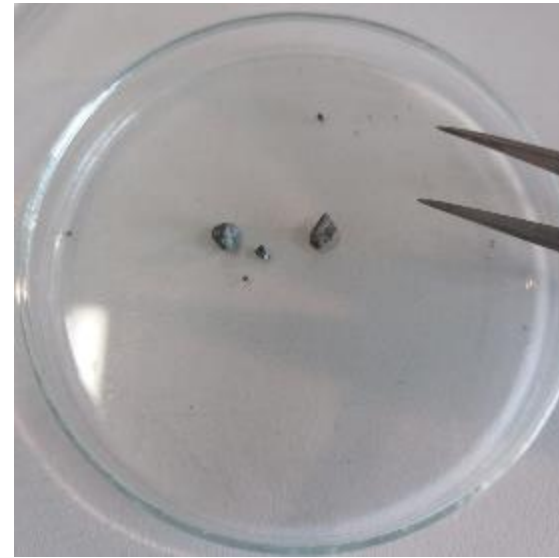


Porto COMP 20.0kV x40 100µm WD11mm





Separation of raw materials into final usable concentrates



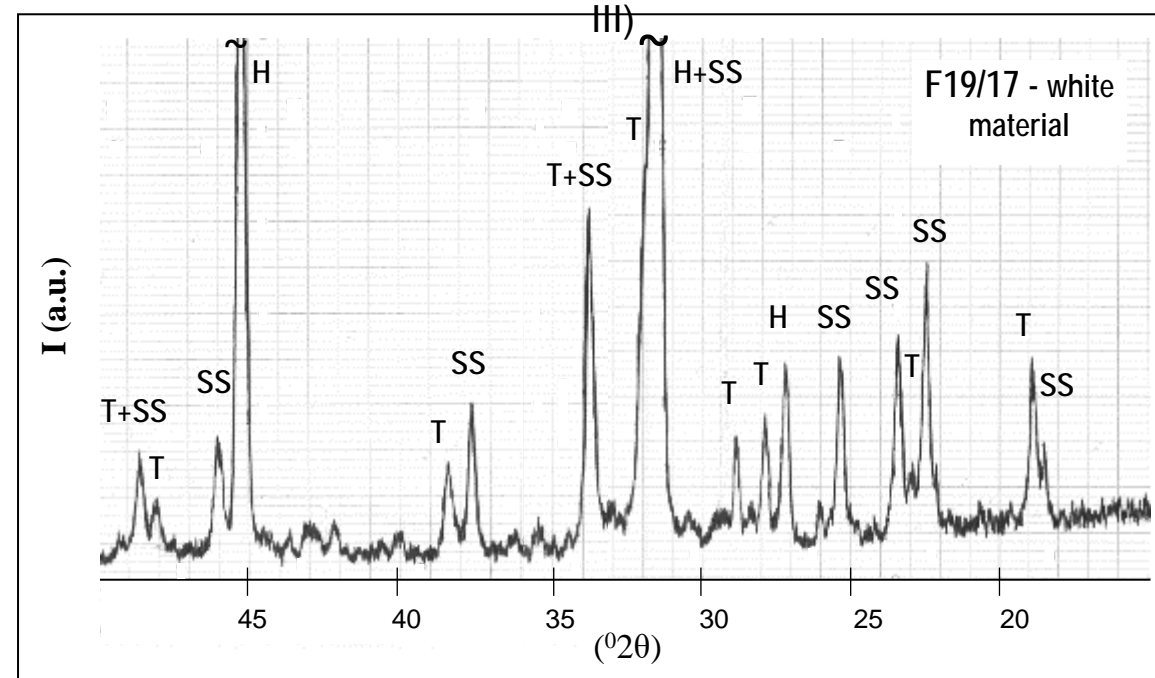


X-ray diffraction (XRD)



Philips PW 1500 powder diffractometer (Bragg-Brentano geometry), equipped with a large-anode copper tube operating at 50 kV - 40 mA and a curved graphite crystal monochromator

XRD pattern. Assigned phases in decreasing percentage:
H, halite (NaCl); **T**, thenardite (Na_2SO_4); **SS** (sodium sulphate, form





Thank you for your attention

daniel.oliveira@lneg.pt

Project Coordination:
Filipe Neves, LNEG
filipe.neves@lneg.pt