

**Serpentinites: from dimension stones to valuable industrial minerals****A. Cavallo<sup>1</sup>, M. Bussolesi<sup>1</sup>, G. Grieco<sup>2</sup>**<sup>1</sup>University of Milano-Bicocca, Department of Earth and Environmental Sciences, Italy<sup>2</sup>University of Milano, ItalyE-mail: [alessandro.cavallo@unimib.it](mailto:alessandro.cavallo@unimib.it)

Serpentinites are used as dimension stones, commercialized as “green marbles” with many different textures and color shades: an excellent example is represented by the Valmalenco area (central Alps, northern Italy). There are two main commercial varieties, depending on texture and microstructures: “schistose” (splitted in thin slabs) and “massive” (polished, sandblasted, etc.). The main rock-forming minerals are represented by antigorite (60 – 90 wt.%) and olivine (up to 30 wt.%), with smaller amounts of clinopyroxene (diopside), chlorite and magnetite. The very fine grain size and the interpenetrated microstructure confer these materials excellent technical properties (compressive and flexural strength, freeze-thaw resistance). The quarrying and processing waste can be estimated around the 40 - 50 % of the extracted material, and at present time there are no virtuous reuses of the waste materials. However, considering the peculiar chemical and mineralogical composition of serpentinitic rocks, there are many possibilities of reuse in the industrial mineral sector. Finely ground antigorite-rich materials could be used as filler for plastics and rubber (instead of talc), whereas olivine-rich wastes as a reactive fixing carbon dioxide (as carbonates, i.e. magnesite) released during the use of fossil fuels. Recently, research has been funded aimed at serpentine carbonation using microwaves, in order to optimize the process and reduce as much as possible energy consumption. In the ceramic industry, the most promising target is represented by forsterite and/or high-MgO ceramics and forsterite refractories (with periclase addition), but also by cordierite ceramics (adding kaolin) and high-hardness vitroceramics. The real possibility of an industrial use of serpentinitic materials will require much more experimental work, because no relevant previous studies are available. Special care must be taken to avoid chrysotile asbestos contamination, which can be occasionally dispersed in the rock mass.

## Mineralogical and isotopic study of magnesite veins in the Evia and Gerakini ultramafites (Greece)

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Magnesite ore deposits are the main source of Mg for the industry and are used in the production of various kinds of magnesia. They are closely associated to ophiolite geological contexts, and are usually hosted within variously altered harzburgites and dunites.

Greece hosts exploitable ophiolite-related magnesite deposits in two areas, located in the Evia island and in the Chalkidiki peninsula. In the present contribution we take into consideration magnesite veins at Kymasi (Evia) and Gerakini (Chalkidiki). The Kymasi magnesites are hosted in peridotites in the tectonic unit of the Pelagonian Zone of Northern Evia. Gerakini is located in the Vardar Zone ophiolite belt, and forms the Gerakini-Ormylia ophiolite complex.

Both areas host major magnesite deposits, mainly comprising shallow stockwork-type ores hosted within variably altered dunites and harzburgites locally intruded by pyroxenitic and gabbroic veins.

At Kymasi, field work was focused on a well exposed network of magnesite veins that show the following zoning from core to rim: a thick massive magnesite central portion, a serpentinized hydraulic breccia with magnesite cement and a partially dolomitized peridotite. The host rock is unaltered peridotite. All contacts are irregular and sharp.

At Gerakini sampling was focused on two active open pits, Ugo and Antonium. Magnesite samples show a variety of textures, comprising massive magnesite, cauliflower magnesite, fibrous magnesite and brecciated magnesite. Host rocks are serpentinized dunites.

XRD data show that, differently from Kymasi, at Gerakini magnesite veins contain a variable amount of dolomite up to 16%.

Mineral chemistry data show that, at Kymasi, high-Cr spinels occur in the breccia, while partially dolomitized peridotite and unaltered peridotite spinels are lower in Cr.

The isotopic analyses show very similar  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values in Kymasi and Gerakini, also consistent with other ophiolite-related magnesite mineralizations in the Balkans. The isotopic values suggest that the  $\text{CO}_2$  was originated from the decarboxylation of organic matter present in the sediments of the area.

Considering the origin of the  $\text{CO}_2$  and the shallow nature of the stockwork mineralization, it can be concluded that both Kymasi and Gerakini magnesites were formed by infiltration of  $\text{CO}_2$ -rich meteoric waters which interacted with peridotites. The interaction caused the leaching of Mg, which was transported by the fluids through preferential pathways, possibly reactivating older shear zones, and finally deposited in the form of magnesite once it reached saturation at shallow depths.

**A preliminary study on the potential of the LARCO laterite ore tailings as secondary source of cobalt**

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Low-emission mobility is an essential component of the broader shift to the low-carbon, circular economy needed for Europe to stay competitive and be able to cater to the mobility needs of people and goods. On this frame, a very important component (and the most expensive one) of all kinds of electric vehicles are their batteries; it is projected that until 2025, the EU-based electric cars battery manufacturers will supply ~6,000,000 batteries for electric cars. The uprising demand for these batteries, subsequently rises the demand for specific metals which are used for their manufacturing, namely Ni, Co and Li. Nickel is used as hydroxide or intermetallic compounds in NMC, NCA batteries, lithium as lithium-cobalt oxide (cathode) and as salt (electrolyte) in Li-ion battery and cobalt is used in cathode materials in LCO, NCA and NMC batteries. Li and Co are also included in the 2020 Critical Raw Materials list of EU, meaning that there is a great risk for their supply. EU should speed up the efforts for discovering new sustainable sources for these metals, both primary and secondary. On this study, the mining tailings of the LARCO laterite ores from Evia were investigated as potential -secondary- sources of cobalt. A total of 10 tailing samples were analyzed for their chemical composition. The results show that cobalt has an average concentration of 614.70 ppm (median value 644 ppm), with values ranging from 377 to 815 ppm, thus making these tailings as a possible source for this metal. Samples are also particularly rich in Ni (average Ni concentration 9,440 ppm), with the small grain size of the tailings being a negative factor for their use as feed in ferronickel metallurgy at the Larymna plant.

### Implementation of a procedure for buffering Acid Mine Drainage waters from pyrite-rich tailings at Fushë Arrëz copper enrichment flotation plant

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The extraction process from metal deposits has the inevitable consequence to generate enormous amounts of waste (close to mines and enrichment plants) mainly solid and in the form of accumulation of sterile minerals or tailings deriving from the processes of concentration and refinement. These waste materials, if not properly treated, constitute a considerable environmental risk. Some of them can be very rich in sulfides, hence the capacity of inducing the formation of high acidic waters rich in Potentially Toxic Elements (PTE).

The present work is focused on the copper enrichment plant of Fushë Arrëz (Northern Albania copper mining district) where a change in tailings environmental impact, due to the transition from double flotation, with separation of pyrite as a by-product, and single flotation, without pyrite separation has been documented. Pyrite, due to its abundance, high reactivity and high S to metal ratio is the main responsible of Acid Mine Drainage (AMD).

The aim here was to define the most suitable procedures for the buffering of leached samples and natural waters from sulfur-enriched mining tailings, through the evaluation of samples chemical parameters and assessment of major, minor and trace elements distribution.

The buffering of the leached products and natural waters was carried out by adding to the solutions fine-grained calcium carbonate supplied by UNICALCE company.

The results show an important reduction in the concentrations of the metals in solution. The metal removal efficiency obtained through this procedure turned out to be excellent and even higher than 90% for most of the PTE considered. In terms of absolute amounts, moreover, almost all the concentrations detected after the buffered remain below the legal limits envisaged for Albanian industrial water discharges. The precipitate produced takes over all the PTE in high concentrations and therefore will require a specific purification or storage treatment.

In order to better understand the buffering process of acid solutions rich in heavy metals and improve their application, two insights are suggested for next steps:

- perform MP-AES analyses at each buffering step allowing, in addition to validating the buffering model created, to yield buffering curves for each ion considered as a function of pH
- perform tests with different buffering materials and subsequently compare the costs and the buffering performance