

Natural analogue of CO₂ mineral sequestration: The Tuscan magnesite deposits

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The magnesite deposit of Malentrata (Tuscany, Italy) was derived from silicification-carbonation of Ligurian serpentinites embedded in pelite-carbonate formations, and represents a natural analogue of *in situ* CO₂ mineral sequestration. Serpentinites were transformed to a brownish friable mineral assemblage of opal, chromian montmorillonite, Fe-rich magnesite and minor iron sulfides and oxides. The serpentinite alteration was accompanied by the formation of magnesite and dolomite veinlets, and large magnesite-dolomite veins along major tectonic structures. The major veins are characterized by the following crystallization sequence: i) early magnesite, ii) green and late pale-brown dolomite cementing the early brecciated magnesite vein infill, and iii) late quartz, chalcedony and opal. The observed mineral assemblage is indicative of low temperature hydrothermal alteration driven by Si- and CO₂-rich fluids under relatively low pH conditions. Geochemical data along transects from carbonated host rocks to carbonate-silica veins suggest a marked variation of fluid composition through the main stages of precipitation. Dolomites are more enriched in Cr, Sr, Y, U and REE with respect to magnesites. Magnesites are the most REE-depleted, whereas green dolomites show quite flat enriched patterns approaching the pattern of sedimentary formations. $\delta^{18}\text{O}$ of magnesites range from 23 to 32‰, and $\delta^{13}\text{C}$ from -2 to 0‰. Both dolomite types are depleted in $\delta^{18}\text{O}$ with respect to magnesite, especially late pale-brown dolomite. $\delta^{13}\text{C}$ of dolomites is similar to magnesite with slightly lower values in green dolomites. It seems to be conceivable that fluids first interacted with serpentinites precipitating magnesite. After the magnesite precipitation, fluids interacted with the sedimentary formations, becoming progressively enriched in calcium and REEs, and depleted in $\delta^{18}\text{O}$ due to the partial equilibration with the pelite portion. At this stage dolomite precipitation recorded geochemical variations of fluids. Malentrata deposit lies at the periphery of Larderello geothermal field and it highlights the near surface local interaction between low temperature fluids and serpentinite bodies in favourable tectonic conditions.

Deciphering arsenic sources in surface waters and the role of bacterial oxidation

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In a geochemical anomaly in As, different potential As contributions to stream waters, such as groundwaters, runoff and As-bearing phase weathering present within the soils were studied with a high sampling frequency. It allowed deciphering the contribution of each compartment to As contamination of surface waters. The role of indigenous bacteria in As oxidation state in ground- and surface waters was also studied in laboratory.

In the soil profile, total As concentrations indicated depletion (1500 to 385 mg.kg⁻¹) during pedogenesis relative to a mineralogical evolution of As-bearing phases upwards the soil profile: from arsenates (Ba-rich pharmacosiderite: 14-26 wt.% As) to Fe-oxyhydroxides (ferrihydrite-like: 4-16 wt.% As; ferrihydrite-type, hematite and goethite: <3 wt.% As). Conversely, an increase of dissolved As concentrations (15-52 $\mu\text{g.L}^{-1}$) was observed in soil solutions.

In stream waters, As concentrations (7.5 to 69.4 $\mu\text{g.L}^{-1}$) were attributed to several inputs: (i) runoff and soil solutions, (ii) waters from former adits (97-120 $\mu\text{g.L}^{-1}$ As), (iii) wetland and groundwaters (up to 169 and 215 $\mu\text{g.L}^{-1}$ As, respectively). The latter inputs were characterized by dissolved As(III) during low flow period which was rapidly oxidized, suggesting the contribution of bacterial oxidation.

Bacterial As oxidation tests showed a decrease of dissolved As(III) concentrations in stream and wetland waters (-17% and -41%, respectively). In groundwaters, a stronger decline for dissolved As(III) (-95% in 15 h) was observed, then followed by an As(III) release (+51%), suggesting the presence of As(V)-respiring bacteria. The study of the As(III)-oxidizing bacterial community (PCR-DGGE method on *aoxB* genes, a genetic marker of these bacteria), showed a divergence in the community structure between (i) surface and wetland waters, and (ii) groundwaters, probably due to variable As concentrations, redox conditions and bacteria number.