

## ***Clumped* isotope thermometry on ultramafic-hosted magnesium carbonates**

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Magnesite (MgCO<sub>3</sub>) and other magnesium carbonates hosted in serpentinized peridotite rocks record the final fate of CO<sub>2</sub>-rich fluids in shallow crustal environments and provide constraints on low-temperature carbon capture and storage in ultramafic rocks. Here we determine *clumped* temperatures of mineralization for magnesium carbonates from a variety of natural ultramafic environments, and we couple our results with a laboratory-based calibration of synthetic magnesite. Our samples include: (a) massive (10's of meters thick and >100's of meters in length and depth) homogeneous, cryptocrystalline magnesite veins from the Red Mountain Magnesite Mine in the Del Puerto ophiolite of the California Coast Ranges (T = 21.5±4°C, n=7, with a maximum temperature of 31°C); (b) surficial nesquehonite (MgCO<sub>3</sub>·3H<sub>2</sub>O), hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O), dypingite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·5H<sub>2</sub>O) and artinite (Mg<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>2</sub>·3H<sub>2</sub>O) from the peridotite-serpentinite belt of the California Coast Ranges (T = 21±4°C, n=6); (c) additional ultramafic-hosted magnesite deposits (Turkey, Austria, Iran) analogous to Red Mountain (T= 30.5±5°C, n=3), and (d) magnesite produced from carbonation of olivine at 60°C, 100 bars pCO<sub>2</sub>, 0.5M NaCl, and variable (20:1 and 50:1) water-rock ratios (T=52±6°C, n=2). We use our results to constrain the δ<sup>18</sup>O composition and origin of the mineralizing fluids of the magnesite deposits at Red Mountain. Nearly identical *clumped* isotope signatures among worldwide magnesite deposits suggest that a similar set of geological processes were associated with carbonation in crustal ultramafic rocks.

## **Characterization of complex Fe-Mn phosphates by LA-ICP-MS methods**

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Ca-phosphates in any of their variants (apatite, merrillite, etc.) are the subject of increasing interest in petrogenesis and mineralogenesis studies of igneous and metamorphic rocks from different geological settings. Their trace element characterization has been sought for and is usually done using LA-ICP-MS methods. Less abundant Fe-Mn phosphates and fluorophosphates are potential indicators of deposits of economic interest but have been so far less investigated for their trace element composition. In an attempt to improve the current knowledge on the latter type, we have analyzed complex phosphates of the triplite-zwieselite (Mn<sup>2+</sup>,Fe<sup>2+</sup>,Mg,Ca)<sub>2</sub>(PO<sub>4</sub>)(F,OH), triphylite-lithiophilite Li(Fe<sup>2+</sup>,Mn<sup>2+</sup>)PO<sub>4</sub> and graftonite-beusite (Ca, Fe<sup>2+</sup>, Mn<sup>2+</sup>)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> series. For each series we have attempted to analyze phosphates covering the widest possible Fe-Mn compositional range. To set up the procedure we first analyzed igneous and metamorphic apatites including the classic specimens from Cerro Mercado (Durango, Mexico), initially on mineral separates and then on thick petrographic preparations. The procedure was subsequently optimized for the analysis of the Fe-Mn phosphates also in thick section. This involved the use of XSeries 2 and UP213 instruments, a SuperCell device, He as transport gas, enhanced vacuum and NIST glasses and Durango apatite for calibration and quality control purposes. Although the absence of specific CRMs implies some limitations, the method set up allows to obtain reliable results for most trace elements in the ppm range and reveals marked differences for the studied series of primary Fe-Mn phosphates, with significant variations also related to the different geological settings. Members of the triphylite-lithiophilite series present extremely low contents in all the analyzed elements, except for Zn (570-8990 ppm). In contrast, members of the triplite-zwieselite series are enriched in Nb (78-537 ppm) and Zn (437-4093 ppm), with variable contents in HREE (0-124 ppm), Ta (4-176 ppm), Y (0-280 ppm), Zr (6-233 ppm), and U (7-50 ppm). Finally, members of the graftonite-beusite series are the richest in REE, with ΣHREE up to 300 ppm and of ΣLREE up to 345 ppm. Other trace elements, such as Zn (1508-4238 ppm), Sr (3-91 ppm) and Y (0-509 ppm) occur also in significant amounts.