

## Pseudomorphic replacement of diopside during interaction with (Ni,Mg)Cl<sub>2</sub> aqueous solutions

A. S. MAJUMDAR\*, H. E. KING, T. JOHN,  
C. KUSEBAUCH AND A. PUTNIS

Institut für Mineralogie, Universität Münster, Corresstraße 24,  
48149 Münster, Germany

\*correspondance: asmajumdar.min@uni-muenster.de

Alteration of peridotite, including serpentinization, has a special place among fluid rock interaction that not only drastically changes rock properties at the ocean floor but also leads to rich ore deposits worldwide. During peridotite serpentinization, olivine and orthopyroxene are more reactive than clinopyroxene. Hence, it may be reasonable to assume that after initial serpentinization of olivine and orthopyroxene, the hot hydrothermal solution rich in metal ions (e.g. Ni) can open further possibilities for relict clinopyroxene to react.

We present a hydrothermal experimental study of diopside-(Ni,Mg)Cl<sub>2</sub> solution interaction to clarify the replacement mechanism and pattern of element mobilization during alteration. Different chloride solutions were used with Ni/Mg ratios of 0, 0.5 and 1. Experiments were carried out in cold seal pressure vessels at 300-600 °C and 1 kbar pressure for 15 days in gold capsules. For 500-600°C NiCl<sub>2</sub> experiments solutions were also spiked with 50% H<sub>2</sub><sup>18</sup>O to study the behaviour of isotopic exchange, hence, the replacement mechanism. Raman, SEM and microprobe analyses were performed on reactive samples to identify the phases and to observe textural and compositional features.

The reactive samples show a sharp compositional and structural interface between diopside and the pseudomorph phases. A complex rim of Ni poor and Ni rich regions are present in NiCl<sub>2</sub> and (Ni,Mg)Cl<sub>2</sub> experiments. Here, the precipitated phases are willemseite and/or nepouite. For MgCl<sub>2</sub> experiments, only talc was detected. The experiment with <sup>18</sup>O-enriched solution documents a shift in the Si-O(bridging)-Si band of willemseite towards lower wavenumbers confirming that diopside pseudomorphism occurs via an interface coupled dissolution-precipitation, where the spatial coupling between dissolution-precipitation is dependent on temperature. The study also shows evidences for Ca transport in the opposite direction to Ni and/or Mg during alteration. This may be important as a geochemical tracer for economic Ni deposits and Ca mobilization during serpentinization.

## Mineralogy and thermodynamics of secondary arsenic phases

JURAJ MAJZLAN<sup>1</sup>, PETR DRAHOTA<sup>2</sup> AND MICHAL FILIPPI<sup>3</sup>

<sup>1</sup> Institute of Geosciences, Friedrich-Schiller-Universität Jena, Germany, Juraj.Majzlan@uni-jena.de

<sup>2</sup> Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University, Prague, Czech Republic, drahota@natur.cuni.cz

<sup>3</sup> Institute of Geology, Academy of Sciences of the Czech Republic, Prague, Czech Republic, filippi@gli.cas.cz

Arsenic is an integral part of the toxic load of many types of mining waste. The parageneses of arsenic minerals in the primary assemblages (rocks, ores) and the secondary assemblages (oxidation zones, polluted soils, waste forms) are quite variable. In this contribution, we will describe different mineral assemblages found at sites polluted by arsenic, including naturally polluted soil profiles, rocky mine dumps, tailings, underground spaces, and caves. Here, the mineralogy is not only dictated by the bulk chemical composition but also by the local conditions and shows surprising variations. For example, although mining waste is commonly dominated by arsenic-rich hydrous ferric oxide and scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O), polluted soils contain more commonly pharmacosiderite [(K,Na,Ba)Fe<sub>4</sub>(AsO<sub>4</sub>)<sub>3</sub>(OH)<sub>4</sub>·6-7H<sub>2</sub>O] and Ca-Fe arsenates such as arseniosiderite. This difference could arise from different availability of element due to different time scales. If so, such differences could suggest how the waste forms could react and transform in the future. In waste forms from material processed by pressure oxidation contain yet different types of ferric arsenates, not known as minerals. Little is known about their solubility and reactivity. The chemical composition of the whole system influences, of course, the nature of the secondary arsenic minerals, and the link between the two can be easily established.

In addition to the crystalline arsenate phases, As(V) can be also incorporated into the crystal structure of iron oxides, especially hematite, as epitaxially intergrown clusters with angelellite-like local structure. This mode of occurrence may be found especially in older systems with relatively low pollution loads.

Thermodynamic data suggest, not surprisingly, that scorodite is the most stable phase in the system Fe<sub>2</sub>O<sub>3</sub>-As<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O. Kaňkite, bukovskýite, As-rich hydrous ferric oxide, FeAsO<sub>4</sub>, and presumably also zýkaite are metastable. The data for more complex ferric arsenates (pharmacosiderite, arseniosiderite, yukonite) are missing; this work is in progress and could reveal interesting relationships between the simpler and more complicated ferric arsenates.