



Fe-Distribution and Hydrogen Generation During Serpentinization

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Serpentinization of peridotite generates large amounts of dihydrogen (H_2, aq), indicated by the presence of Ni–Fe alloys and low-sulfur-fugacity sulfides, e. g. awaruite and pentlandite, in serpentinites. Hydrogen is produced when ferrous iron in olivine is oxidized by water to ferric iron in secondary magnetite and serpentine. This process is strongly dependent on bulk rock composition, water-to-rock ratio and temperature. These relations were examined in thermodynamic reaction path models (using the EQ3/6 computer code) with dunitic and harzburgitic rock compositions.

The model results were compared with electron microprobe analyses, bulk magnetization measurements, and Mößbauer spectroscopy of partially to fully serpentinized dunites and harzburgites from Ocean Drilling Program Leg 209, Hole 1274A, Mid-Atlantic Ridge 15°N. These samples have mesh rims that reveal a distinct in-to-out zoning, starting with brucite (Mg# 80) at the interface with olivine, then a zone of serpentine (Mg# 95) + brucite ± magnetite, and finally serpentine + magnetite in the outermost mesh rim. The composition of co-existing serpentine and brucite in pseudomorphic mesh rims is virtually constant in most samples from 32 to 147 meters below seafloor, suggesting similar alteration conditions of olivine downhole.

Bulk magnetization measurements of microdrilled mesh rims in combination with thin section petrography revealed a positive correlation of magnetite content with extent of serpentinization. Where relic olivine is present, the magnetite content is significantly lower than in fully serpentinized rocks. In these domains with sparse magnetite, Mößbauer spectra revealed $Fe^{3+}/\sum Fe$ values between 0.30 and 0.48 for paramagnetic minerals in the mesh rims (i. e., secondary hydrous phases). In heavily to completely serpentinized rocks with abundant magnetite, $Fe^{3+}/\sum Fe$ values of the paramagnetic phases are consistently higher and range from 0.53 to 0.68.

In the EQ3/6 runs, a serpentine solid solution model that includes greenalite and hisingerite ($Fe_2Si_2O_5(OH)_4$) was used in investigating the distribution of iron between serpentine and magnetite and its oxidation state in serpentine. Our model computations predict that above 330 °C and water activities near unity, the dissolution of olivine and coeval formation of serpentine, magnetite and dihydrogen is significantly obstructed by the dearth of silica. At these temperatures, hydrogen fugacities are too low for awaruite and pentlandite to be stable. When temperatures drop below 320–330 °C, brucite becomes stable and hydrogen generation is facilitated, because the reaction of olivine to serpentine, magnetite and brucite requires no external silica. The $MgO-FeO-Fe_2O_3-SiO_2-H_2O$ and $Fe-Ni-Co-O-S$ phase relations observed in the mesh rims suggest that serpentine and brucite from Hole 1274A likely formed at temperatures between 150 and 250 °C and water-to-rock ratios (w/r) between 5 and 0.1. However, formation of awaruite must have taken place during main stage serpentinization at temperatures between 200–250 °C and w/r < 1, when alteration conditions were sufficiently reducing. Likewise, the model predicts the $Fe^{3+}/\sum Fe$ ratios of mesh-rim serpentine/brucite observed in incompletely serpentinized rocks of serpentine (0.3 to 0.5) at low w/r ratios and $T < 250$ °C. The calculation results furthermore indicate that elevated $Fe^{3+}/\sum Fe$ ratios (0.5 to 0.7) measured in fully serpentinized rocks appear to correspond to higher w/r ratios and less reducing conditions.

Our study indicates that unprecedented details about the reaction sequences during serpentinization may be obtained from merging careful petrographic, magnetic, and spectroscopic analyses with comprehensive thermodynamic modeling.