Interfacial reactions during olivine replacement

H.E. KING[1]*, H. SATOH[2], T. GEISLER[3] K. TSUKAMOTO[4] AND A. PUTNIS[1]

[1]Institut fuer Mineralogie, Westfaelische Wilhelms-Universitaet Muenster, Germany
(*correspondence: hking_01@uni-muenster.de)
[2]Mitsubishi Materials Corporation, Japan
[3]Steinmann Institut, Universitaet Bonn, Germany
[4]Department of The Earth and Planetary Science, Tohoku University, Japan

Olivine-fluid interactions have a variety of applications in environmental remediation schemes, e.g. CO_2 sequestration and sulphate-rich acidic solution neutralization. We have conducted experiments to examine olivine reactivity within these systems, including mineral carbonation (200 °C, carbonated saline solution) and sulphuric acid neutralization (90 °C). Furthermore, we have used *in situ* phase-shift interferometry (PSI) to gain new insights into surface specific olivine dissolution.

The role of the interfacial solution composition was most pronounced in experiments with sulphuric acid, which produced an amorphous silica pseudomorph after olivine at high acid concentrations. Incorporation of ^{18}O into the silica layer in an isotope tracer experiment indicates that the replacement reaction occurred via an interface-coupled dissolution-reprecipitation mechanism. The formation of a pseudomorph in 3.6 M and 2 M solutions suggests that at these conditions olivine dissolution was the rate-limiting step. However, in 1 M solutions the formation of the amorphous silica layer controlled the rate, uncoupling the spatial relationship between dissolution and reprecipitation so that no pseudomorph was produced.

Dissolution of different olivine surfaces in saline solutions were studied with PSI, and showed that the fastest dissolving surface supersaturated the interfacial solution to precipitate a new phase at acidic conditions. This phase is predicted to be similar to the amorphous silica-enriched phase observed to form in the carbonation experiments indicating that the interfacial solution composition plays a critical role under a wide range of conditions.

Sulfur isotope studies in organic matter via SIMS using a statistical approach with heterogeneous standards

H.E. KING JR.[1], MINDY M. ZIMMER[1,2], WILLIAM C. HORN[1] AND WILLIAM A. LAMBERTI[1]

[1]ExxonMobil Research and Eng. Co., Annandale NJ
(correspondence hubert.e.king@exxonmobil.com)
[2]current address Los Alamos National Lab, Los Alamos NM)

Solid bitumen, often found in rocks associated with a hydrocarbon phase, retains a paleo-signature reflecting the evolution of the hydrocarbon. For example, the $^{34}S/^{32}S$ ratio can provide information on the relative importance of thermal sulfate reduction over bacterial sulfate reduction during diagenesis. Such bitumen, distributed as small globules or grain coatings throughout the rock matrix, is a challenge to analyze. A technique with high-spatial resolution, Secondary Ion Mass Spectrometry (SIMS), is an excellent method, but there are challenges in applying this technique to such materials.

SIMS analysis of mineral phases is readily performed because standards allowing correction for instrument and matrix isotope fractionation have been developed. There are no comparable standards for sulfur isotopes in bitumen. Here we introduce the use of sulfur-bearing organic solids such as petroleum coke as such standards. They posses the required similarity in chemical bonding environment to that in bitumen. However to utilize these solids required that we develop a method to overcome their intrinsic chemical inhomogenity. For example, there are finely divided sulfate phases distributed in the organic matrix. Utilizing SIMS imaging to avoid secondary phases and a statistical analysis technique to mitigate the influence of unresolved secondary phases, we found that consistent correction factors for both instrument and matrix fractionation can be obtained. We have generated a Calibrated Matrix Correction that allows the systematic analysis of $\delta^{34}S$ values for bitumen, demonstrating those results by analyzing several bitumens from Brooks Range, Alaska and LaBarge, Wyoming.