## Probing crystal growth mechanisms with non-traditional isotopes

LYNDA B. WILLIAMS AND RICHARD L. HERVIG

Arizona State University, Dept. Geological Sciences, Tempe, AZ 85281-1404 (Lynda.Williams@asu.edu, rick.hervig@asu.edu)

Non-traditional stable isotopes are useful for studying the substitution of elements in specific sites in clay minerals during nucleation and growth. Boron substitutes in the tetrahedral sites of illite, while Li substitutes into octahedral sites. Their isotopic exchange with pore fluid is a sensitive indicator of when Si-O or M-O bonds are broken, and therefore provide insights to reaction mechanisms.

We conducted a hydrothermal experiment reacting smectite to illite in a B-rich solution at 300°C, 100MPa. The fluid's isotopic composition was changed after 65 days to examine the rate of illite re-equilibration during crystal growth. The bulk clay (circles) contained tetrahedral and interlayer-B. The samples were then NH<sub>4</sub>-exchanged to remove interlayer-B. The remaining clay contains only tetrahedral B and was size-separated into fine (<0.2 $\mu$ m; squares), medium (0.2-2.0 $\mu$ m; triangles) and coarse (>2.0  $\mu$ m; diamonds) fractions.

Bulk clays retain variable amounts of the fluid B in the interlayer with little isotope fractionation ( $\pm 3\%$ ). The fine fraction approaches equilibrium quickly, indicating constant nucleation. The coarser fractions have not re-equilibrated. Thus, the boron isotope ratio of different size fractions of clays may record a history of fluids present during diagenesis.



## Boron isotope changes during illitization

## Experimental calibration of the Fe isotope fractionation between pyrrhotite and silicate melt

J. SCHUESSLER, R. SCHOENBERG, H. BEHRENS AND F. VON BLANCKENBURG

Institut für Mineralogie, Universität Hannover, Callinstr. 3, D-30167 Hannover, Germany (j.schuessler@mineralogie.uni-hannover.de)

While systematic differences in the Fe isotope composition of minerals in ultramafic rocks were found in several studies [1, 2, 3], others did not reveal any measurable inter-mineral high temperature Fe isotope fractionation [e.g., 4]. We tested the possibility of high temperature iron isotope fractionation by a first experimental study.

We investigated iron isotope fractionation in the pyrrhotite-silicate melt system, using a hydrous peralkaline rhyolitic glass powder and various amounts of elemental sulphur as starting materials. Pyrrhotite (Fe<sub>1-x</sub>S) was crystallised at a pressure of 500 MPa and temperatures between 840 and 1000 °C. Additionally, experiments with <sup>57</sup>Fe-enriched glass and natural pyrrhotite were performed to study the kinetics of Fe isotope exchange between pyrrhotite and silicate melt and to verify that experimental results represent equilibrium conditions. The Fe isotope composition of pyrrhotite and silicate glass were measured by MC-ICP-MS upon separation of the two phases and chemical purification of iron [5].

The  $\delta^{56}$ Fe values of pyrrhotite are significantly lower (e.g.,  $\Delta^{56}$ Fe<sub>pyrr-melt</sub> = -0.18 ± 0.02 ‰ (2 $\sigma$ , n=4) at 900 °C) than those of the coexisting silicate melt. This isotope fractionation can be attributed to the difference in the iron oxidation state between pyrrhotite and silicate melt. While trivalent iron dominates in the melt, pyrrhotite contains almost exclusively Fe(II). The Fe(II)-bearing pyrrhotite then incorporates preferentially lighter iron isotopes.

Further investigation on the Fe isotope fractionation between other mineral phases and silicate melts is needed, but the presented experimental results, suggest that resolvable Fe isotope fractionation might be expected in other igneous systems, too.

## References

- [1] Williams, H. M. et al. (2004) Science, 304, 1656-1659.
- [2] Weyer, S. et al.(2004) Beih. z. Eur. J. Mineral., 16, 156.
- [3] Zhu, X. K. et al. (2000) EPSL, 200, 47-62.
- [4] Beard, B. L. & Johnson, C. M. (2004) GCA, 68, 4727-4743.
- [5] Schoenberg, R. & von Blanckenburg, F. (2005) *IJMS, in press*