TEM/EELS measurement of $Fe^{3+}/\Sigma Fe$ in biotite near a fracture

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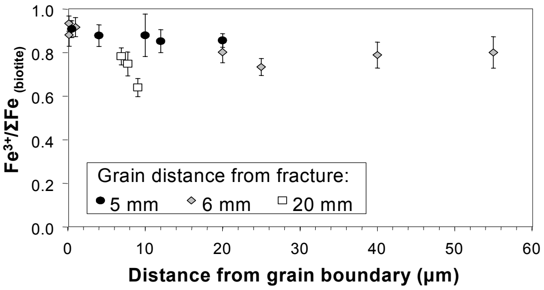
The valence state of Fe in minerals, may be used as a paleoredox tool for studies of past climate change or deep geological waste disposal applications. $Fe^{3+}/\Sigma Fe$ ratios in primary silicates may preserve a record of past oxidation even if reductive dissolution later removes Fe oxyhydroxide evidence that O_2 once was present.

We have modified a TEM electron energy loss spectroscopy (EELS) method (van Aken and Liebscher 2002) for measuring $Fe^{3+}/\Sigma Fe$. Mineral standards of known $Fe^{3+}/\Sigma Fe$ were used to calibrate a relationship based on $I(L_3)/I(L_2)$, the intensity ratio of Fe L_3 and L_2 edges in EELS core loss spectra. Measurements of $Fe^{3+}/\Sigma Fe$ were then made on biotite grains located adjacent to a shallow fracture in the Lac du Bonnet granite batholith (Whiteshell, Manitoba).

This biotite has high $Fe^{3+}/\Sigma Fe$, even at distances a few cm from the fracture, providing evidence of a reaction with oxygenated groundwater at shallow depths. There may be zonation of $Fe^{3+}/\Sigma Fe$ inwards from the grain boundaries, but it is not clearly discernable at our scale of investigation (Fig. 1).

Figure 1: Biotite $Fe^{3+}/\Sigma Fe$ versus distance from the nearest visible grain boundary. Error bars show 95% confidence limits.



Analytical TEM can detect mineral alteration at the nm scale, appropriate for O_2 diffusion along mineral grain boundaries. This spatial resolution is not available with other $Fe^{3+}/\Sigma Fe$ methods, such as Mossbauer spectroscopy.

Reference

van Aken, P.A. and Liebscher, B., (2002). *Phys Chem Minerals* **29**. 188-200.

Lithium-geospeedometry: Quantifying rapid geological processes

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Lithium diffusion in plagioclase has been known to be extremely rapid for a number of years [1] and hence the distribution of Li within and between phases may record the rates of short-lived, or low-temperature, processes. We have developed a Li-geospeedometer based on the down temperature diffusion of Li from plagioclase into clinopyroxene to allow us to quantify rapid geological processes.

High temperature experiments were performed to quantify the temperature dependence of the equilibrium distribution of Li between plagioclase and clinopyroxene between 900°C and 1200°C. Lithium partitioning between these phases is highly sensitive to temperature changing by an order of magnitude over this temperature range. At lower temperatures Li partitions more strongly into clinopyroxene than at higher temperatures.

High temperature experiments have also been undertaken to determine the diffusion coefficient of ^6Li in clinopyroxene between 800°C and 1100°C. Self diffusion of lithium in clinopyroxene is approximately two orders of magnitude slower than in plagioclase over this temperature interval – still extremely rapid compared to most cations.

These new experimental data, along with the published diffusion coefficient for Li in plagioclase [1] calibrate the Li-geospeedometer for Li exchange between plagioclase and clinopyroxene during cooling. We have applied this geospeedometer to determine the cooling rate of the sheeted dike complex of the oceanic crust. We find that the upper half of the sheeted dike complex cools very rapidly (~500°C/hr) indicating that this can supply the heat required to drive hydrothermal megaplumes. The lower portion of the sheeted dike complex cools much more slowly (~5°C/hr) supply a longer lasting heat (and perhaps nutrient) source to the overlying hydrothermal system.

Reference

[1] B. J. Giletti, T. M. Shanahan, *Chem Geol* v139, 1997.