# VSI study of biotite dissolution at acidic pH and 25-50˚C

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Generally, the dissolution rates of the phyllosilicates that comprise the mica group (e.g. muscovite, biotite and flogopite) were obtained from experiments in which ground powders were used, and the calculated rates were normalised either to total or edge surface area, derived from BET measurements. Using the vertical scanning interferometry (VSI) technique we attempt to compute biotite dissolution rates from quantifying surface normal retreat of the cleavage (001) surface at pH 1 and 25, 40 and 50 ºC. The advantage of these measurements is that allows us to obtain biotite dissolution rates from mineral surface retreat, and thus avoiding the need to normalize the dissolution rates with externally measured surface areas.

Single biotite fragments of approximately 100 $mm^2$ were placed in 250 mL of 0.1 M $HNO_3$ solution (pH 1) and 25, 40 and 50 ºC for almost two weeks. During this time span the cleavage surface was examined by VSI after 4, 7 and 13 days. On the one hand, dissolution features were observed on the cleavage surface, and on the other hand, the dissolution rates were computed from surface retreat compared to a non-reacted reference surface.

The calculated biotite dissolution rates, with an average error of ~10 %, were $2.5 \times 10^{-8}$, $1.1 \times 10^{-8}$ and $0.3 \times 10^{-8}$ mol $m^{-2}$ $s^{-1}$ at 50, 40 and 25 ºC, respectively, which are higher than those calculated from the total mineral surface area, although rates normalized to total surface area may have little relevance for micas, since reactive sites probably are concentrated on edge surface [1]. VSI examinations of the reacted cleavage surface show that biotite dissolution was controlled by preferential surface edge dissolution.

The calculated activation energy of the biotite dissolution at pH 1 from the rates obtained at 25, 40 and 50 ºC is 14.35 kcal $mol^{-1}$ ($R^2$ = 0.997), which is similar to that of biotite dissolution at very acidic pH [2].

[1] Kalinowski & Schweda (1996) *GCA* **60**, 367-385 [2] McMaster *et al*. (2008) *MinMag* **72**, 115-120

# Spin transition in Fe-bearing perovskite: Implications for the lower mantle

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Using lattice dynamical calculations based on density functional perturbation theory we are able to disentangle a part of the complex phase diagram and spin behavior of the $(Mg,Fe)SiO_3$ perovskite (pv). To do this we investigate the dynamic stability of Pbnm $FeSiO_3$ pv and show the existence of unstable phonon modes. We track the eigen-displacements of the phonons modes to find low-spin and intermediate spin states. On solid-state physical basis we explore a set of hypothetical structures with various spin configurations and considerably lower enthalpy than the parent orthorhombic Pbnm structure. We show that the spin evolves along a high-spin to mixed high- and intermediate spin to low-spin transition sequence. We also analyze the thermal behavior of both high-spin and low-spin phases and we discuss a first thermal phase diagram.

We show that the elastic moduli and the bulk seismic wave velocities are weakly affected by the spin transition. However, the intrinsic differences in seismic anisotropy between the high-spin and low-spin phases of Fe-bearing pv coupled with lattice preferred orientation that can develop during mantle flow lead to distinct seismic signatures between the top and the bottom of the lower mantle [1]. These signatures are detectable by seismic observations and they need to be taken into account in tomographic studies of the Earth's lower mantle.

Finally, we find that the electronic gap widens during crossover to the low-spin phase. This has a direct influence on the electircal conductivity and agrees qualitatively with in situ measurements [2].

[1] Caracas, Mainprice, and Thomas (2010) *Geophys. Res. Lett.* **37**, L13309. [2] K. Ohta, *et al*. (2008) *Science* **320**, 89.