

The apparent activation energy for biotite dissolution by *in situ* Atomic force microscopy (AFM) observations

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In this study we used *in situ* AFM imaging of biotite (001) surfaces to observe dissolution processes in oxalic acid and hydrochloric acid solutions in real time. In oxalic acid solutions at pH 2 and 1 we observe the combined dissolution processes of slow etch pit formation, followed by relatively fast etch pit growth. The etch pit depth is found to be consistent with the thickness of 1 *tot* layer (~1 nm). Measurements of the fractional surface area covered by etch pits over time provide dissolution rates in the acid solutions. Experiments over a range of temperature, 10°C < T < 35 °C, in the pH 1 solution allow an estimate of the apparent activation energy, $E_a = 49 \pm 2 \text{ kJmol}^{-1}$ using the Arrhenius equation. We find that the average radius of etch pits grows linearly with time for all T, and use these growth rates to obtain a second value of $E_a = 53 \pm 3 \text{ kJmol}^{-1}$. We also find a linear relationship between the dissolution rate and the density of step edges on the surface for all values of T. However, E_a is found to vary between ~ 40 kJmol⁻¹ and >100 kJmol⁻¹ at low and high step density, respectively. This variation may reflect the greater energy required for etch pit formation compared with etch pit growth. In an HCl solution of pH 1 we do not observe the formation of discrete etch pits, but a more general degradation over the entire biotite (001) surface. We conclude that etch pit occurrence in the oxalic acid solution proceeds through chelation of aluminium ions in the (001) surface by the oxalate ligand. This may destabilize the silicate structure, leading to the removal of the entire *tot* layer, as observed. In the HCl solution the aluminium cations are less soluble due to the lack of organic ligand so the silicate structure remains intact.

Metal silicate partitioning of Ge, Mo, Ga and P: Constraints on core formation

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Siderophile element signatures in Earth's mantle are a result of segregation of the iron rich core from the silicate mantle. It is generally argued that during the metal silicate differentiation process these elements were substantially partitioned into the core leaving behind lithophile elements in the silicate mantle. Several core formation models have been proposed to account for the observed abundance of elements in mantle rocks. A recently proposed model [1] suggests that the core formed at the base of a magma ocean which deepened with accretion and in which conditions became more oxidising with time. This also accounts for 5-7% Si in the core.

To test this hypothesis of early reducing magma ocean [1] we are studying the metal silicate partitioning behaviour of selected siderophile and nominally lithophile elements, characterizing the dependence of the metal silicate partition coefficient, D, on oxygen fugacity. We report new experimental results on the partitioning behaviour of Ga, Ge, Mo and P, and these are compared with our previous work on Si, Ta, Nb and V. All these elements can exist in variable and high oxidation states and their partitioning could also be sensitive to silicate melt composition [2]. Experiments were made at 2 GPa and 2000 K, over a range of relative oxygen fugacities from ~IW-2 to IW-6. Silicate melts range from basaltic to peridotitic in composition. The melt compositional parameter, NBO/T, is used as a proxy for silicate melt composition, and has values from 0.7 to 4. Isobaric, isothermal data for each element were regressed using the equation: $\ln D^{\text{met/sil}} = a + b fO_2 + c(\text{NBO}/T)$. Regressions show that at the experimental conditions Ge has a likely valence state of +2, Ga, Nb and V exist in 3+ valence states, Si shows a valence state of +4, whereas P and Ta appear to exist in a 5+ valence state. Observing the partitioning behaviour of these elements over the redox range investigated, Si exhibits the least siderophile tendency and it appears unlikely for 5-7% Si to sequester into the core under reducing conditions without disturbing the mantle's budget of other siderophile and refractory lithophile elements. Further experiments are in progress to provide more constraints on the influence of fO_2 and melt composition on the metal silicate partitioning of these elements.

References

- [1] Wade & Wood (2005), *EPSL* **236**, 78-95
[2] Walter *et al.* (1995), *Science* **270**, 1186-1189