Zoisite – an effective trace element vehicle at HP metamorphic processes

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Delamination processes occurring as a result of crustal thickening may cause significant continental crustal recycling into the mantle. Caused by the formation of garnet-rich HPassemblages, plagioclase-rich rocks of the lower crust will experience a fast sinking into the subcontinental mantle (Wittenberg, 2000) The resulting processes will lead to a redistribution of trace elements between high pressure phases. This study is aimed at understanding which phases are controlling the transport of trace elements from delaminated plagioclase-rich rocks into the mantle. The experiments were performed at 1.5 to 4.0 GPa and 900° to 1100° C in a pistoncylinder (P<2.5 GPa) and a belt-apparatus (P>2.5 GPa). The starting materials (glasses) were made from a natural plagioclase-cumulate powder, enriched with a CaF₂/AlF₃mixture (to act as a flux), and doped with the elements Sr, La, Nd, Sm, Eu, Gd, Y, Yb (for REE 500µg/g of each of the elements; for Sr 500µg/g and 5000 µg/g). The starting glasses were also prehydrated at high pressure and contained 3.7 wt% H₂O. Glasses and mineral phases were analysed by EMP (Cameca SX 100) and identified by powder-diffraction.

In all runs zoisite, pyroxene, and a varying amount of melt were observed. Most runs also contained garnet and kyanite or corundum. Zoisite was also found in flux-free experiments and can be a stable phase at mantle conditions.

Zoisite is the phase in which most trace elements were incorporated. The concentrations of the doped trace elements could be analysed by EMP in zoisite, but need to be analysed by high resolution in-situ techniques in the other phases The $D_{sm}^{zo/melt}$ is > 4 and increases with pressure



as well as with temperature (Fig. 1). In the presence of a flux (Ca-Al-rich systems) zoisite will be formed easily and hence incorporate very effectively lithophile elements such as REE and Sr. If present the garnet will incorporate the HREE whereas other trace elements will be preferentially fractionated into zoisite. Thus, the redistribution of trace elements with crustal signatures into the mantle are not only dependent on the behaviour of major phases such as garnet, but may also be controlled by zoisite.

Reference

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Chemical weathering rates of volcanic glasses

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Volcanic activity produces glassy material like ash, pumice and scoria, which is very common on the volcanic islands and mountains spanning the Pacific. Its subsequent weathering generates Andisols, a very fertile soil type that supports a dense vegetation cover in moist climates, like Hawaii, Chile, and South Japan. Environmental conditions like precipitation rates and vegetation along with the chemical composition of the volcanic glass and the soil solution strongly influence the rate of weathering.

This study has focussed on the compositional effect of volcanic glasses on the dissolution rates under acidic conditions. The geometric surface area normalized dissolution rates of the volcanic glasses increase linearly with decreasing silica content of the glasses at pH 4, 25°C and far from equilibrium. The far from equilibrium dissolution rate of basaltic glass, at Earth's surface conditions, can be described with two variables only: temperature and the aqueous activity ratio a_{H}^{3}/a_{Al}^{3+} . The glass dissolution is promoted by anions that form complexes with Al³⁺ like oxalate and fluoride. The maximum effect of 1 mmol oxalic acid on the dissolution rate of basaltic glass is 50 fold increase at pH 4.5 and 25°C. Under similar conditions 90 mol fluoride addition (1.7 ppm) yields 10 times higher dissolution rates for volcanic glasses of all composition. While fluoride can be a considerable dissolution promoting agent during and shortly after volcanic eruptions, where it can reach concentrations up to 1200 ppm, organic acids, secreted by the vegetation, are always important in soils. Together with the carbonic acid from soil, organic agents provide a favourable low pH and at the same time complex the aqueous Al³⁺. Hence the biosphere has a significant effect on the weathering rate of volcanic glasses.

Volcanic glass lifetimes from basaltic to rhyolitic composition and metal/element release rates per volume (Andisol) soil per year (assuming stoichiometric dissolution) have been computed. This information is crucial for soil scientists as the individual metals act as nutrients as well as growth inhibitors or toxins depending on their solution concentration. For example, the reduction in Al^{3+} not only enhances the glass dissolution but also creates a healthier plant growing environment as aluminium is a plant toxin.