

Compositional gradient of Cpx produced by fluid assisted eclogitization

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The Precambrian granulite facies assemblages ($P \leq 10$ kbar, 800°C) of the anorthositic rocks of the Bergen Arcs, Western Norway was overprinted by eclogite facies assemblages ($P=15-20$ kbar, $650-700^\circ\text{C}$) along shear zones and fluid pathways associated with the Caledonian orogenic cycle (Jamtveit *et al.* 1990).

The aim of this study is to investigate the mechanism of fluid-mineral interaction that take place as the granulite facies clinopyroxene is altered to omphacite using microscopy and micro-analytical techniques (SEM, EMP and TEM).

The investigated sample comes from the margin of a shear zone and contains relicts of garnet and clinopyroxene while the former plagioclase domains are reacted to kyanite, omphacite, amphibole, clinozoisite and white micas (paragonite and phengite). Relict clinopyroxene in contact with plagioclase domains is replaced by the following sequence of reaction zones: 1) a core of Al-rich diopside (granulite facies), locally with domains of intergrown garnet and diopside. 2) An inner zone consisting of coarsely intergrown pyroxene (Jd_{24}) and amphibole (symplectite A). 3) An intermediate zone of porous pyroxene (Jd_{43}) with inclusions of dolomite. 4) An outer zone consisting of grains of omphacite (Jd_{59}) surrounded by symplectites of amphibole and plagioclase (symplectite B).

The reaction zones that developed around the granulite facies pyroxene core have a total width of ca 500 μm and formed during reaction between the infiltrating fluid and the original pyroxene.

References

Jamtveit B., Bucher-Nurminen K., and Austrheim H. (1990), *Contrib Mineral Petrol.* **104**, 184-193.

Minerals into molecules

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Why Small?

Questions posed about minerals are now often molecular. For answers, we need experimental models that are also molecular. They must be sufficiently complex to look like minerals but small enough to treat at a sophisticated level using computer methods. Here we review experiments on nanometer-size aqueous oxide clusters where we measure rates of steady oxygen-isotopic exchange between structural sites in the molecules and bulk solution using ^{17}O -NMR. In all cases, the reactions are steady elementary or near-elementary isotope exchanges and the molecule doesn't dissociate.

We show that: (1) The reactivities of functional groups at mineral surfaces are often estimable using these clusters and (2) Little can be reliably known about reactions at mineral surfaces without such experimental models--Our instincts are often worse than wrong--they are often misleading.

Aqueous Oxide Nanoclusters

One molecule we review is a 2.5-nm cluster that isolates $>\text{Fe}^{\text{III}}\text{-OH}_2$ sites for kinetic characterization. Using this 2.5 nm cluster, we discuss how acid-base chemistry affects the rates of dissociation of $>\text{Fe-OH}_2$ functional groups on mineral colloids and how the rates of ligand substitution on minerals can be estimated accurately. Does charging affect these labilities? Does size matter? Is there a unique nanogeochemistry at work here?

We also review work on the Lindqvist anions, which are 0.86 nm diameter molecules that can be protonated stepwise, like a mineral surface. For these clusters, the reactivities of oxygens actually invert when isoelectronic metal substitutions are made. We show that protonation of *any* oxygen in the Lindqvist ions labilizes all exchangeable oxygens in the structure. Thus, a view of oxide reactivity where protons are only local is incorrect.

Finally, we review the data on Al(III) polyoxocations where oxygen-isotopic exchanges into the bridging oxygens is complicated, and much different than at clays (Rosenqvist and Casey, 2006), but substitution at the bound waters is simple, robust and immensely useful (see Wang *et al.*; 2007).

References

Wang J., Rustad J. R., and Casey W. H. (2007) Calculation of water-exchange rates on aqueous polynuclear clusters and at oxide-water interfaces. *Inorg. Chem.* **46**, 2962-2964.
Rosenqvist, J. and Casey, W. H. (2004) The flux of oxygen from the basal surface of gibbsite ($\alpha\text{-Al}(\text{OH})_3$) at equilibrium. *Geochim. Cosmochim. Acta* **68**, 3547-3555.