Breakdown mechanisms of titanclinohumite in antigorite serpentinite

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The recycling of water in the deep mantle strongly relies on the stability of hydrous minerals during subduction and the water storage capability of nominally-anhydrous minerals. Many authors have stressed the importance of the humite-group minerals for the storage of water in the mantle. The recycling of water by titanclinohumite in olivine-bearing rocks depends on the stability of titanclinohumite during subduction, which in turn depends on the subduction thermal field and the F/OH ratio of this mineral.

Veins with OH-titanclinohumite (OH-Ti-Chu) and olivine occur close to clinopyroxenite layers scattered through the antigorite serpentinites from the Cerro del Almirez ultramafic massif (Sierra Nevada, Betic Cordillera, S. Spain) [1][2]. They formed at 1.3 GPa and 475°C, due to simultaneous breakdown of former Ti-rich clinopyroxene and brucite in the presence of 6 vol.% of free water. Breakdown of Ti-Chu single crystals in these veins to an olivine+ilmenite framework at 620-640°C and 1.7-2.0 GPa was gradual: small relict patches of Ti-Chu appear even at some distance from the reaction front and ilmenite grains coarsen and become less frequent. Detailed TEM data of the textural breakdown sequence suggests both progressive transfer of Ti to ilmenite and progressive release of H_2O during the breakdown of Ti-Chu. This textural features points to a very limited availability of water during Ti-Chu breakdown suggesting that veins operated as closed systems. At higher T conditions, antigorite dehydration reaction took place giving place to the complete destruction of OH-Ti-Chu. Thus, OH-Ti-Chu from Atg-serpentinite can be precluded as an efficient water or titanium carrier into deep mantle in hot subduction zones.

[1] Trommsdorff, López Sánchez-Vizcaíno, Gómez-Pugnaire & Muntener (1998) *Contrib Mineral Petr* **132**, 139-148.
[2] López Sánchez-Vizcaíno, Gómez-Pugnaire, Garrido, Padrón-Navarta & Mellini (2009) *Lithos* **107**, 216-226.

Phosphate forms predominately monodentate complexes at the surface of goethite

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The manner in which phosphate adsorbs to the surface of goethite has importance in many areas of geochemistry, including oxoanion bioavailability, mineral dissolution, and surface complexation modeling. The prevailing view for the past two decades is that phosphate adsorbs in a predominantly bridging-bidentate fashion. However, we recently showed that the analogous oxoanion, arsenate, is in fact, predominantly monodentate coordinated at the goethite surface [1]. These results for arsenate have prompted us to reexamine phosphate coordination at the surface of goethite.

We performed simultaneous infrared spectroscopic and potentiometric titrations on four different goethites: α-FeOOH with surface areas of 43 and 104 m^2/g, and α-FeOOD with surface areas of 34 and 57 m^2/g. The total phosphate concentrations ranged from 0.4 to 3.1 $\mu mol/m^2$, and the pH (or pD) was titrated between 2.5 and 11. We also isolated the spectra of the different protonation and deuteronation states of phosphate, pentaamminecobalt(III) phosphate (a modentate coordinated complex), and bisethylenediamine-cobalt(III) phosphate (a bidentate coordinated complex).

A principal component analysis of the spectra from any single surface titration shows two effects in the data. By analogy to similar trends in the arsenate-goethite system, we interpret these effects as due to a transition from an un- to a singly-protonated complex from high to moderate pH, and from a singly- to a doubly-protonated complex from moderate to low pH. The pH trends in the Type-B OH stretching region are also analogous to the arsenate-goethite system, and they are consistent with an unprotonated complex at high pH, a singly-protonated complex at moderate pH, and a doubly-protonated complex at low pH. Finally, the spectra in the PO stretching region for phosphate adsorbed on α-FeOOD at low pD reveal a PO stretching band that is otherwise hidden behind the FeOH bending modes of α-FeOOH. This previously unobserved band suggests that the symmetry of the phosphate surface complex at low pD is likely C_{2v} or less.

In summary, we conclude that, analogous to the arsenate-goethite system, phosphate is coordinated in a predominately monodentate fashion and is unprotonated at high pH, singly-protonated at moderate pH, and doubly-protonated at low pH.

[1] Loring *et al*. (2009) *Chem. –Eur. J.*, in press.