

Is there a reversible step in ^{45}Ca sorption onto pure calcite?

J. LY, E. TERTRE, C. BEAUCAIRE AND V. MEVELLEC

CEA, Centre d'Etudes de Saclay, DANS/DPC/SECR/L3MR,
91191 Gif sur Yvette, France.

Metal sorption onto carbonate minerals have been intensively interpreted in literature by two reaction steps: (1) a first one rapid and completed within few hours and (2) a second one slower, eventually irreversible and occurring at a constant rate (Davis *et al.*, 1987; Zachara *et al.*, 1991; Mevellec, 2000). The first step is often attributed to an ion exchange process, but its reversibility is rarely investigated. Consequently, discrimination of the global sorption phenomenon into two different mechanisms is not always justified.

Therefore, we have investigated both sorption and desorption of Ca, radiotraced with isotope ^{45}Ca , onto synthetic pure calcite in aqueous solutions saturated with respect to calcite and in equilibrium with the atmospheric CO_2 . Batch experiments were performed as a function of time and at different pH using anionic chemical buffers having no affinity towards calcite. The distribution coefficient of ^{45}Ca was calculated from radiochemical measurements of the supernatants before and after sorption, and the total Ca aqueous concentration was measured by ion - chromatography.

As mentioned by previously cited authors, our results show that whatever the pH, K_d 's of ^{45}Ca increase with time without reaching a stationary state within two weeks. Moreover, K_d 's calculated with desorption experimental data are systematically higher than those calculated with the sorption ones. In order to test the occurrence of a first reversible ion exchange step, we applied the approach of Badillo-Almaraz and Ly (2003) put forward for the interpretation of Ca sorption onto hydroxyapatite. More specifically, on the basis of isotopic equilibrium principle and from the knowledge of the isotopic ratios ($^{45}\text{Ca}/\text{Ca}_{\text{tot}}$), it is possible to calculate "reversible" K_d 's of ^{45}Ca for both sorption and desorption steps. Doing this, we observe that both calculated K_d 's values are similar, whatever the time and pH. In these conditions, we are able (1) to evidence the reversible step of retention of Ca and more, (2) to quantify the amount of Ca sorbed on the calcite surface, which can be compared to surface crystallochemical data.

References

- Badillo-Almaraz V.E. and Ly J. (2003). *J. Colloid Interf. Sci.* **258**, 27-32.
 Davis J.A., Fuller C.C. and Cook A.D. (1987), *Geochim. Cosmochim. Acta* **51**, 1477-1490.
 Mevellec V. (2000). Education of Training, CEA Internal Report.
 Zachara J.M., Cowan C.E. and Resch C.T. (1991), *Geochim. Cosmochim. Acta* **55**, 1549-1562.

P-T conditions and oxygen fugacity estimates suggest suprasubduction setting of Voykar ophiolites, Polar Urals

Z. E. LYASKOVSKAYA^{1,2}, V.G.BATANOVA¹ AND I.A. BELOUSOV¹

¹Vernadsky Institute of Geochemistry, Moscow, Russia
(sobolev@geokhi.ru)

²Moscow State University, Moscow, Russia

Mantle section of Voykar ophiolites, Polar Urals, Russia contains exceptionally fresh harzburgites, dunites and pyroxenites. Dunites and pyroxenites indicate melt percolation event dated by Re-Os isotopes as 0.6 Ma old (Batanova *et al.*, 2007). Host harzburgites yields much older ages (up to 2.5 Ga). Here we report estimations of P-T conditions and oxygen fugacity for harzburgites, dunites and pyroxenites based on mineral compositions.

P-T conditions of harzburgites correspond to $T=950\text{ C}$ and $P= 1.2\text{-}1.4\text{ GPa}$ (Wells, 1977; Mercier, 1980). Oxygen fugacities $-1.5\text{-}2.5\text{ log units}$ higher than QFM (Ballhaus, 1991). Pyroxenites yield $T= 950\text{-}1050\text{ C}$ and P around 1.4 GPa . The oxygen fugacity of pyroxenite and dunites still has to be evaluated.

The obtained high oxygen fugacities and low temperatures suggest suprasubduction settings for Voykar ophiolites.

References

- Ballhaus C. *et al.*, (1991). *Contrib. Mineral. Petrol.* **107**, 27-40.
 Batanova V.B. *et al.*, (2007). *Geophysical Research Abstracts* **9**, 10328, EGU 2007,
 Mercier J. C. C. (1980). *Tectonophysics* **70**, 1-37.
 Wells P. (1977) *Contrib. Mineral. Petrol.* **62**, 129-139