

Interactions of phosphate and phosphonate with the calcite surface

J. STELLING*, A.K. NOTHSTEIN AND T. NEUMANN

Karlsruhe Institute of Technology (KIT), Institute of Mineralogy and Geochemistry, D-76131 Karlsruhe, Germany (*correspondence: stelling@kit.edu)

Crystal growth mechanisms of calcite have been studied in detail in the past [1, 2]. The ability of calcite to adsorb P as phosphate from raw, sea and artificial water [3, 4] has been investigated intensively to recover P as a valuable nutrient [5]. Moreover, a detailed understanding of the interaction between phosphonates and calcite is of great interest for large-scale application as scale inhibitor, dispersant or chelating agent [6]. To date, understanding atomic-level processes that govern the kinetics of calcite growth with respect to phosphate and phosphonate anions is still incomplete.

As part of the ReCaWa joint project (Reactivity of Calcite/Water Interfaces), we investigate the sorption and coprecipitation processes of phosphate and phosphonate on calcite surfaces from (super)saturated calcite solutions. Solutions were prepared from p. a. grade chemicals (CaCl₂, NaHCO₃) in double distilled water (18.2 MΩ·cm), with pH adjusted to 8.2 and I=0.1 mol/L. Phosphate (H₃PO₄, Na₃PO₄·6H₂O) or phosphonate (etidronic acid, HEDP) were added in concentrations from 3–1000 μmol/L and 10–25 μmol/L, respectively. For batch experiments differing amounts precipitated calcium carbonate or limestone powder with varying specific surface area (SSA) and crystal morphology were added to the solutions. Additional and upcoming coprecipitation experiments under strongly defined conditions are performed using a mixed flow reactor (MFR) to allow coprecipitation of homogeneous phosphate or phosphonate containing calcite onto the calcite seed powder.

Experimental results show that phosphate uptake is a function of SSA and formation of HEDP precipitates dependent on the calcite morphology, respectively. Forthcoming analytical work includes the identification of different fixation mechanisms and phosphorus-containing phases using XRD and XAFS spectroscopy at grazing incidence.

[1] Morse *et al.* (2007) *Chem. Rev.* **107**, 342–381. [2] Larsen *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 2099–2109. [3] Donnert *et al.* (1999) *Environ. Technol.* **20**, 735–742. [4] Song *et al.* (2006) *Chemosphere* **63**, 236–243. [5] Gilbert (2009) *Nature* **461**, 716–718. [6] Nowack (2003) *Water Res.* **37**, 2533–2546.

Geochemistry of lamprophyres in rare-metal districts related to granitoids

M. ŠTEMPROK^{1*}, TH. SEIFERT² AND D. DOLEJŠ¹

¹Faculty of Science, Charles University, 12843 Praha 2, Czech Republic

(*correspondence: miroslav.stemprok@natur.cuni.cz)

²Technical University Bergakademie, 09596 Freiberg, Germany

Lamprophyres occur occasionally in mafic-silicic dyke suites of rare-metal (RM) granitoids in Paleozoic provinces of Western and Central Europe, Central Kazakhstan, the Altai, and in Mesozoic provinces of Transbaikalia, Yakutia, Chukotka and Alaska, which host RM (Sn, W, Nb, Ta, Mo, Be) mineralization. We evaluate 190 whole-rock chemical analyses of lamprophyres and variable sets of trace elements in order to uncover any genetic relationships between the melts derived from metasomatized upper mantle and enrichment in RM and alkalis. The lamprophyres correspond to minettes and kersantites with minor spessartites, and have 40–65 wt. % SiO₂, 0.8–9.6 wt. % K₂O, up to 17.8 wt. % MgO, and up to 1450 ppm Cr and 515 ppm Ni. The highest molar MgO/MgO+FeO^{TOT} ratios up to ~0.75 indicate no substantial modification by fractionation or crustal assimilation. The Zr-Hf and U-Th ratios are not decoupled, and the Nb-Ta ratios approach the primitive mantle values. However, absolute concentrations of these elements, which are also considered to be the least mobile in aqueous fluids, show large to extreme enrichments: Zr (27–1420 vs. 190 ppm in calc-alkaline lamprophyres [1], 193 ppm in the upper continental crust [2]), Hf (3.5–36 vs. 5.2 ppm [1], 5.3 ppm [2]), U (0–29 vs. 3 ppm [1], 2.7 ppm [2]), Th (4–75 vs. 9 ppm [1], 10.5 ppm [2]), Nb (2–150 vs. 13 ppm [1], 12 ppm [2]), Ta (0–16 vs. 0.9 ppm [1], 0.9 ppm [2]). These levels in lamprophyres of the RM districts exceed the average abundances of some elements in calc-alkaline lamprophyres or in the differentiated upper continental crust by one to two orders of magnitude. They are also systematically enriched in F (0.04–2.85 vs. 0.11 wt % [1]), Rb (43–1490 vs. 70 ppm [1]), Cs (2.4–122 vs. 3 ppm [1]), Li (14–447 vs. 44 ppm [1]), and Sn (1–417 vs. 2 ppm [1]) partly due to superimposed greisenization. However, the overall enrichment pattern of lamprophyres and mineralized granites suggests that the source of some components in RM districts can be traced to mantle-derived melts, as previously proposed for the Cornubian province [1].

[1] Rock (1991) *Lamprophyres*. Blackwell, 285 pgs. [2] Rudnick & Gao (2003) *Treatise on Geochemistry* **3**, 1–64.