

Transitions and twin wall conduits: controls on chemical transport in minerals

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Many rock-forming minerals display symmetry-changing structural phase transitions in response to changing temperature, pressure or chemical composition. As a consequence a hierarchical microstructures of transformation twins may develop [1]. It has long been recognised that these offer the potential for modifying the diffusion rates and transport characteristics of chemical species within the host minerals. Using the α - β phase transition in quartz as a model example, we have investigated the significance of a fairly typical structural phase transition on the rates and mechanisms of ionic diffusion.

Using β -eucryptite as a Li^+ ion source [2], we have measured diffusion of Li^+ into a natural single crystal of quartz as a function of temperature through the phase transition from low (trigonal) quartz to high (hexagonal) quartz. As this transition is encountered, a changing pattern of Dauphiné twins develops, with the twin wall density increasing on heating towards the transition temperature, T_c , and an incommensurate phase stable with a couple of degrees of the transition. We find that Li^+ ion transport peaks in the vicinity of the incommensurate phase, and the temperature dependence of diffusion indicates that the activation energy for diffusion in the high-temperature phase is around half that measured in the low-temperature phase.

The increase in Li diffusion into quartz very close to T_c can be explained in terms of the increased density of domain walls, if Li^+ diffuses faster in the domain wall than in the bulk α -quartz structure. This implies that domain walls act as conduits for diffusion, as has been noted previously in measurements of Na^+ into the WO_3 perovskite structure. Additional effects due to changes in elasticity through the structural phase transition may also modify the transport behaviour in the bulk, and account for the differences in diffusion coefficients in the low- and high-temperature phases.

In materials science applications, the phenomenon of domain wall transport could be exploited in device fabrication at mesoscopic scales. In Earth sciences, domain wall transport could be envisaged as a significant process in those phases which display transformation twin (ferroelastic) microstructures, ranging from numerous framework silicates in the crust, to silicate perovskites in the lower mantle.

[1] Salje, E.K.H., Bismayer, U., Hayward, S.A., and Novak, J. (2000) *Mineral. Mag.*, 64, 201-11.

[2] Sartbaeva, A., Farnan, I., Redfern, S. A. T., Kristensen, J. H. (2001) *Bull. Soc. Fr. Minéral. Cristallogr.*, 21, 108.

Coordination of some metals sorbed at the calcite-water interface

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Metal incorporation into calcite has been shown to be strongly site selective on the common (10.4) face. Multiple surface sites are distinguished by different geometrical arrangements of CO_3 groups, and the nonequivalent sites are segregated between structurally distinct surface steps. Adsorption of metal species at the calcite-water interface is an essential step in the overall incorporation process, and it may also be an important mechanism for sequestration of toxic metal species in natural waters. In view of these surface site differences, individual coordination preferences of various metal species may control both their site preferences and their extent of uptake. We have used EXAFS spectroscopy to characterize the coordination of Zn(II), Cu(II), and Pb(II) species sorbed at the calcite-water interface at pH 8.3. Our results show distinct surface site coordinations that differ from the coordination of these same species substituted into calcite, and allow us to explain surface site preferences.

Zn(II), Cu(II), or Pb(II) was added to pre-equilibrated calcite suspensions at pH 8.3 with maximum metal concentration below saturation with respect to possible solubility-limiting phases. Calcite solids were recovered by filtration after 48 h; moist paste samples were loaded into sealed sample holders for EXAFS data collection at beamline X11A or X18B at NSLS. Fitting was done using WinXAS and theoretical phases and amplitudes calculated with FEFF7.

EXAFS fit results for adsorbed Zn(II) show a Zn-O first-shell distance of 1.95 Å, consistent with tetrahedral coordination by four oxygens. A fitted Zn-Ca distance of 3.45 Å confirms that Zn(II) forms an inner-sphere complex at a Ca surface site. Adsorbed Cu(II) atoms are Jahn-Teller distorted, with the equatorial oxygen atoms located at a radial distance of 1.95 Å. No axial oxygen contribution could be identified, but a Cu-Ca shell was found at $R=3.9$ Å, which indicates the formation of inner-sphere Cu(II) complexes at the calcite surface. Incorporated Cu(II) atoms occupy the Ca site within the calcite surface as Jahn-Teller distorted octahedra with the equatorial oxygen shell at 2.01 Å. Fit results for Pb(II) yield a first shell of approximately four oxygens at 2.36 Å. A Pb-Ca distance of 4.05 Å verifies that metal binding at the mineral surface takes place via inner-sphere complexation.

The coordination of adsorbed Zn(II) and Pb(II) differ from their regular octahedral coordination when substituted in the Ca site of calcite, and differences in coordination also occur between the adsorbed and incorporated Cu(II). We note that Zn, Pb, and Cu exhibit similar site preferences on calcite (10.4) surfaces. It remains to be determined if and how these preferences for surface coordination may influence distribution coefficients.