Raman spectroscopic insight into structural changes in berlinite with high pressure and temperature

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Berlinite ($AlPO_4$) and α-quartz are structural isotypes, which are related to each other by the coupled substitution 2 Si = Al + P. The SiO_4 tetrahedra along the *c*-axis in α-quartz are replaced in berlinite by alternating AlO_4 and PO_4 tetrahedra. This preferred ordering results in a doubled *c* unit-cell parameter. The frequencies of Raman modes of berlinite and α-quartz are very similar because the atomic masses of Al + P are almost the same as that of two Si atoms [1]. However, detailed inspection reveals a greater complexity in the Raman spectrum of berlinite [2]. To obtain more information on the relationships to the berlinite structure, we studied the strong A_1-Raman lines at 462 and the 1111 cm^{-1} at temperatures up to 800 °C and pressures up to 10 GPa.

The positions of both bands shift in the opposite direction with pressure (*P*) and, likewise, with temperature (*T*). The 1111 cm^{-1} Raman line is accompanied by a less intense band at 1104 cm^{-1}. With increasing *P*, the 1111 cm^{-1} band shifts towards lower wavenumbers and that at 1104 cm^{-1} to higher wavenumbers. Both lines thus display the same frequency at about 1.4 GPa at 23 °C. With further increase in *P*, they become fully separated above 5 GPa. Both Raman lines originate from stretching vibrations of the PO_4 tetrahedra. The opposed behavior with pressure is tentatively interpreted as being caused by the alternate succession of the AlO_4 and PO_4 tetrahedra along the *c*-axis, which permits a different compression/extension of the P-O1 and P-O2 distances.

The results also indicate the great potential of berlinite as a pressure sensor for diamond-anvil cell experiments, including studies at elevated *T*. A relative shift, defined by the difference of the shifts in the wavenumber between the 462 and the 1111 cm^{-1} lines with *P* and *T*, can be used as pressure gauge. Moreover, this sensor may be applicable at higher pressures than α-quartz [3] because no high-pressure polymorph isomorphic to coesite or stishovite is known.

[1] Scott (1971), *Phys. Rev. B* **4**, 1360-1366. [2] Gregora *et al.* (2003) *J. Phys.: Condens. Matter* **15**, 4487–4501. [3] Schmidt & Ziemann (2000), *Am. Mineral.* **85**, 1725-1734.

Effect of ionic strength on Ca isotope and Sr incorporation into calcite

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Chemical reactions in nature lead to stable isotope variations in part because diffusivities and reaction rates are mass-dependent. For crystals grown from aqueous solution, there is no general theory that relates reaction rate to mass, but the contribution of isotope-specific reaction rates to the net isotope composition of a mineral must be related to processes occurring at the mineral-fluid interface.

Laboratory experiments have shown that the Ca isotope composition ($\delta^{44}Ca$) of calcite precipitated from aqueous solution varies considerably (up to 1.5‰) and correlates with the crystal growth rate (*R*). Generally, inorganic calcite precipitation experiments yield calcite crystals that are enriched in the light isotope of Ca relative to the parent solution. The degree of light isotope enrichment correlates with Sr/Ca in calcite. These observations indicate that variations in $\delta^{44}Ca$ in calcite reflect a mass dependence on reaction rate coefficients (*k*) and that the physical process responsible for mass discrimination is also responsible for trace element discrimination. We postulate that dehydration/rehydration kinetics of Ca^{2+} and Sr^{2+} and/or the presence of impurities on the mineral surface are controlling the kinetic isotope and trace element effects. If true, the presence of other ions (e.g. NH_4^+) in solution should perturb the stability of the hydration shell of Ca^{2+} and Sr^{2+} and also interfere with their incorporation into the mineral lattice.

We present results from inorganic calcite precipitation experiments using two solutions that differ in ionic strength (*I*=0.095 vs. *I*=0.485 mol/l). In low ionic strength experiments, we observe correlations between $\delta^{44}Ca$, Sr/Ca and *R* that are in excellent agreement with results from a previous study that used a similar parent solution composition (Tang *et al.*, *GCA*, 2008). In our initial experiments at high ionic strength, values of $\delta^{44}Ca$ vs. *R* and Sr/Ca vs. *R* lie off the previous trends, but $\delta^{44}Ca$ and Sr/Ca co-vary such that $\delta^{44}Ca$ vs. Sr/Ca is relatively independent of solution composition. Additional experiments are underway and results will be discussed in the context of molecular-scale processes - and their liquid composition-dependence – controlling isotopic and trace element incorporation into minerals.