

s11.m1.o3 **Crystal-chemistry of the Si-P replacement in minerals.** F. Brunet¹, C. Chopin¹, G. Chazot² and R. Miletich³, ¹Lab. de Géologie, ENS-CNRS, Paris (France), ²Lab. de Géologie, Univ. Blaise Pascal, Clermont-Fd (France), ³Lab. for Crystallography, ETHZ, Zürich (Switzerland)

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The ionic radius difference between Al³⁺ and Si⁴⁺ and between P⁵⁺ and Si⁴⁺ is very similar. Although there is plethora of examples of aluminum-substituted silicates, wide P⁵⁺-Si⁴⁺ replacements are very much less documented in nature. Several reasons can be invoked: low abundance of P in the Earth, supremacy of apatite, Ca₅(PO₄)₃(OH,F), that tends to concentrate all the available phosphorus and/or a crystal-chemical control. Actually, all these factors are likely to operate.

On a crystallographic point of view, all phosphate minerals are orthophosphates and one could therefore expect that P only enters orthosilicate structures. Phosphate-silicate isomorphism is common (e.g. berlinite-quartz or xenotime-zircon) but does not necessarily imply mutual solubility. Some rare silico-phosphate minerals also occur in nature (e.g. harrisonite, ideally, Ca(Fe,Mg)₆(SiO₄)₂(PO₄)₂, or attakolite, CaMn(Al,Fe)₄(HSiO₄)(PO₄)₃(OH)₄). Among the major silicates, quartz although isostructural to berlinite, AlPO₄, is always devoid of phosphorus. Natural olivine and garnets contain minor amounts of phosphorus (tenths of weight % P₂O₅ at most). Actually, phosphoran olivine reported in meteorites and from two terrestrial occurrences can incorporate up to 6 weight % phosphorus oxide. Synthetic garnets grown at 3 GPa, 850°C display B₂O₅ content of 2 wt%. It should be noted that in these two silicate structures, SiO₄ tetrahedra are isolated what could potentially favor phosphorus introduction. On the other hand, in feldspars, SiO₄ tetrahedra are highly polymerized, and B₂O₅ contents as high as 1.2 weight % have been reported. Even much higher B₂O₅ contents were analysed in synthetic feldspars.

In the apatite and ellenbergerite structures, the situation is totally different since they represent the only naturally occurring complete phosphate-to-silicate series. What is then the singularity of these two structures?

In addition to its stability in almost all geological contexts, the apatite structure displays an enormous chemical variability that makes it a good candidate for nuclear waste confining material.

Contrary to apatite both ellenbergerite phosphate and silicate endmembers are very rare minerals. With a dense structure, based on chains of face-sharing octahedra, ellenbergerite is restricted to high or very-high pressure environments. Therefore, in the case of ellenbergerite, pressure seems to be the factor that controls the P⁵⁺-Si⁴⁺ replacement.

s11.m1.o4 **Harmonic and anharmonic aspects of the dynamics of silica polymorphs at extreme temperatures.** E. Bourova¹, S. C. Parker², P. Richet¹. ¹Institut de Physique du Globe de Paris, France ²University of Bath, U.K.

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The polymorphs of SiO₂ attract great attention because of their considerable importance in mineralogy and geophysics. Of particular interest are the mechanisms of phase transitions and the behaviour of these polymorphs at high temperatures and pressures which are not fully understood.

Some of the specific areas in need of more work are: (1) the mechanisms of the high temperature anomalous volumetric changes in the important silica polymorphs, quartz and cristobalite and (2) the detailed dynamical behaviour at the atomic scale.

Furthermore, at low temperatures, the nature of excess vibrational contribution in specific heat C_p is also still discussed.

Therefore, silica represents a challenging object for numerical simulation. There are also other reasons to study silica using computational approach: corresponding structures are well defined; a lot of experimental data on its behaviour is available to test the models; elaborated potential models of ion interactions in SiO₂ work well under normal conditions.

We have studied anharmonic aspects of high temperature dynamics of polymorphs of silica, such as α-β transition in cristobalite, and volume decrease in β-phases at very high temperatures. To achieve this goal, we used the molecular dynamics code DLPOLY_2.0¹ and the lattice dynamics code PARAPOCS²

The primary effect of the anharmonic interactions on the phonon frequencies can be estimated by comparing the changes in the phonon spectra at different temperatures obtained using quasi-harmonic approximation (PARAPOCS). Next, we have applied principal mode analysis of molecular dynamics trajectory of cristobalite at different temperatures. From combination of obtained apply principal mode analysis results and PARAPOCS simulations, we can be able to estimate this anharmonicity. A similar approach was also applied at low temperature, and we present here a new approach for investigating the low temperature vibrational anomalies.

[1] Forester T. R. and W. Smith, The DL_POLY_2 user manual. Version 2.11, CCLRC, Daresbury Laboratory, Daresbury, 1998

[2] Parker S.C. and G.D. Price, Computer modelling of phase transitions in minerals, *Advances in Solid - State Chemistry*, v.1, 295-327, 1989.