Experimental evidence of six-fold oxygen coordination for phosphorus and XANES calculations

A.-M. Flank¹, N. Trcera¹, F. Brunet², J.-P. Itié¹, T. Irifune³, P. Lagarde¹

1. Synchrotron Soleil, L’Orme des Merisiers, BP 48, 91192 Gif sur Yvette, France
2. Laboratoire de Géologie, CNRS-ENS-UMR8538, 24 rue Lhomond, 75005 Paris, France
3. Geodynamics Research Center, Ehime University, Matsuyama 790-8577, Japan

Abstract. Phosphorus, a group V element, has always been found so far in minerals, biological systems and synthetic compounds with an oxygen coordination number of four (i.e., PO₄ groups). We demonstrate here using phosphorus K-edge XANES spectroscopy that this element can also adopt a six-fold oxygen coordination (i.e., PO₆ groups). This new coordination was achieved in AlPO₄ doped SiO₂ stishovite synthesized at 18 GPa and 1873 K and quenched down to ambient conditions. The well-crystallized P-bearing stishovite grains (up to 100µm diameter) were embedded in the back-transformation products of high pressure form of AlPO₄ matrix. They were identified by elemental mapping (µ-XRF). µ-XANES spectra collected at the Si and P K edges in the Si rich region with a very low concentration of P present striking resemblance, Si itself being characteristic of pure stishovite. We can therefore infer that phosphorus in the corresponding stishovite crystal is involved in an octahedral coordination made of six oxygen atoms. First principle XANES calculations using a plane-wave density functional formalism with core-hole effects treated in a supercell approach at the P K edge for a P atom substituting an Si one in the stishovite structure confirm this assertion. This result shows that in the lower-mantle where all silicon is six-fold coordinated, phosphorus has the crystal-chemical ability to remain incorporated into silicate structures.

1. Introduction
Pressure-induced solid-solid phase transitions are often characterized by an increase of the coordination number. For example, transformation from a tetrahedral to an octahedral oxygen coordination is well known for the silica polymorphs where SiO₄ turns above 8GPa into SiO₆ in the stishovite form (rutile like structure), a high-pressure dense silicate structure of primary geophysical importance [1].

Furthermore with a mantle abundance below 0.25 wt%, phosphorus has been shown to be mainly hosted by silicates (e.g., olivine) in the Earth’s upper-mantle, and is known to partly replace tetrahedral silicon in rock forming silicates[2 and references therein]. Although it is of primary importance for phosphorus geochemistry in the deep earth, there is no data about the possibility of such replacement in silicates where silicon stands in an octahedral configuration. First principle XANES calculations tested at the silicon and phosphorus K edges on reference compounds, and
applied to a P atom substituting an Si one in the stishovite structure are presented which confirm the conclusions of reference [2].

2. Experimental and calculation methods
A homogeneous mixture (2 to 1 molar proportion) of amorphous silica (SiO$_2$) and AlPO$_4$ (berlinite form), respectively, was held at 18 GPa, 1873 K for 7 hours in a split-sphere multi-anvil (2000 tons) using WC anvils of 5-mm-truncation edge-length. After experiment, the sample is embedded in a P-free epoxy, cut and polished. Phase identification was performed using a micro-focused X-ray diffractometer equipped with a rotating Cu anode. Energy dispersive electron spectrometry (FE-SEM EDS) analyses of the experimental product were made using synthetic AlPO$_4$ – berlinite as P and Al standards and SiO$_2$ as a Si standard.

The run product was further characterized using synchrotron radiation (absorption and fluorescence) on the LUCIA beamline while it was located at the Swiss Light Source [3], (PSI-SLS and SOLEIL). Elemental mapping has been obtained by synchrotron X-ray fluorescence measurement. Thanks to the focusing optic of the beamline (two mirrors in the Kirkpatrick-Baez configuration) the spot size was smaller than 6 x 7 µm$^2$ (FWHM). The counting rate on each image has been normalized to the incident photon flux outgoing from the double Si (111) crystal monochromator set to 2200 eV (above the phosphorus K-edge), and from the dead-time of the silicon drift diode fluorescence counter. These counting rates have not been corrected from self-absorption effects because no elemental concentrations were intended to be extracted from this mapping. X-ray absorption measurements have also been done using the same experimental set-up.

The method used to calculate the XANES spectra of model compounds is a self-consistent full-potential approach based on the Density Functional Theory (DFT) in the Local Density Approximation (LDA): it uses a plane wave basis set, norm-conserving Troullier-Martins pseudopotentials and periodic boundary conditions. Reciprocal-space integrations are performed using a Monkhorst-Pack k-point grid. All-electron wave functions are reconstructed using the Projector Augmented Wave method and the cross-section is computed as a continued fraction (see [4-5] for more details about the calculation). The calculations were performed at the Si K edge for quartz and stishovite and at the P K edge for berlinite. Another calculation was performed at the P K edge for stishovite where the absorbing silicon atom has been substituted by an absorbing P atom. The pseudopotentials of the absorbing atoms were obtained by considering only one 1s electron on their electronic configuration. For all the calculations, the self-consistent potential was obtained in the LDA as formulated by Ceperley and Alder [6] with a cut-off energy of 90 Ry for the plane-wave expansion, and a 1x1x1 k-point grid. The cross section was calculated using a 3x3x3 k-point grid for quartz and stishovite and 2x2x2 k-point grid for berlinite. The continued fraction is calculated with a constant broadening parameter of 0.5 eV for all the calculations. As periodic boundary conditions are used, the core-hole electron interaction is taken into account in a supercell approach that permits to isolate the absorbing atom. Convergence is reached for the following size of supercells: 2x2x2 for quartz, 2x2x3 for stishovite and 2x2x1 for berlinite.

In order to highlight the possible influence of the Si substitution by a P atom in stishovite, the mineral structure was relaxed using the first principles calculations based on the DFT-LDA, keeping fixed the size of the supercell whereas all atomic positions are relaxed. The relaxation was performed using plane wave basis set, norm-conserving Troullier-Martins pseudopotentials, periodical boundary condition and a 2x2x2 k-point grid and a cut-off energy of 100 Ry.

3. Results and discussion

3.1 XANES calculations for crystalline materials
In figure 1 Si K edge XANES spectra for Si 4-fold coordinated to O in quartz and 6-fold coordinated in stishovite [7] are presented. This XANES data can serve as fingerprints of the local structural
environment of the elements of interest: the XANES of phosphorus (figure 2) in AlPO₄ (berlinite quartz homeotype family) characteristic of P in tetrahedral coordination is nearly identical to that of tetrahedral silicon in quartz, while it clearly differs from that of octahedral silicon, in stishovite. Moreover, a positive energy shift of a few eVs between the leading edges appears in going from quartz to stishovite. Corresponding XANES calculations are also presented in these figures which show a good agreement with experiment.

Figure 1. XANES measurements beyond the silicon K-edge, in model compounds (black curves) with end-member compositions compared to the results of the calculations (red line for quartz where Si is 4-fold coordinated, green line for stishovite where Si is 6-fold coordinated).

Figure 2. XANES measurements beyond the phosphorus K-edge, in the model compound AlPO₄ (black curve) (P 4-fold coordinated), compared to the results of the calculation (green curve).

3.2 P hosted in stishovite
The experimental product recovered at ambient conditions (figure 3), is composed of SiO₂-stishovite containing 0.99 (0.09) wt% P₂O₅ and 1.37 (0.11) wt% Al₂O₃ (numbers in parentheses represent 1 sigma error based on 96 analyses) along with the back-transformation products of high-pressure form of AlPO₄. Beside stishovite, X-ray diffraction indicates that the low-cristobalite form of AlPO₄ crystallized along with an unidentified phase with prominent diffraction lines at 4.43, 3.91, and 2.59 Å. Well crystallized P-bearing stishovite grains (up to 100µm across) coexist with smaller AlPO₄ grains (a few micrometers) (figure 3a). The spatial distribution of Al, Si and P was followed by µ-XRF (figure 3 b-d), and XANES at the P, Si and Al K edges were collected on two points of interest POI1 and POI2, corresponding respectively to the stishovite (high silicon content) and AlPO₄ (regions with high and similar Al and P content) grains.
Figure 3 Spatial distribution of aluminium, silicon and phosphorus determined from synchrotron X-ray fluorescence. (a) Optical microscope image collected in reflection mode. The horn-shape sample area corresponds to the very bottom of the platinum container in the vicinity of the W-Re thermocouple. Stishovite grains occur as faceted crystals less than 50 µm across. They are easily identified by their high silicon content on the silicon map (POI1 area). Phosphorus is present in the POI1 area but in very small amount. AlPO₄ grains, of quench origin, are poorly crystalline and display a much lower optical reflectivity. The frame (dashed line) outlines the area investigated by x-ray fluorescence. (b) Aluminium spatial distribution. (c) Silicon map. (d) Phosphorus map.

The spectra of phosphorus and silicon collected on POI1, i.e., the region where phosphorus is a minor element in stishovite microcrystals, are displayed in figure 4. There is a striking resemblance between the XANES of phosphorus in POI1 and that of silicon in pure stishovite. They both display a positive energy shift with respect to their tetrahedral counterparts (quartz or berlinite): 2.4 eV for silicon and 2 eV for phosphorus. We can therefore infer that phosphorus in the corresponding stishovite crystal is involved in an octahedral coordination made of six O atoms.

The phosphorus K-edge in POI2 (AlPO₄ composition) and in pure AlPO₄ berlinite are displayed in figure 5. The spectrum measured at POI2 displays the main spectral characteristics of phosphorus in four-fold oxygen coordination, as found in AlPO₄-berlinite, i.e., an intense white line and a sharp resonance located at 2172 eV. The fine structures in between appear to be modified in the POI2 spectrum. This could be due to a modification of the Al site as it is expected for an InPO₄ structure where the In (Al) site is in an octahedral configuration. This structure becomes stable at high pressure and high temperature for most of the berlinites [8]. Furthermore compared to AlPO₄, the edge is located at the same energy position. Therefore it can be concluded that phosphorus in POI2 is in a tetrahedral oxygen site.

To confirm this “fingerprints” assumptions, we did calculations at the P K edge on the stishovite crystal, replacing one silicon atom by a P one. Results are presented in figure 6. With a relaxation of the structure as described previously, the agreement with the experiment is improved.
4. Conclusion

In this study, we report compelling evidence of octahedral phosphorus surrounded by oxygen. The synthesis of compounds containing phosphorus surrounded by 6 oxygen atoms in an octahedral configuration has remained a challenge. This coordination number was attained by incorporating phosphorus as a minor element in SiO₂-stishovite. In the lower mantle where all silicon is six-fold coordinated, we show here that phosphorus has the crystal-chemical ability to remain incorporated into silicate structures. Beyond the pure crystal-chemical aspects, the experimental evidence, reported here, of six-fold coordination for phosphorus incorporated as minor element in a dense silicate structure is also particularly relevant to phosphorus geochemistry in the deep Earth. There are experimental and natural evidences that phosphorus dissolves into silicates at the pressures and temperatures of the upper-mantle [2]. From our study, even a dense silicate structure such as the rutile-type can host, under six-fold coordination, phosphorus in amounts exceeding its chondritic abundance. The relatively high P₂O₅ content analyzed in decompression products of Ca-perovskite (between 0.1 and 0.5 wt% P₂O₅; [9]) included in a lower-mantle diamond suggests that significant amount of this element can be brought by the down-going slab to the top of the lower mantle.

Figure 4 XANES measurements beyond the silicon and the phosphorus K-edges in POI1; phosphorus and silicon spectra have been vertically shifted for the sake of clarity. The corresponding energy scales are on top of the diagram for phosphorus K-edge and at the bottom for the silicon K-edge. The energy span of each spectrum is the same. The spectra are normalized.

Figure 5 XANES measurements beyond the phosphorus K-edge for P in POI2 compared to the spectrum of P in berlinite (tetrahedral oxygen environment). The spectra are normalized.
This six-coordinated phosphorus in stishovite is also confirmed clearly by recent $^{31}$P and $^{27}$Al Nuclear Magnetic Resonance spectroscopy in samples synthesized by methods similar to those reported here [10].

Acknowledgments

We are grateful to the machine and beamline groups at SLS-PSI whose outstanding efforts have made these experiments possible. Authors wish to acknowledge Delphine Cabaret for her help in the theoretical part of this work, and for giving us an access to her code. The theoretical part of this work was supported by the French computational institute of Orsay (Institut du Développement et des Ressources en Informatique Scientifique) under project Nos. 92015.

References

[1] Yagi T. and Akimoto S. (1976) Tectonophysics 35, 259-270.
[2] Brunet F., Flank A.-M., Itié J.P., Irifune T., Lagarde P. (2007), American Mineralogist, 92, 989-993.
[3] Flank A.-M., Cauchon G., Lagarde P., Bac S., Janousch M., Wetter R., Dubuisson J.-M., Langlois F., Idir M., Moreno T., and Vantelon D. (2006) Nuclear Instrumental Methods B, 246, 269-274.
[4] Taillefumier M, Cabaret D, Flank A-M, Mauri F (2002) Phys Rev B 66:195107(1–8)
[5] Cabaret D, Gaudry E, Taillefumier M, Sainctavit P., Mauri F (2005) Physica Scripta T115:131-133
[6] Ceperley D.M. and Alder B.J (1980), Phys.Rev. Lett. 45, 566
[7] Andrault D., Neuville D.R., Flank A.-M., and Wang Y. (1998) American Mineralogist, 83, 1045-1053.
[8] Badro J., Itié J.P. and Polian A. (1998), European Physical Journal B 1, 265-268
[9] Joswig W., Stachel T., Harris J.W., Baur W.H., and Brey G.P. (1999) Earth and Planetary Science Letters, 173, 1-6.
[10] Stebbins J.F., Kim N., Brunet F., Irifune T (2009) Eur. J. Mineral. (2009), 21, 667-671