Experimental evidence of sixfold oxygen coordination for phosphorus

FABRICE BRUNET,1,* ANNE-MARIE FLANK,2 JEAN-PAUL ITIÉ,2 TETSUO IRIFUNE,3 AND PIERRE LAGARDE2

1Laboratoire de Géologie, CNRS-ENS—UMR8538, 24 rue Lhomond, 75005 Paris, France
2Synchrotron-SOLEIL, BP48, 91192 Gif s/Yvette, France
3Geodynamics 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 using phosphorus K-edge XANES spectroscopy that this element can also adopt a sixfold oxygen coordination (i.e., PO6 groups). This new coordination was achieved in phosphorus-doped (1 wt% P2O5 level) SiO2-stishovite synthesized at 18 GPa and 1873 K and quenched to ambient conditions. This change of phosphorus coordination at high pressure within a dense silicate structure is particularly relevant to phosphorus mineralogy (and geochemistry) in the deep Earth. 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, in the fourfold-coordinated silicon sites. In the lower mantle where all silicon is sixfold coordinated, we show here that phosphorus has the crystal-chemical ability to remain incorporated into silicate structures.

Keywords: Phosphorus, coordination, XANES, stishovite, berlinite, lower mantle

INTRODUCTION

Pressure-induced transformation from a tetrahedral to an octahedral oxygen coordination is well known for the silica polymorphs where SiO4 turns into SiO6 in the stishovite form (Stishov and Popova 1961; Chao et al. 1962). It is also observed for GaO4 in GaAsO4 (Badro et al. 1997a) and GaPO4 (Badro et al. 1998), for AsO4 in GaAsO4 (Badro et al. 1998) and AlAsO4 (Badro et al. 1997b) as well as for GeO4 in GeO2 quartz or in GeO2 glasses (Itié et al. 1989). However, up to now, this transformation has never been observed for the PO4 tetrahedron. Although the electronic structure of phosphorus would allow higher coordination, phosphorus adopts a fourfold coordination, especially when surrounded by oxygen atoms. Sixfold coordination can be achieved with halogens as first neighbors (Wells 1975) or in some high-pressure forms of semiconductors like InP (Menoni and Spain 1987) or GaP (Baublitz and Ruoff 1982). The PO4 tetrahedral unit appears extremely stable even under the effect of high pressures as compared to GaO4, AsO4, GeO4, or SiO4 tetrahedra. Molecular dynamic simulations have shown that phosphorus remains in a tetrahedral configuration to at least 80 GPa (Tse and Klug 1992). The remarkable stability of the PO4 configuration is at the origin of the reversibility of the phase transformation observed for AlPO4 under pressure (Kruger and Jeanloz 1990). The synthesis of compounds containing phosphorus surrounded by 6 oxygen atoms in an octahedral configuration has remained a challenge. In this study, we report compelling evidence of octahedral phosphorus. This coordination number was attained by incorporating phosphorus as a minor element in SiO2-stishovite, a high-pressure dense silicate structure of primary geophysical importance.

EXPERIMENTAL METHODS

A homogeneous mixture (2 to 1 molar proportion) of amorphous silica (SiO2) and AlPO4 (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 (see Brunet et al. 2006 for details of the cell assembly). After recovery, the sample was 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 AlPO4-berlinite as P and Al standards and quartz as Si standard.

The run product was further characterized using synchrotron radiation (absorption and fluorescence) on the LUCIA beamline (Flank et al. 2006, 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 µm (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 for 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.

RESULTS AND DISCUSSION

The experimental product recovered at ambient conditions (Fig. 1), 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 (Kruger and Jeanloz 1990). Besides stishovite, X-ray diffraction indicates that the low-cristobalite form of AlPO4 has crystallized along with an unidentified phase with prominent diffraction lines at 4.43, 3.91, and 2.59 Å. Field-effect SEM characterization of the run product shows well-crystallized P-bearing stishovite grains (up to 100 µm across). AlPO4 grains are smaller (a few micrometers) and display a crumbled morphology, which could suggest (partial) back-transformation upon quench (Fig. 1). X-ray