Direct EXAFS evidence for incorporation of As$^{5+}$ in the tetrahedral site of natural andraditic garnet

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ABSTRACT

Exceptionally high-quality X-ray absorption spectroscopy (XAS) spectra of the As K-edge measured on a garnet from the Central Oslo Rift (Jamtveit et al. 1993) are presented and interpreted. The best fit to the extended X-ray absorption fine structure (EXAFS) spectrum indicates that arsenic occurs predominantly as As$^{5+}$ in the tetrahedral Si$^{4+}$ site. The first shell As-O bond lengths of 1.69 Å are identical to those observed for As$^{5+}$ in sodium arsenate and the edge position of 11872 eV is also characteristic of As$^{5+}$. Determination of oxidized As within the structure places an important constraint on fluid chemistry, but perhaps even more importantly, EXAFS fitting of outer shells (As-Ca 3.07, 3.75, 5.71, 6.11 Å; As-Fe/Al 3.47, 5.35 Å; As-Si 3.88, 5.60, 5.91 Å) in this high-quality data set gives unequivocal evidence that AsO$_4^{2-}$ substitutes for SiO$_4^{4-}$ in the garnet tetrahedral site. This, to the best of our knowledge, is the first such XAS study yielding direct evidence, through outer shell fitting, for both the coordination environment and oxidation state of arsenic within (as opposed to sorbed onto) a silicate mineral.

Keywords: Arsenic, garnet, XAS, EXAFS, oxidation state, coordination

INTRODUCTION

Despite extensive interest, reflected in numerous X-ray absorption spectroscopy (XAS) studies of the solid phase speciation of arsenic (Morin and Calas 2006; Coker et al. 2006; Pascua et al. 2005; Canes et al. 2005; Savage et al. 2005; Thoral et al. 2005; Sherman and Randall 2003; Bostick and Fendorf 2003; Tournassat et al. 2002; Farquhar et al. 2002), there is a paucity of XAS data on the oxidation state and especially the coordination environment of arsenic in, as opposed to sorbed onto, silicate minerals. Such data are potentially invaluable to the interpretation of XAS spectra of soils and sediments in which arsenic may occur either within the bulk structure or sorbed onto several different phases as a range of different surface complexes, each with As in a unique coordination environment (Rowland et al. 2005; Gault et al. 2003a, 2003b, 2005; Hudson-Edwards et al. 2005; Paktunc et al. 2003, 2004; Morin et al. 2003; La Force et al. 2000).

As$^{5+}$ substitution for tetrahedral silica in silicate minerals was postulated over 40 years ago (Esson et al. 1965) as one of several ways to explain the presence of trace arsenic in sulfide-poor rocks, but previously this coordination environment for As has never been directly observed via XAS. The paucity in data stems from the fact that arsenic is a major component of only a small number of mostly unusual silicate minerals. These include meidaite, (Mn,Ca)$_6$(V,As)Si$_4$O$_{10}$(OH)$_2$ (Gramaccioli et al. 1981), and ardennite, (Mn,Ca,Mg)$_6$(Al,Mg,Fe)$_6$(V,As)Si$_4$O$_{10}$(OH)$_2$ (Donnay and Allmann 1968), where As$^{5+}$ substitutes for V$^{4+}$ in a tetrahedral site in both structures, and filatovite, K[(Al,Zn)$_2$(As,Si)$_3$O$_{10}$] (Filatov et al. 2004), in which As$^{5+}$ substitutes for Si$^{4+}$ and in which (As,Si)O$_4$ tetrahedra are surrounded by (Al,Zn)O$_4$ tetrahedra and vice versa. Incorporation of As$^{5+}$ into the feldspar-like tetrahedral framework is possible as charge is balanced through the incorporation of Zn$^{2+}$ or Al$^{3+}$ into adjacent tetrahedral sites.

Only recently has the oxidation state of arsenic in a small number of silicate minerals been determined, but problems with data quality due to the extremely low concentrations of As have hindered the determination of the full coordination environment. Pascua et al. (2005) obtained first shell information, showing that most (~70 to 90%) of the arsenic present in hydrothermally precipitated phases from northwestern Japan was As$^{5+}$. As$^{5+}$ was indeed also found to be present and was postulated to be incorporated into amorphous silica and perhaps into the smectite stevensite, but the mode of incorporation of oxidized As$^{5+}$ could not be unambiguously determined. Hattori et al. (2005) analyzed As in forearc mantle serpentinites and found most to be present as oxidized As$^{5+}$, with As$^{5+}$ representing over 80% of the arsenic inventory in some samples. They concluded that at least some of this As$^{5+}$ was likely to be structurally incorporated within antigorite, substituting for Si$^{4+}$ and maintaining charge balance via a coupled substitution of the form:

$$\text{Al}^{3+} + \text{As}^{5+} \leftrightarrow 2 \text{Si}^{4+}$$

Neither study was able to obtain information beyond the first shell and so assignment of As$^{5+}$ to the tetrahedral site, although likely, was not directly determined. Indeed, Hattori et al. (2005) reported a coordination number for arsenic of 5.2; but of course with As concentrations as low as 6 ppm it is understandable that spectra were difficult to interpret. Therefore, it is clear that analy-