

## **Direct EXAFS evidence for incorporation of As<sup>5+</sup> 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<sup>5+</sup> in the tetrahedral Si<sup>4+</sup> site. The first shell As-O bond lengths of 1.69 Å are identical to those observed for As<sup>5+</sup>-O in sodium arsenate and the edge position of 11872 eV is also characteristic of As<sup>5+</sup>. 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<sub>4</sub><sup>3-</sup> substitutes for SiO<sub>4</sub><sup>4-</sup> in the garnet tetrahedral site. This is, to the best of our knowledge, 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