

Reduction of Antimony by nanoparticulate Fe₃O₄ and FeS

R. KIRSCH^{1,2}, A.C. SCHEINOST^{1*}, A. ROSSBERG¹,
D. BANERJEE¹ AND L. CHARLET²

¹Inst. of Radiochemistry, FZD, Dresden, Germany, and ROBL at ESRF, BP220, 38043 Grenoble, France

(*correspondence: scheinost@esrf.fr)

²LGIT, BP 53, 38041 Grenoble, France

Antimony finds a wide range of industrial applications, e.g. in flame retardants, brake pads and as a lead-alloy in storage batteries and ammunition and is widely distributed in the environment. Sb may occur in several oxidation states (-III, 0, III, V). Under oxic conditions, Sb⁰ oxidizes prevalently to Sb^V, forming the anionic species Sb(OH)₆⁻ which is strongly sorbed by Fe oxides [1]. In contrast, Sb^{III} forms an uncharged complex Sb(OH)₃(aq), which is more mobile. Under anoxic conditions, Sb^V and Sb^{III} may be reduced by Fe^{II}-bearing minerals. Magnetite (Fe^{II}Fe^{III}₂O₄) and mackinawite (FeS) have been shown to reduce e.g. Se [2], As [3], and Pu [4]. We therefore investigated the reaction of Sb^{III} and Sb^V with these two minerals at approximately 1ppm O₂ (v/v) using Sb-K XAS.

When Sb^{III} was reacted with magnetite at pH 4.7 to 7.6 during 1 h to 67 d, the oxidation state was stable and only one Sb species was identified by EXAFS. Sb^{III} is coordinated with 4 to 5 iron atoms at a distance of 3.6 Å. FEFF Monte Carlo simulations revealed formation of a highly ordered surface complex on the {111} faces of magnetite. The trigonal pyramidal SbO₃ units occupy positions of Fe^{III} tetrahedra, that would be ideally coordinated to six FeO₆ octahedra via corner-sharing. The experimental Fe coordination numbers below six suggest that Sb occupies positions near edges of the {111} faces. When Sb^V was reacted with magnetite, reduction to Sb^{III} increased linearly between pH 4.5 and 6.5, with little influence of reaction time. The Sb^{III} produced by the surface reaction formed the same surface complex as after direct addition of Sb^{III}.

In the presence of mackinawite, Sb^V was completely reduced to Sb^{III} within 30 d and in the pH range 4.3 - 8.4. The local structure shows Sb^{III} surrounded by three sulfur atoms at a distance of 2.5 Å as in Sb₂S₃. The lack of more distant atomic shells suggests a highly disordered structure. Again the resulting surface complex is the same as after direct addition of Sb^{III}. Cryo-XPS measurements of shock-frozen samples show that the S 2p spectra remain unchanged before and after Sb^V reduction, while a Fe^{III}-shoulder emerged in the Fe 2p spectra after reduction, indicating that Sb^V was reduced by Fe^{II} and not by S. In no case, reduction to an oxidation state below III was observed.

[1] Scheinost *et al.* (2006) *Geochim. Cosmochim. Acta* **70**, 3299-3312. [2] Scheinost & Charlet (2008) *Environ. Sci. Technol.* online. [3] Gallegos *et al.* (2007) *Environ. Sci. Technol.* **41**, 7781-7786. [4] Powell *et al.* (2004) *Environ. Sci. Technol.* **38**, 6016-6024.

Olivine morphology and the origin of main group pallasites

S.A. KISSIN

Dept. of Geology, Lakehead Univ., Thunder Bay, ON P7B 5E1 Canada (sakissin@lakeheadu.ca)

Introduction

The main group pallasites (PMG) were defined by Scott [1] with later modifications by Wasson & Choi [2], who defined anomalous members with anomalous metal compositions (PMGam) and those with anomalous olivine compositions (PMGas) as well as anomalous metal compositions. Shapes of olivine crystals have been investigated in detail by Scott [3] and Buseck [4] whose results are in agreement as to the morphologies of the olivine crystals of the pallasites. The shapes of macrophenocrysts range from rounded to highly angular, although microphenocrysts are rounded, with few exceptions.

Relation between Metal Composition and Olivine Morphology

Examination of the data available reveals that there are 18 PMG, 5 PMGam and 3 PMGas whose compositions and olivine morphologies are both well characterized. Of the PMG, 17 have angular olivines and 1 has rounded olivines. Of the 8 anomalous pallasites, 5 have rounded olivines and 3 angular ones. Thus, there is an apparent relationship between olivine morphology and chemical classification of PMG

Discussion

Olivine morphology clearly has a bearing on the genesis of pallasites. Wasson & Choi [2] demonstrated that the metal compositions of PMG members can be produced by a fractional crystallization model based the same system as that which produced the group IIIAB iron meteorites. This model is consistent with the hypothesis that the pallasites represent the core-mantle interface in a parent-body. Scott [5], however, has summarized some of the difficulties with this model. However, textural evidence clearly indicates that PMG have been subject to shock disruption followed by injection of metal. The rate of rounding of olivines in molten metal has been shown to be very rapid [6] indicating that the rounded olivines of the PMG members have experienced a history different from that of those with angular olivines.

[1] Scott (1977) *GCA* **41**, 349-360. [2] Wasson & Choi (2003) *GCA* **67**, 3079-3096. [3] Scott (1977) *GCA* **41**, 693-710. [4] Buseck (1977) *GCA* **41**, 711-740. [5] Scott (2007) *LPS* **38**, Abstr.2284. [6] Saiki *et al.* (2003) *MAPS* **38**, 427-444.