Structural investigation of platinum solubility in silicate glasses

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INTRODUCTION

Platinum is a strategic element that is relatively insoluble in oxide glasses (usually less than a few parts per million). However, for some silicate melts containing large amounts of alkaline-earth elements, it is possible to dissolve larger amounts of Pt (i.e., >10 ppm). The Pt found in some synthetic silicate glasses is derived from corrosion of Pt-crucibles by the melt (Fairbairn and Schairer 1952; Ginther 1971; Higby et al. 1990) which imparts a yellowish color to glasses richest in Pt. For example, in low-silica calcium aluminosilicate glasses/melts prepared at one atmosphere pressure, enhanced Pt solubility can be observed (Dablé 1996; Azif et al. 1996; Amossé et al., unpublished manuscript) and may be as high as ~200 ppm as observed here (Table 1). Based on indirect solubility and electrochemical measurements, the enhanced solubility of Pt in CAS melts under oxidizing conditions is related to the presence of oxidized valence states of Pt. Depending on the interpretation of experimental solubility data, Pt is thought to be in the +2 (Borisov et al. 1996) or +6 (Dablé 1996) valence state.

High Pt contents (above 100 ppm) are also observed in some oxide glasses used for nuclear waste storage (Kelm and Oser 1991; Pacaud et al. 1991). This Pt is generated by the decay of highly radioactive isotopes after storage for a few years. A better understanding of the structural factors that govern the enhanced solubility of Pt in oxide glasses will help, for instance, to better extract this precious element from nuclear waste glasses.

To explore the structural origin of the enhanced solubility of Pt in CAS melts, we have undertaken an X-ray absorption fine structure (XAFS) spectroscopy study of Pt in various yellowish glasses from the CAS system containing trace amounts (as low as 20 ppm) of Pt. XAFS spectroscopy was used to determine the oxidation state of Pt in these glasses as well as its coordination environment. In addition, bond-valence considerations were used to derive plausible models of the medium-range structural environment around Pt in these glasses. Finally, structural information from this study was correlated with the solubility of Pt in these glasses/melts.

EXPERIMENTAL DETAILS

Glass synthesis

The nomenclature used to represent glass compositions here is Ca_xAl_ySi_2 where x and y represent, respectively, the mol% SiO_2 and Al_2O_3 components in the glass. The glasses were prepared by mixing reagent grade oxides SiO_2, Al_2O_3, and CaCO_3 in the desired amounts (Neuville 1992) (Fig. 1). The powders were slowly decarbonated at 1200 K and melted at 1900 K for 3–4 hours in a Pt crucible. The glasses were quenched from the melts by rapidly cooling the bottom of the crucible in water. The Pt present in the glasses derives directly from corrosion of the Pt-crucibles. In these glasses, the highest Pt contents were found in the most yellow glasses. Chemical analyses are in Table 1.

Pt-model compounds

Various model compounds representative of the coordination chemistry of Pt were investigated, including: metallic Pt, α-PtO_2, Na_2Pt(OH)_6, K_2PtCl_6, and (NH_4)_2PtCl_6 (Bandel et al. 1979; Siegel et al. 1969; Takazawa et al. 1984). Metallic Pt

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