

PGE complexes at superliquidus temperature: Embryos for platinum-group minerals?

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Even though As, Sb, Te, and Bi are mere trace elements in magmatic sulfide melts, minerals of the platinum-group elements (PGE) with these ligands are exceptionally common. Obviously, at subsolidus temperatures, there is a marked chemical preference of the PGE to bond with the chalcogenes and semimetals and form discrete arsenides, antimonides, tellurides, and bismuthinides. The question addressed here is if similar PGE-ligand preferences also exist at supersolidus and superliquidus temperature. Should such proposition be proven correct, we could argue that discrete crystalline PGE-chalcogene and PGE-semimetal phases have their chemical equivalents at superliquidus conditions in the form of PGE-As, Sb, Te, and Bi molecular associations, complexes or even poly-atomic clusters [1]. We could even go as far as proposing that the crystallization of a discrete PGE phase with a specific metal-ligand combination merely reflects the re-organization to larger units, of PGE-ligand molecules or complexes with the same PGE-ligand combination.

Experiments were carried out in an Ir-Pt-As-bearing, monosulfide (mss)-saturated Fe-Cu-S system at 950°C at minimum and maximum sulfur fugacities as bracketed by the Fe-FeS (metal-troilite) and Fe_{1-x}S-S₂ (mss-sulfur) equilibria. Copper was added to expand the two-phase (mss-melt) stability field such that mss grains coexisted with sulfide melt pools sufficiently large for contamination-free laser-ablation analysis. Platinum, Ir, and As were added to the sulfide matrix at the tens of ppm levels. The molecular As/PGE bulk ratios varied from 0, 1, 2, 3 and 5. In charges with high sulfur fugacity, i.e. when all As is present as cation [2], the partition coefficients of Pt, Ir and As are insensitive to the As/PGE atomic bulk ratio. At low sulfur fugacity, in contrast, when all As is dissolved as anions, the mss-sulfide melt partition coefficients of Pt and Ir decrease with increasing atomic As/Pt; D_{Ir} (mss/sulfide melt) slightly and D_{Pt} (mss/sulfide melt) sharply by almost one order of magnitude. The results can only be rationalized if PGE minerals such as IrAs₂ (iridarsenite) or PtAs₂ (sperryllite), and potentially many more discrete PGE phases with rare elements as ligands, have their equivalents at superliquidus temperature in the form of Ir-As, Pt-As etc. molecules, complexes or even poly-atomic clusters [1].

[1] Tredoux *et al.* (1995) *S Afr J Geol*, **98**, 157-167. [2] Helmy *et al.* (2010) *Geochim Cosmochim Acta*, **74**, 6174-6179.

Geochemical roles of thioanions of the heavier metals and metalloids

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Where sulfide replaces oxygen in sedimentary environments, many elements' aqueous geochemistry is altered profoundly. Among first row transition metals, the primary effect is reduction (e.g. Cr^{VI}→Cr^{III}, Mn^{IV}→Mn^{II}, Fe^{III}→Fe^{II}, Cu^{II}→Cu^I). Secondarily (i.e. at higher sulfide concentrations), sulfide complexes can form through replacement of O, N or Cl atoms in first coordination shells of the reduction products. In contrast, for many heavier metals and metalloids, the primary effect is ligand replacement, with reduction occurring secondarily, if at all. Thus thioanions may form with trace elements in their highest oxidation states (e.g. Re^{VII}S₄⁻, Mo^{VI}S₄²⁻, As^VOS₃³⁻, Sb^V₂S₆²⁻). In each of these known cases, the thioanion a) is stabilized at geochemically reasonable sulfide concentrations (10⁻⁶ to 10⁻⁴ M) at near-neutral pH and b) appears not to precipitate a binary sulfide solid phase under conditions ordinarily found in nature.

Owing to experience with first-row transition metals, geochemists have tended to attribute behavior of heavier metals and metalloids in sulfidic waters to reduction rather than ligand exchange. Although the determining role of ligand exchange in Mo's behavior in sulfidic waters has become accepted over the past 15 years, belief in Re's reduction in these waters still prevails. I will present a new, ligand-exchange model for Re's response to sulfide that is analogous to that recently proposed to explain Mo behavior in euxinic waters [1]. The model can explain important features of Re's geochemistry, including its precipitation exclusive of Mo in suboxic environments and its precipitation at a nearly constant ratio to Mo in sulfidic environments.

Because thioanions can act as multidentate, sulfur-donating ligands, they may influence the geochemistry of other trace metals. Both As^{III} and Mo^{VI} thioanions are now known to form extraordinarily stable complexes with coinage metals (Cu, Ag, Au). It can be expected that the same will eventually be demonstrated for thioanions of other elements, especially Sb and Bi.

[1] Helz, G. R.; Bura-Nakić, E.; Mikac, N.; Ciglenečki, I. (2011) *Chem. Geol.* in press.