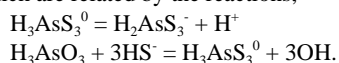


Spectrophotometric study of thioarsenite speciation in high temperature aqueous solutions

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Arsenic sulphides occur commonly in natural waters, especially in hydrothermal systems. For example, in the Rotokawa geothermal system in New Zealand bright yellow and orange precipitations of amorphous arsenic sulphides are observed around near-boiling springs. In addition, the deep fluids have arsenic concentrations up to 3-4 ppm (Krupp and Seward, 1990). The lower temperature hydrothermal chemistry of arsenic also has some relevance to understanding the metabolic processing of arsenic by thermophiles in the near surface environment of hydrothermal systems. Unfortunately, thioarsenite speciation in aqueous solutions is not well determined; there is no agreement in the literature, although there are experimental solubility data, Raman spectroscopic measurements, and theoretical calculations in As-S-H₂O aqueous system. The present study involves the determination of the stabilities and stoichiometry of thioarsenous species in aqueous solutions from 25 to 300°C by means of high temperature uv-vis spectrophotometry. Absorbance measurements were carried out in a flow-through Ti-Pd alloy cell with windows of uv-quality fused silica. Spectra were collected using a Cary 5E double beam spectrophotometer. Solution preparation and handling as well as pH determination were carried out in such a way as to exclude any contact with air and in some cases also without any gaseous phase to avoid losses of H₂S. Rank analysis of the absorbance matrix indicated the presence of the three species in solution, one of which could be ascribed to the HS⁻ ion charge-transfer-to-solvent transition. The other two absorbing species we ascribed to be H₃AsS₃⁰ and H₂AsS₃⁻, which are related by the reactions,



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The relationship between volatile element patterns and chondrule textures in CRs and OCs

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The chemical complementarity between chondrules and matrix has been considered to show that they represent material condensed at different temperatures¹. The nature of the chemical complementarity is, however, different between different meteorites, e.g. Renazzo and Semarkona, and here we show that chemical differences correspond to textural differences that yield insight into the nature and environment of chondrule formation.

Volatile-depleted CR chondrites preserve evidence of extensive volatilization during chondrule formation rapidly followed by incomplete recondensation, onto chondrule rims for moderately volatile elements and in the matrix for the most volatile elements such as S, Ga, Ge etc². The matrix represents a large fraction of CR [31.1% in Renazzo] chondrites and CR chondrules are often irregular in shape and preserve evidence of formation by the agglomeration of smaller droplets in a dust-rich environment.

Ordinary chondrites on the other hand, are less volatile-depleted and contain less matrix [15.6% in Semarkona]. In contrast to CRs, a large fraction of the chondrules are volatile-enriched and volatile elements such as S are concentrated in veneers around chondrules. This indicates that recondensation after chondrule formation was dominantly onto chondrules rather than in the sparse matrix. OC chondrules are typically spherical, but also preserve evidence for having agglomerated together and with their surrounding matrix at temperatures above the glass transition temperature, as they are frequently molded around one another.

We interpret this as evidence that (i) matrix must have been present in the same nebular region as the chondrules when these were still hot, (ii) the first stages of accretion followed chondrule formation rapidly enough that the matrix-chondrule system remained closed, (iii) chondrules had cooled down to lower temperatures in OCs than in CRs when this event took place, which allowed a more complete recondensation. This argues against the x-wind model³ for chondrule formation, according to which volatiles lost from chondrules ought to be decoupled from them. It is consistent, however with the predictions of the shock-wave model⁴.

References

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