

Methylated arsenic-sulfur compounds in ground water

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Arsenic (As) speciation was determined by anion-exchange chromatography-inductively-coupled plasma-mass spectrometry (AEC-ICP-MS) in ground waters from a site impacted by methylated arsenic biocides. Aside from the expected four conventional As species arsenite, arsenate, monomethylarsenate (Me1As(V)) and dimethylarsenate (Me2As(V)), up to 9 additional As species were encountered. Among these, the five major species were the As(III) compound monomethylarsenite Me1As(III), and the four thio-substituted methylated As(V) compounds monomethylmonothioarsenate Me1As(V)-S1, monomethyldithioarsenate Me1As(V)-S2, dimethylmonothioarsenate Me2As(V)-S1 and dimethyldithioarsenate Me2As(V)-S2. All five compounds were identified by retention time matching to synthesized standards, and the last four identifications were additionally confirmed by electrospray-tandem mass spectrometry (ES-MS-MS) in collected AEC fractions. None of these As species have been identified in ambient waters before.

These novel As species not only occurred in most of the collected ground water samples, but usually also collectively constituted a major fraction of the total dissolved As concentration (TDAs) present. Average and maximum (in parentheses) relative concentrations measured (expressed in % of TDAs) were 5.3 (39.0) for Me1As(III), 10.2 (43.1) for Me1As(V)-S1, 2.1 (15.1) for Me1As(V)-S2, 3.1 (10.8) for Me2As(V)-S1 and 1.7 (9.0) for Me2As(V)-S2. The highest fractions of metabolites of the original biocides Me1As(V) and Me2As(V) were found in samples with intermediate TDAs concentrations, i.e. between the original emission site and the edge of the propagation plume, indicating that these novel metabolites play a role in the environmental transport and fate of the As biocides at this site. Although Me2As(V) and its metabolites were generally present at lower concentrations than Me1As(V) and its metabolites (as a result of the emission history), the fraction of dimethylated metabolites was higher on average than that of monomethylated metabolites, indicating that Me2As(V) is more reactive in the observed transformations than Me1As(V).

A preservation study of six selected samples over a period of 24 weeks showed that the novel As species were reasonably stable in unpreserved samples, but had a tendency to convert back to their original precursors, Me1As(V) or Me2As(V), respectively, over time. Cryofreezing on-site generally seemed to yield the best As speciation preservation, but unpreserved samples yielded comparable results. Acidification caused immediate and significant changes in As speciation, and must consequently be avoided for sites where these novel As species are or may be present.

The perovskite – post-perovskite phase transition of CaIrO₃ during experimental deformation: Implications for the D'' layer

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The existence and the seismic properties of the D'' layer have been explained by the occurrence of a MgSiO₃ post-perovskite structure (pPv) that forms at a pressure of approximately 125-130 GPa above the core-mantle boundary. However, the deformation-induced lattice-preferred-orientation (LPO) of the pPv phase is still controversial, since the extremely high pressure precludes the direct use of MgSiO₃ for controlled deformation experiments, and different analogue substances appear to yield different LPO for a given strain field. While diamond-anvil-cell (DAC) experiments with MgGeO₃ indicated (100) and/or (110) slip planes, controlled deformation experiments with CaIrO₃ resulted in a (010) slip plane with a [100] Burgers vector. The difference between both approaches was that the CaIrO₃ experiments were deformed from the start in the pPv field, while the DAC experiments started in the Pv field and crossed the pPv phase boundary during deformation.

In order to see whether the differences in the LPO measurements result from these different conditions, we performed CaIrO₃ deformation experiments in axial compression with the d-DIA multi-anvil press in the Pv stability field and crossing the Pv-pPv stability field boundary during deformation. Experiments with CaIrO₃ Pv were performed at 1450°C and 1GPa with a strain rate varying between 10⁻³-10⁻⁵ s⁻¹. Interestingly, only the high strain rate experiments resulted in a weak texture, thus suggesting diffusion accommodated grain boundary sliding as the dominant deformation mechanism.

For investigating the Pv-pPv phase transition, the temperature was lowered to 1200°C during deformation. The resulting samples consist of a mixture of pPv and metastable Pv. Relict Pv crystals often contain conjugate sets of polysynthetic twins that are oriented at ca. 45° to the axis of greatest shortening. Post-Perovskite appears to nucleate preferentially along these (110) twin planes. LPO measurements of pPv in these samples show an alignment of (100) and (110) perpendicular to the compression direction, similar to the LPOs found in DAC experiments. Thus, we are able to distinguish between deformation- and transformation-induced LPO in pPv.

In the D'' layer both texture types of pPv may occur: the transformation-type LPO in regions where material descends from the Pv stability field, and the deformation-type LPO where horizontal shear flow is dominant. These regions will also have different seismic anisotropy signatures and could be distinguished seismologically.