

## Gold and Silver in hydrothermal fluids and vapors: Insights from *in situ* XAFS spectroscopy

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Our current knowledge of the aqueous complexes transporting gold and silver in ore-forming hydrothermal fluids is limited essentially by bulk solubility measurements, and very few direct data are available about Au and Ag species structures and their interactions with the solvent. Here we present new data on Au and Ag complexing with chloride and sulfide in aqueous solution to 450°C and 1 kbar, obtained by *in situ* X-ray absorption fine structure spectroscopy using a recently designed optical cell [1].

Results show that  $\text{AuCl}_2^-$  is the major  $\text{Au}^{\text{I}}$  species in acidic chloride solutions, in agreement with the available solubility studies. This complex is characterised by a linear geometry and Au-Cl distances of 2.27 Å, and shows no spectroscopically detectable solvation shell. In contrast, the speciation of  $\text{Ag}^{\text{I}}$  in acidic-to-neutral fluids in a wide range of NaCl concentrations (to ~6 m) is dominated by  $\text{AgCl}_3^{2-}$  and  $\text{AgCl}_2^-$  solvated by 1 to 2 water molecules in the 1<sup>st</sup> coordination shell of the silver ion, with average Ag-Cl distances decreasing from ~2.45 Å at 150°C to ~2.35 Å at 450°C. These differences in species structure and solvation are responsible for the contrasting vapor-liquid partitioning of Ag and Au in the  $\text{H}_2\text{O}$ -NaCl system [2].

Results in the system Au-S- $\text{H}_2\text{O}$ -NaOH are consistent with complexes having two S ligands in a linear geometry around Au at 2.29 Å. Our data confirm the formation of the famous  $\text{Au}(\text{HS})_2^-$  complex at pH 4 to 8 [3], but reveal the predominance of new complexes like  $\text{H}_2\text{SAuHS}^0$ ,  $\text{SO}_2\text{AuHS}^0$  or Au-polysulfides at pH<3. These species are likely to be responsible for the enhanced gold transport by acidic S-rich vapor and fluid phases as observed in natural fluid inclusions and model systems [4].

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## Equilibrium iron isotope fractionation at super-high pressures

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Equilibrium iron isotope fractionation at super-high pressures was estimated from the Fe partial phonon density of states (PDOS) obtained in inelastic nuclear resonant X-ray scattering synchrotron radiation experiments using the method established in [1, 2]. Isotope fractionation coefficients (IFC) between metallic iron and ferripericlasite ( $\text{Fe}_x\text{Mg}_{1-x}\text{O}$ ) and ferriperovskite ( $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ ) are presented in Table 1.

Mineral pair	T, K	P, GPa	$\alpha^{57/54}\text{Fe}$ , ‰
$\text{Fe}_{0.25}\text{Mg}_{0.75}\text{O}$ - Fe	2000	0	-0.017
	4000	0	-0.002
	2000	110	0.010
	4000	110	0.001
$\text{Fe}_{0.05}\text{Mg}_{0.95}\text{SiO}_3$ - Fe	2000	0	-0.032
	4000	0	-0.006
$\text{Fe}_{0.4}\text{Mg}_{0.6}\text{SiO}_3$ - Fe	2000	130	0.240
	4000	130	0.062

**Table 1:** Equilibrium iron isotope fractionation between metallic iron and ferripericlasite and ferriperovskite.

The PDOS are taken from [3-5]. The  $\beta$ -factor of perovskite at ambient pressure is computed from Moessbauer data [6]. As it follows from Table 1, the iron IFC change their magnitudes and signs at low-mantle pressures. The  $^{57/54}\text{Fe}$  equilibrium isotope fractionation factor between mantle and core was estimated from the IFC in Table 1. This factor varies from 0.025‰ (at 4000 K) to 0.12‰ (at 2000 K) exceeding significantly 0.02‰ at 2000 K obtained in [7] from Moessbauer-derived IFC [8] at ambient pressure.

This study gives grounds to suggest that the abundance of Earth mantle samples in heavy iron isotopes results from the high-pressure Earth core formation.

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