

Halogens and noble gases subducted into the mantle: constraints from mantle wedge peridotites and olivines in arc lavas

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Findings of subducted halogens and noble gases with seawater and sedimentary pore-fluid signatures in exhumed mantle wedge peridotites and eclogites from the Sanbagawa-metamorphic belt, southwest Japan [1, 2], as well as that of seawater-derived heavy noble gases (Ar, Kr, Xe) in the convecting mantle [3], challenge a popular concept that the water flux into the mantle wedge is controlled only by hydrous minerals in altered oceanic crust and sediment resulting in that subduction volcanism acts as a 'subduction barrier' which efficiently recycles volatile components contained in subducted slabs back to the Earth's surface. To verify whether and how such subduction fluids modify the composition of the mantle beneath subduction zones, we determined noble gas and halogen compositions of mantle wedge peridotites and olivines in arc lavas.

MORB-like ³He/⁴He and halogen ratios of olivines in lavas from the northern Izu-Ogasawara arc and a peridotite from the Horoman alpine-type peridotite complex in northern Japan indicate insignificant contribution to the mantle wedge of radiogenic ⁴He and porefluid-like halogens both observed in the subduction fluids in the Sanbagawa samples to a depth ranging from 40 to 100 km [1, 2]. A hotter mantle wedge than those of mature subduction zones is proposed for the Sanbagawa subduction system [4], in contrast the Izu subducting slab is relatively cold and would therefore lose relatively little water at equivalent depths to other slabs [5]. This implies a relatively small amount of the pore water subduction fluids would be released from the Izu slab at a sub-arc depth (150-200 km) resulting in further subduction to great depths in the mantle.

The mechanism by which the seawater-like noble gases are delivered to the convecting mantle remains to be elucidated. Serpentinized lithosphere of subducting slab is probably the best candidate, because if the hydration of the lithosphere by pore fluids is operating in a closed system, subduction of the serpentinized lithosphere can transport pore-fluid derived noble gases and halogens into the deep mantle [1, 2]. This is supported by a recent observation of noble gases and halogens in exhumed serpentinites similar to that of seawater and sedimentary pore fluids [6].

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Gold complexation within a halophilic cyanobacterium

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Introduction

Understanding the biogeochemical processes that transform gold are important in improving our ability to identify anomalies within dispersion halo environments, and potentially to recover trace amounts of gold [1]. Cyanobacteria have been implicated as potential gold nanofactories [2], and may contribute to gold nanoparticle formation in placer environments [3].

Octahedral platelet and nanoparticle gold precipitation has been observed after exposure of bacteria, e.g., *Plectonema boryanum* 485 [4], to HAuCl₄. The mechanism by which gold nanoparticles form within these cells is not well understood; however, adsorption of Au(I) to sulfur was reported following the addition of HAuCl₄.

Results and Discussion

X-ray analysis of near edge spectra (XANES), a synchrotron method, showed that the reaction of a halophilic *Plectonema sp.*, with 0.5 mM HAuCl₄ reduced Au(III) to Au(I), which then formed complexes with sulfur. At higher gold concentrations (5 mM) Au(III) was reduced to elemental Au.

To investigate Au binding to known sulfur-containing proteins we probed glutathione (GSH), using Electrospray Ionization Mass Spectrometry (ESI-MS). GSH reduced Au(III) chloride to Au(I) and coordinated the Au through its cysteine residue (Figure 1). GSH binds Au as a monomer and as a dimer.

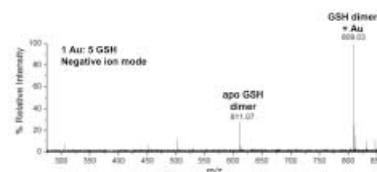


Figure 1. ESI-MS of a glutathione (GSH) complex with Au(I). HAuCl₄ added to 40 μM GSH for a final ratio of 1 Au: 5 GSH.

Cells reacted with 0.5 mM HAuCl₄ were lysed by liquid homogenization. Visualization of disrupted cells using phase contrast light microscopy revealed cell debris, and examination of whole mounts using TEM showed some cell envelope fragments. We recovered a soluble- and a cell envelope-fraction that bound Au. AAS and ESI-MS of the soluble fraction demonstrated the presence of low molecular weight Au-binding peptides. Occurrences of low molecular weight cysteine-rich metallothionein proteins in some species of marine cyanobacteria [5, 6] are targeted as possible gold-complexing organic compounds [7].

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