# Volatile subduction in serpentinites

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Serpentinites represent the main pathway for $H_2O$ and Cl subduction. The fate of noble gases in subducted serpentinites is also fundamental to investigating mantle convection and evolution.

Antigorite-schists from Erro Tobbio (Western Alps, Italy) have atmospheric noble gas concentrations an order of magnitude higher than typical basalts and Br/Cl-I/Cl similar to marine pore fluids. Fluid inclusions formed during initial antigorite breakdown have $^{36}Ar$ concentrations of ~5-100 ppb; $^{84}Kr/^{36}Ar$ plus $^{130}Xe/^{36}Ar$ compositions from seawater up to 2-3 times seawater; and enrichments in Br and I relative to Cl. The products of final antigorite breakdown represented by chlorite-harzburgites from Almirez (Betic Cordillera, Spain), have noble gas concentrations similar to gas-rich basalts and contain fluid inclusions with: ~0.8-5 ppb $^{36}Ar$; $^{84}Kr/^{36}Ar$ plus $^{130}Xe/^{36}Ar$ values of ~4-5 times seawater; and the lowest measured Br/Cl and I/Cl values. Taken together these data suggest: the 'noble gas subduction barrier' is ~85 % efficient for Ar; the heavy noble gases are subducted preferentially; and noble gases are subducted more efficiently than halogens or water.

Noble gas subduction is decoupled from $H_2O$ and explains the heterogeneity of heavy noble gases in the mantle. Slab devolatilisation leads to widespread 'atmospheric contamination' of noble gases in arc and back-arc basalts. Whereas, deep-subduction of atmospheric Xe>>Kr>Ar explains the low $^{40}Ar/^{36}Ar$ ratios and high relative abundance of atmospheric-Xe in Ocean Island Basalts. This realisation makes it possible to correlate the heavy noble gases with subducted lithophile elements for the first time.

# Gold adsorption and reduction by non-metabolizing bacterial cells

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Bacteria can adsorb Au from solution and precipitate it as cell-bound nanoparticles, but the underlying mechanisms are poorly understood. We examined the initial interactions between aqueous Au (III)-chloride complexes and bacteria by measuring the effects of non-metabolizing cells on the speciation and distribution of Au. We conducted batch Au (III) removal experiments, measuring the kinetics and pH dependence of Au removal, and tracking valence state transformations and binding environments using x-ray absorption spectroscopy (XAS). We used *Bacillus subtilis* or *Pseudomonas putida* cells suspended in 5 ppm Au (III)-(hydroxide)-chloride, 0.1 M $NaClO_4$ solutions. Both species removed > 85% of the Au from solution after 2 h below pH 5. Above pH 5, the extent of Au removed from solution after 2 h decreased with increasing pH, with ≤ 10% removal of Au from solution above pH 7.5. Au removal with both bacterial species was rapid at pH 3, and slowed with increasing pH. Reversibility experiments demonstrated that once the Au was removed from solution, adjusting the pH did not resolubilize the Au. However, cysteine caused Au to desorb, suggesting that the Au was not internalized within the bacterial cells during the experiments. XAS analysis indicated that ≥ 95% of cell-bound Au was Au (I), adsorbed to sulfhydryl and carboxyl or amino cell wall sites, with no Cl atoms present in any of the surface complexes. Bacterial exudates alone, with no cells present, also reduced aqueous Au (III), but this reduction was slow, and does not explain the presence of Au (I) on the bacterial cell walls in our experiments.

Our results suggest that Au removal occurs as a pH-dependent two-step adsorption-reduction process. The speciation of the aqueous Au and the bacterial surface controls the rate of Au removal from solution. Under low pH conditions, the cell walls are only weakly negatively charged, and aqueous Au complexes adsorb readily and rapidly, and the adsorbed Au is then reduced to Au (I) by oxidized components within the bacterial cell walls. With increasing pH, the cell wall becomes more negatively charged, slowing adsorption significantly. Both species exhibit nearly identical adsorption and reduction behavior, so it is possible that the adsorption and reduction steps that bacterial cell walls promote represent common initial steps in the formation of Au (0) nanoparticles from solution.