

Oxidation Rates of Hg⁰ in Geothermal Fluids

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Introduction

Elemental mercury is the predominant form of mercury found in chemical surveys of wells at New Zealand geothermal fields. Hg⁰ is dominant in all gaseous samples throughout geothermal power stations, even at very high H₂S levels. In order to model the geochemical behaviour of the dissolved elemental mercury, we have begun an experimental programme to measure the rates of Hg⁰ oxidation under various conditions applicable to natural geothermal systems as well as in geothermal power stations.

Experimental

De-aerated water saturated with Hg⁰ and water containing the reactants (e.g. dissolved air, H₂S, Cl⁻) are separately injected into a nominal 500 ml glass flask which closely approximates a well-mixed reactor. At a total flow rate of 2 ml/min the mean residence time is 232 minutes, and steady state is reached in 800 minutes. Analysis of the effluent determines the proportion of oxidised mercury as well as other constituents such as SO₄ and pH, Cl⁻, and H₂S.

Results

Initial experiments showed that, within the analytical uncertainties, mixing Hg⁰ saturated water with air saturated water (1:1, effluent pH 5.7) resulted in no oxidation of Hg⁰ at 25°C or 50°C. This supports earlier studies where the oxidation of Hg⁰ by molecular oxygen appears to be kinetically inhibited. Although Tubino and de Magalhães (1995) showed that Hg⁰ was easily oxidised by O₂ in the presence of Cl⁻, this is not supported by our experiments so far. At 25°C and 0.05 mol/dm⁻³ NaCl the rate of oxidation was slow, 0.1 (g/hr at a total Hg⁰ flux through the reactor of 2.4 (g/hr. In the presence of H₂S, the rate appears to be sensitive to pH. In future experiments, improvements will be made to better control the redox state of the fluid in the reactor.

pH	H ₂ S	SO ₄	Total Hg Flux	Hg Oxidation
	ppm	ppm	(g/hr	(g/hr
7.7	7.0	0.6	2.6	1.2
5.5	10.0	-	2.6	0.06

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References

de Magalhães M.E. and Tubino M., (1995), *The Science of the Total Environment*, 170, 229-239.

Combined Sr, Pb and O isotopic tracing of origin and migration of the Neolithic Alpine Iceman

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A perfectly preserved Neolithic human mummy was discovered in a high-altitude Alpine glacier in northern Italy in 1991. This ~5300 year old mummy ("Iceman") with its entire equipment was found in-situ and provides a unique opportunity to investigate circumstances of 'real' life and death during the late Neolithic.

Here we utilize radiogenic (Sr, Pb, Nd) and stable isotope (O, C) geochemistry to answer questions regarding origin and migration of the Iceman. Using tooth enamel and bone, insights can be gained about the earliest childhood and the last ~10-20 years of adult life, respectively, because human hard tissues mineralize at different ontogenetic stages. Radiogenic isotopes allow reconstruction of the provenance of the Iceman relative to the local geological environment. Stable isotopes provide information about altitude and position relative to the main Alpine watershed. Soils from Neolithic to Copper Age archaeological sites, ice from the finding site as well as modern waters and teeth have been analyzed for comparison.

Radiogenic isotopic compositions of enamel and bones were determined utilizing three sequential leaching steps for each sample to detect possible post-mortem alteration. Three fragments of Iceman enamel are characterized by similarly high ⁸⁷Sr/⁸⁶Sr ratios of 0.7203-0.7206, consistent with compositions of gneisses and schists e.g. close to the finding site. Sites overlying limestone or widespread Permian volcanic bedrocks can be excluded as the Iceman's childhood area. Two compact hipbone samples have lower ⁸⁷Sr/⁸⁶Sr ratios of 0.7175 and 0.7181. Hence, in contrast to a constant food source during his earliest childhood, the Iceman used food from (and migrated to) a different region during his last ~1-2 decades of life.

¹⁸O-analyses of river waters from valleys north and south of the finding site, the latter being located at the main Alpine watershed, have revealed large differences predominantly between north and south but also east and west. The preliminary ¹⁸O analysis of enamel can only be reconciled with waters from the south using the constant oxygen isotope fractionation of human bodies, hence excluding a northern origin of the Iceman. This is also consistent with ¹⁸O data of modern teeth. Bones are significantly lighter in ¹⁸O when compared to enamel, implying that the Iceman has spent his childhood at lower altitudes than his later adult life. Further calibrations of oxygen isotope analyses are underway.