Fractionated mercury isotope in sediments: A quest for processes

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Analyses of mercury isotopes in sediments from lakes and oceans have revealed mass independent fractionation (MIF) effects. MIF of Hg isotopes can provide constraints on models of Hg cycling in aquatic systems. Isotope ratios ^{198}Hg/^{202}Hg, ^{199}Hg/^{202}Hg, ^{200}Hg/^{202}Hg, ^{201}Hg/^{202}Hg and ^{204}Hg/^{202}Hg have been measured in mercury vapor generated by reduction of sample solutions with $SnCl_2$ in a continuous- flow cold-vapor generator connected to a Thermo-Finnigan Neptune MC-ICPMS, using a standard-sample bracketing technique, relative to the NIST SRM 3133 Hg-standard. When corrected for mass dependent fractionation, only values for ^{199}Hg/^{202}Hg and ^{201}Hg/^{202}Hg yield non-zero residuals. These residuals are expressed as Δ^{199}Hg and Δ^{201}Hg respectively and have negative or positive values indicating depletion or enrichment.

Lake Erie and Yucatan limestone are enriched in the odd A isotopes. The absolute value of enrichment/depletion generally increases with the depth of the sediment but is not correlated with the total concentration of Hg in the sediments. The primary species of Hg in sediments are Hg(II) and MeHg. The former is scavenged from the water column because of its high reactivity with particulates and MeHg is produced in the anaerobic sediments by sulfate reducing bacteria. Lab experiments have shown that photo-reduction of Hg(II) and MeHg in water yields residual water enriched in the odd_A isotopes (positive Δ^{199}Hg and Δ^{201}Hg) and liberates elemental Hg that should be depleted in Δ^{199}Hg and Δ^{201}Hg. Lake Erie and Yucatan sediments might have a large proportion of Hg derived from the water column that retain the odd A isotope enrichment signature. Lake and spring sediments were highly enriched in organics and exhibit negative values of Δ^{199}Hg and Δ^{201}Hg. The slight depletion of the odd N isotopes in these sediments might be due to the organics, mostly plant materials that derive their ^{199}Hg and ^{201}Hg depletion from the atmosphere and they overwhelm the proportion of enriched ^{199}Hg and ^{201}Hg signature that comes from the adsorped Hg(II) in water. From the range of values of the Δ^{201}Hg/Δ^{199}Hg ratios, we infer multiple isotope effects responsible for the MIF.

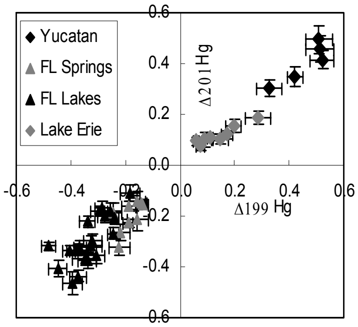

Figure 1: MIF of Hg in sediments.

High-pressure melting relations in Fe-C-S systems: Implications for metallic cores in planetary bodies

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The density deficit of the Earth's outer core with respect to that of pure metallic Fe-liquid suggests presence of ~10% light elements in Earth's outer core. The presence of minor elements such as S, C, O, H, Si, and P is also argued for cores of other planetary bodies. However, experimental data on the effect of light elements on melting relations of Fe in multi-component systems and the mutual solubility of various light elements in molten Fe has been limited.

We investigated the near-liquidus phase relations in Fe-C-S ternary at 2-6 GPa and 1050-1700 °C. Experiments were performed in a piston cylinder and a multi-anvil device using MgO (Fe-5wt.%C-5wt.%S and Fe-5wt.%C-15wt.%S) and graphite (Fe-13%S, Fe-5%S, Fe-1.4%S) capsules. Run products were analyzed for Fe, S, C, and O using electron microprobe.

Liquidus temperature increases from ~1125 °C to ~1410 °C and from ~1100 °C to ~1300 °C from 2 to 6 GPa for Fe-5wt.%C-5wt.%S and Fe-5wt.%C-15wt.%S respectively. The crystalline phase at the liquidus is Fe_3C at 2-4 GPa and Fe_7C_3 at 6 GPa and pure Fe starts crystallizing only with further drop in temperature of ~75 (at 2 GPa) to 200 °C (at 6 GPa) below the liquidus. The melt in equilibrium with crystalline Fe-carbide is S-rich with C/(C+S) weight ratio as low as 0.01 at low-T and high extent of crystallization. For Fe-5wt.%C-5wt.%S, a single liquid is observed above the liquidus at all pressures. But for Fe-5wt.%C-15wt.%S, super-liquidus conditions produce two immiscible liquids at 2-4 GPa and a single liquid at 6 GPa. Liquid immiscibility in Fe-C-S system with high S content can be reconciled with our graphite saturated experiments that show a decrease in C solubility in molten metallic liquid with increasing S content.

Our results along with the 1 atm phase relations in Fe-C-S systems indicate that the mutual solubility of C and S in molten Fe is enhanced with pressure and no liquid immiscibility induced compositional stratification is expected for planetary cores with pressures $\geq$ 6 GPa. But for planetary bodies with core pressures $<$ 6 GPa, a compositional stratification with sulfide-rich outer core and Fe_3C-Fe bearing inner core can be produced.