Goldschmidt 2000
September 3rd–8th, 2000
Oxford, UK.

Journal of Conference Abstracts
Volume 5(2), 591

Mercury Isotopic Analyses by Single- and Multi-Collector Magnetic Sector Inductively Coupled Plasma Mass Spectrometry

Bjoern Klaue (bklaue@umich.edu) & **Joel D. Blum** (jdblum@umich.edu)

University of Michigan, Geology, 2534 CCLittle Building, Ann Arbor, MI, 48109, USA

Mercury is an intriguing element to study because it: (a) is highly volatile; (b) has seven stable isotopes with a relatively large mass range (196-204 amu); (c) forms bonds that have a high degree of covalent character; and (d) exists in more than one oxidation state. These factors suggest that it may undergo kinetic isotopic fractionation in natural systems (Nier, 1950). However, neither the true isotopic composition nor the fractionation of Hg isotopes has been studied in detail with modern instrumentation. The Hg isotopic composition has been analyzed by gas source mass spectrometry (Zadnik, 1989) but the reported abundances show large inconsistencies (De Bievre, 1984). Interest in measurements of the Hg isotopic composition has been spurned by reports of large ^{196}Hg/^{202}Hg anomalies in meteorites (Lauretta, 1999). These measurements were performed by neutron activation analyses (INAA) and have not been confirmed by other techniques. Due to mercury's high volatility and ionization potential, isotopic measurements cannot be performed by thermal ionization mass spectrometry (TIMS). Analysis by gas source mass spectrometry and single-collector inductively coupled mass spectrometry are typically limited to a precision of 0.1%, which is insufficient for the expected levels of natural isotopic fractionation of Hg. Multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) offers an efficient way to achieve high precision isotopic measurements for elements that were previously impracticable or impossible to analyze (e.g., Halliday, 1999). Thus, we developed a cold-vapor generation MC-ICPMS method, which allows high precision Hg isotopic analyses down to the 0.005% precision level. Cold-vapor or Hg(0) generation with Sn(II) as the reducing reagent allows the fast and selective chemical separation of mercury from the matrix. External mass fractionation correction is achieved by mixing the sample Hg-vapor online with a dry aerosol of the NIST 997 thallium isotopic standard reference material. The external inter-element fractionation correction is mainly intended to improve the internal precision of MC-ICPMS measurements but typically fails to also accurately correct for absolute isotopic ratios within a few hundred ppm (Rehkaemper, 1998). The thallium external correction is a well-established method for lead isotopic measurements but even for the chemically and electronically similar elements Tl and Pb the external correction yields absolute ratios that are slightly different from the certified values (Rehkaemper, 1998). Because there are no certified Hg isotopic standards to test the accuracy of the measurements, we compared the results of the MC-ICPMS ratios (Tl external correction, power law) with single-collector ICPMS data (direct measurement). The Finnigan "ELEMENT" single-collector magnetic sector ICPMS applied for this study can be tuned to exhibit no or very little absolute mass fractionation using well known standards of Pb (NIST 981) or Tl (NIST 997). Precision levels of 0.05 to 0.1% can be achieved. However, the VG Elemental "P54" MC-ICPMS typically shows a mass fractionation of ca. 1% per amu in the 200 (amu) mass region which requires external correction procedures. The absolute Hg isotopic composition measured with both instruments agrees within 0.1% for all but one ratio (201/202, 0.3% deviation), which proves that the external Tl correction procedure yields reasonably accurate Hg isotope ratios for MC-ICPMS. The MC-ICPMS method was applied to a number of terrestrial and extraterrestrial samples to establish the range of isotopic variations for Hg. Due to the lack of a Hg isotopic reference material we have chosen a purified native mercury product form the Alamaden mine in Spain (the world largest known Hg deposit) as a relative "zero" standard. Analyses of a number of independent ore samples from the same mine revealed no significant differences between the Hg(0) product and the ores. We analyzed cinnabar and native mercury samples from 7 mines throughout the world and found fractionation of up to -0.15% for the Hg 198/204 ratio. While the cinnabar samples from most mines displayed only small differences in the 0.01 - 0.03% range, we observed the largest fractionation for samples of cinnabar and native mercury from the same mines. This is consistent with the possibility that partial condensation or evaporation during ore deposition is a common mechanism of Hg fractionation. We will further investigate the extend of Hg isotopic fractionation in natural systems and the possibilities of using Hg isotope ratios as a tracer for pollution sources, geochemical, and biogeochemical processes.

De Bievre P, Gallet M, Holden NE & Barnes IL, *J. Phys. Chem. Ref. Data*, **13**, 877, (1984).

Halliday AN, Christensen JN, Lee DC,Rehkaemper M, Hall CM & Luo X, *Inorganic Mass Spectrometry, fundamentals and applications, M Dekker Inc., NY*, Chap. 13, (1999).

Lauretta DS, Devouard B & Buseck PR, *Earth Planetary Sci. Letters*, **171**, 35-47, (1999).

Nier AO, *Phys. Rev.*, **79**, 450, (1950).

Rehkaemper M & Halliday AN, *Int J. Mass Spectrom*, **181**, 123-133, (1998).

Zadnik MG, Specht S & Begemann F, *Int. J. Mass Spectrom*, **89**, 103-110, (1989).