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# Plasma Centrifuge and Isotopic Fractionation in MC-ICP-MS

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Isotopic studies of various elements have been rapidly expanding in the past several years since the advent of MC-ICP-MS. It is becoming increasingly apparent that we need an adequate description of mass bias phenomena in MC-ICP-MS. It is generally thought that mass bias in ICP-MS results from space-charge effects behind the skimmer cone and through the lens where a fraction of lighter isotopes fail to enter the mass analyzer (Douglas and Tanner, 1998). To first order, the empirical "exponential fractionation law" observed on TIMS (Russell et al., 1978) worked surprisingly well to correct for such effects. But in detail, the law breaks down and fails to explain the observed data. Most notable is the "$^{208}$Pb depletion problem" that was observed on all existing MC-ICP-MS instruments (9th Goldschmidt Conference at Harvard, 1999).

We challenge the prevailing notion that no fractionation occurs during ionization in the ICP and introduce the concept of "plasma centrifuge" from *Plasma Physics* to explain secondary isotopic fractionation effects that are not fully removed by the exponential law.

Rotation and separation of isotopes in plasma centrifuges have been studied for four and half decades (Slepian, 1955). When the cylindrical, axi-symmetric, and fully ionized plasma column is subject to uniform, axial magnetic field B (the case for our ICP-MS ion source), it provides the conditions for a plasma centrifuge, producing isotope fractionation. The charged particle forward spirals inside the cylindrical solenoid of the load coil. The lighter ions fly in a tighter spiral, while the heavier ones take wider trajectories. When the ions leave the solenoid, the B field becomes weaker, the spiral trajectory will become bigger as it inversely correlates with B, further separating isotopes of different masses. Using a fluid model, the cylindrical plasma column rotating as rigid body was described as: $R(r)/R(o) = \exp[(\Delta M)\omega^2 r^2/2kT]$ where R(r) and R(o) are the ratios of the heavier to lighter ion species at radius r and at the rotation axis, respectively, $\Delta M$ is the mass difference between two ion species, $\omega$ the angular rotation rate ($\omega = B.q/m$), and T is the temperature. The fractionation increases exponentially as the square of the radial distance from the plasma axis. The above equation indicates that centrifugal isotope separation exponentially depends on the ratio between the difference in ordered rotational kinetic energies of the isotopes and the random thermal energy. At the plasma-sample interface, the 1% of analyte ions being sampled and entering the skimmer cone is already depleted to some degree in heaviest isotopes by a few epsilon compared to the light isotopes based on the prevailing plasma conditions in MC-ICP-MS and observed isotope data. From this point on, space charge effects may take over.

Based on the isotopic data obtained with MC-ICP-MS [Mo (see Yin and Jacobsen, 1998) and Nd as two end member examples], it appears to us that "space charge effects" (for the light isotope depletion) as well as "plasma centrifuge" (heavy isotope depletion) are operational in ICP-MS. High precision multiple collection ICP-MS offers us the best chance to study this phenomenon in detail.

We propose that the *Plasma Centrifuge Hypothesis* be tested and studied by optimizing and changing systematically a few crucial analytical parameters, such as sampling depths (defined as the distance from the tip of the sampling cone to the nearest turn of the load coil) and sample cone orifice diameter. Another way of studying the problem is by careful examination of existing isotope data obtained with MC-ICP-MS and applying the exponential law to the data to remove the first order space charge effect and then inverting the data to obtain certain parameters of plasma centrifuge, such as separation factor, collection radius, plasma rotation rate. Pending good weather, we hope to present results at the meeting.

The plasma centrifuge mechanism may explain why $^{208}$Pb, the most abundant and heaviest isotope of Pb, is depleted in MC-ICP-MS measurements. We will show that the approach of changing Tl isotopic ratio (Rehkämper and Halliday, 1998; Belshaw et al., 1998) is not valid and does not solve the problem.

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