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IN-SITU GEOCHRONOLOGY: EXTENDING LARIMS TO Pb-Pb ISOCRHONS

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Introduction: We have previously described development of Laser Ablation Resonance Ionization Mass Spectrometry (LARIMS) for in-situ determination of the radiometric age of rocks using isotope ratios of Rb and Sr [1,2]. LARIMS uses laser resonance excitation of the target elements, which provides elemental selectivity, thus eliminating isobaric interferences with little or no sample preparation and allowing thousands of samples to be measured in significantly shorter periods of time than traditional methods. We have recently begun research that aims to extend the Rb-Sr capability to include Pb-Pb measurements. Preliminary measurements of Standard Reference Material 612 (SRM-612) from the National Institute of Standards and Technology (NIST) demonstrate that resonance ionization of Pb can measure samples with as little as 0.12 ppm total Pb.

Background: In-situ LARIMS will enable measurements of 1) isotope geochemistry relevant for chronology and igneous evolution, 2) light isotopes relevant for habitability, life, and climate history, as well as 3) elemental abundances relevant to understanding local and regional geology. In particular, the elemental selectivity of LARIMS makes isotopic geochronology measurements possible that heretofore required extensive sample preparation and were thought to be practically impossible for in-situ measurements. For example, we have used Rb-Sr LARIMS to analyze a piece of the Martian meteorite Zagami and the Duluth Gabbro, a lunar analogue. In these measurements, we obtained isochron ages consistent with the published ages within 200 Ma.

Pb-Pb geochronology is well-suited for LARIMS analysis. The use of a single element simplifies the laser system and eliminates inter-element fractionation that can be problematic in Rb-Sr analysis or other multi-element LARIMS measurements. In general, there is less interference at masses corresponding to Pb isotopes than at lighter masses. However, there are potential interferences such as Hg and HfO_2, which have been known to cause problems in Inductively Coupled Plasma Mass Spectrometry (ICPMS) of Pb isotopes [3]. LARIMS enables a simple check for interfering species by detuning the laser wavelength off the Pb resonance. The resonance ionization signal for the desired species should disappear when the resonance laser is detuned. Any residual signal is due to an interfering species.

Three resonance ionization laser schemes were examined for initial LARIMS analysis of Pb: 1) a 2+1 scheme that uses $\lambda_1 = \lambda_2$ = 450.3 nm (the first transition in this scheme is a simultaneous two-photon excitation), 2) a 1+1+1 scheme using λ_1 = 283.3 nm, λ_2 = 600.2 nm and $\lambda_3 \quad < 1270$ nm, and 3) a 1+1 scheme that uses $\lambda_1 = \lambda_2$ = 283.3 nm. One-photon resonance excitations have cross-sections that are orders of magnitude greater than either two-photon resonance excitations or photoionization processes. Therefore, although schemes 1) and 3) have the advantage of requiring fewer lasers, they also require high-intensity blue or UV wavelengths. This adversely affects the selectivity of the resonance ionization process. Scheme 2) uses low-intensity UV and visible wavelengths and a high-intensity IR wavelength. This is the preferred scheme and was selected for our initial Pb LARIMS measurements.

Preliminary Results: A laser system capable of producing the required wavelengths for scheme 2) was assembled. A Nd:YAG laser pumped dye laser produces 566.6 nm light, which is frequency-doubled in a beta barium borate crystal. A second Nd:YAG pumped dye laser produces the 600.2 nm light for the second resonance in scheme 2). The fundamental of one of the Nd:YAG lasers (1064 nm) is used for the final photoionization step. We focus the fifth harmonic (213 nm) of another Nd:YAG laser onto the sample to ablate material off the surface. Electric fields suppress the ions created in the ablation process, preventing these ions from entering the mass spectrometer. The three resonance ionization laser lasers spatially overlap the ablated plume about 1 mm off the surface. These three resonance ionization wavelengths are synchronized in time with each other but delayed with respect to the ablation laser pulse. For Pb, the resonance ionization signal peaks at about 9 μsec delay. The electric field that initially suppressed ablated ions is reversed before the resonance lasers are fired, thus extracting the ions selectively created by resonance ionization into a multi-bounce time-of-flight mass spectrometer (MBTOF-MS). The MBTOF-MS separates the isotopes in time, allowing analysis of isotope ratios.

We have used this technique to analyze NIST SRM-612, a glass wafer containing 38.57 ppm Pb along with a number of other constituents. The mass spectrum shows all of the Pb isotopes, with the even isotopes in the expected ratios. However, we have found that the Pb-207 peak height is very sensitive to the exact wavelength of the 600.2 nm light used for the second excitation. The height of this odd isotope can be significantly modified with minute changes in the 600.2 nm wavelength that don't affect the peak heights of the even isotopes. This is due to the well-known odd-even isotope anomaly in resonance ionization. Because of the sensitivity of the Pb-207 peak to the exact wavelength, a standard with known Pb isotope ratios is analyzed frequently to allow calibration of the isotope ratios. In very preliminary LARIMS spectra obtained for SRM-612, the measured Pb-208 signal-to-baseline noise is over 600:1. This corresponds to a minimum detection limit of 0.12 ppm total Pb. We anticipate improving the signal-to-noise with optimization of TOF voltages and ablation laser intensity.

Future Work: We are in the process of measuring an isochron for a sample of Duluth Gabbro and anticipate having results available for the conference.

We are also exploring the use of fiber lasers for LARIMS analyses of Pb. Fiber lasers are small, lightweight, and extremely robust, making them ideal for space missions. We are presently developing fiber lasers for our Rb-Sr LARIMS work and we have investigated ways to efficiently combine wavelengths from Er-, Yb-, and Tm-doped fibers to generate both the 283.3 nm wavelength and 600.2 nm wavelength needed for Pb LARIMS. Concepts utilizing wavelengths readily generated in these fibers have been developed.

References:

1. F.S. Anderson, J. Levine, and T.J. Whitaker, Rapid Comm. in Mass Spect., 2015, 29, 191-204.
2. F.S. Anderson, J. Levine, T.J. Whitaker, Rapid Comm. in Mass Spect., 2015, 29, 1457-1464.
3. R.W. Hinton and J V Long, Earth Planet. Sci. Lett 1979, 45, 309-325.