IN SITU ZIRCON LU-HF ISOTOPIC ANALYSES ON THE SAPPHIRE 1700 MC-ICPMS: EXAMPLE FROM THE SAN GABRIEL ANORTHOSITE, CA AND IMPLICATIONS FOR PLANETARY ANALOGS

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Introduction: The mineral zircon is the primary choice for U-Pb geochronology. The coupling of these ages to the zircon's Lu-Hf isotopic composition provides a powerful tool for elucidating magmatic sources, as well as elucidating the temporal evolution of the crust-mantle system. The number of published studies with Lu-Hf in zircon measurements has increased rapidly with the development and improvement of laser ablation inductively coupled mass spectrometry (LA-ICPMS) [e.g., 1]. On a smaller scale, there has also been an increase in studies using the Lu-Hf isotopic system in zircon to advance our understanding of the formation of non-terrestrial planetary bodies (e.g. petrogenesis of lunar [2] and martian zircon [3]).

From a precious extraterrestrial sample perspective, with limited amount of sample available, there is a need to continuously document the capabilities and limitations of semi-destructive *in-situ* geochemical measurement techniques. Here, we report the *in-situ* zircon Lu-Hf measurement capabilities of the Sapphire 1700 MC-ICPMS, a first, and discuss a Mesoproterozoic analog sample. Namely, a pegmatitic zircon from the San Gabriel Mountain anorthosite, CA.

Samples and Analytical Methods: *In-situ* Lu-Hf, U-Pb, optical profilometry, and cathode luminescence measurements were collected in the Astromaterials Research and Explorations Science (ARES) division at NASA-JSC. *In-Situ* U-Pb geochronology was conducted on a Thermo-Scientific Element-XR ICP-MS coupled to a Photon Machines 193 nm laser ablation system. U-Pb utilized a 25 μm spot, ablated for 30 s at 5Hz and 5 J/cm^2, resulting in crater depths of ~20 μm. Reference zircon 91500 [4] was used as a primary reference material, with downhole fractionation corrections performed using the "U-Pb Geochronology" data reduction scheme in Iolite™ [5]. Concordia ages calculated using IsoplotR [6].

In-Situ Lu-Hf isotope measurements were conducted on a Nu Instruments™ Sapphire 1700 MC-ICPMS coupled to an Applied Spectra™ iX-fs-Tandem LA-LIBS 1030 nm laser ablation system. For the initial laser session (standards-only), a 40 μm spot was ablated for 20 s at 8 Hz and an energy density of ~6 J/cm^2. The second laser session, containing the San Gabriel zircon, utilized the same instrument settings, however a 60 μm spot was used and placed directly over the previous U-Pb spots. Zircon standards were treated similarly, with 25 μm spots placed according to the U-Pb methods prior to Lu-Hf analyses. Masses 170 to 180 were measured simultaneously on 11 faraday cups using 10^{11} Ω resistors and an integration time of 0.1 s. Zircon Mud Tank was used as the primary calibration standard [7], with secondary zircon standards (Penglai [8], RAK-17 [9], 91500 [10], Plesovice [11], R33 [12]) encompassing a full range of Lu/Hf and Yb/Hf ratios. Data reduction, including Yb and Lu interference corrections, were completed using the Iolite data reduction scheme developed and described in [13].

Results & Discussion: A major concern in the *in-situ* measurement of the Lu-Hf system is the correction for the Lu and Yb interference on Hf. As a result, initial experiments were conducted solely on natural zircon standards before subsequent measurements on zircon from the San Gabriel anorthosite.

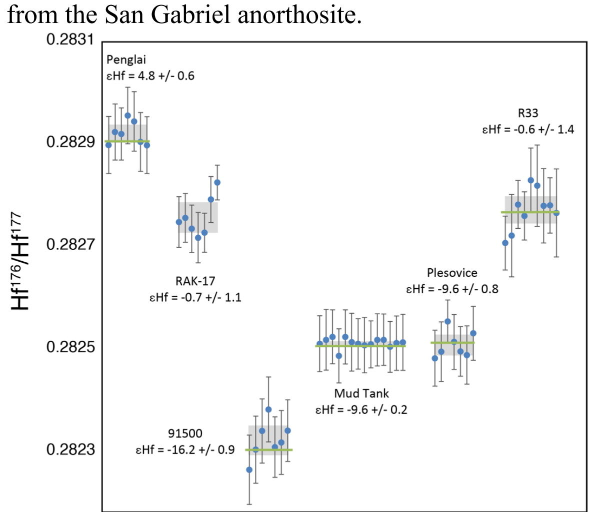

Figure 1. Results of in-situ Lu-Hf measurements on various natural zircon standards. Data at 2SE. Grey box is weighted mean, green line is "true" value.

Standards & Interference Correction: With a 40 μm spot producing ~20 μm depth craters, individual analysis precision for measured $^{176}Hf/^{177}Hf$ is ~50 ppm for a total Hf beam of ~5 V, while the typical precision for a weighted mean is ~20 ppm (for n ~8). The natural zircon standards used cover a range of $^{176}Lu/^{177}Hf$ and $^{176}Yb/^{177}Hf$ values from ~0.00002 to ~0.003 (Mud Tank) and ~0.001 to ~0.1 (R33), respectively. By using Mud Tank, with its low Yb and Lu concentrations, as the primary zircon standard, we can demonstrate the effectiveness of our Lu and Yb interference corrections from a "worst case" scenario. Following the correction scheme of [13], we reproduce $^{176}Hf/^{177}Hf$ values well within the published "true" values for each zircon (Fig. 1), with zircons R33 and RAK-17 zircons constraining the accuracy of the interference correction at high Yb and Lu concentrations.

San Gabriel Zircon: Part of larger San Gabriel Mountain's geologic setting includes the San Gabriel Anorthosite Complex, a massive anorthosite which mimics other terrestrial anorthositic bodies that are often used as geochemical analogs for lunar anorthosites. Likewise, A pegmatitic sample was taken within the San Gabriel Anorthosite Complex (Fig. 2B).

The megacryst zircon is characterized by highly fractured euhedral prismatic grains that display mosaic textures (Fig. 2B,C). Although highly fractured, a collection of 15 U-Pb laser ablation spot analyses produce a concordant age of 1159.7 ± 4.2 Ma (2 SE) (Fig. 2A). This age is slightly younger than the generally published age of 1.19 Ga for the anorthosite complex [e.g., 14], as well as the minimum metamorphic age of 1186 Ma reported for associated granulite facies gneiss [15] adjacent to the anorthosite.

Hf analyses collected from the same locations are generally homogenous (Fig. 3) and can help elucidate the origins of both the fluids causing the pegmatitic textures, as well as the sources for the massive anorthositic magmatism. A two-stage depleted model age points towards a mantle source with a minimum age

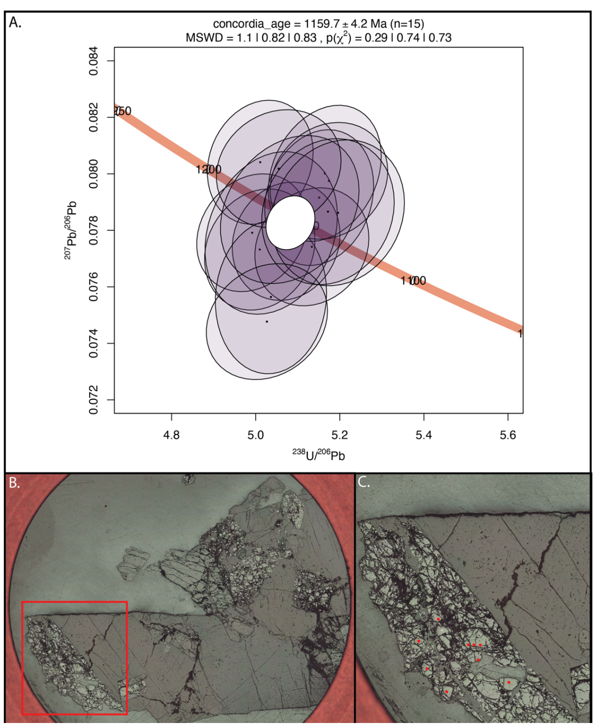

Figure 2. a) Tera-Wasserburg Concordia diagram for U-Pb analyses of pegmatitic San Gabriel zircon. b) Reflected light mosaic of sample with zoomed area (c) showing some of the analyses locations.

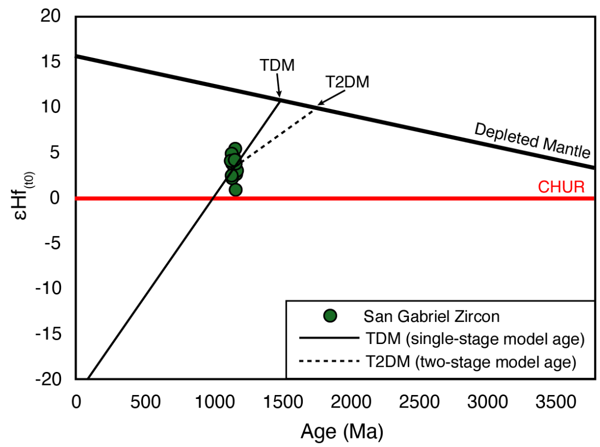

Figure 3. Initial εHf for San Gabriel Zircon with single (solid) and two-stage (dashed) depleted mantle (DM) model ages. Error not shown (2SE ~2 εHf units).

similar to the ~1.7-1.8 Ga Proterozoic basement rock of the area (i.e. Mendenhall Gneiss).

Conclusions: The described LA-MC-ICPMS setup produces accurate *in-situ* Lu-Hf isotopic measurements in zircon for samples with a range in Lu and Yb concentrations. High precision measurements can be made with minimal ablated volumes, but improvements can likely be made with adjustments to the instrumental setup (i.e. slower ablation, addition of N_2 gas).

The advanced capabilities of the Sapphire MC-ICPMS hosted in the Center for Isotope Cosmochemistry & Geochronology will be a key part of NASA's sample mission return isotope geochemistry and geochronology capabilities. Laser ablation studies afford high resolution (5 – 60 µm) *in-situ* analyses that, in combination with the high mass resolution and multiple detectors of the Nu Sapphire 1700, will expand capabilities to perform isotopic tracer and geochronologic studies of astromaterials.

Measurement of the pegmatitic zircon from the San Gabriel anorthosite provides an internal readiness case for sample return, in particular for forthcoming ANGSA felsites (e.g., Erickson et al., this meeting).

Acknowledgments: We thank Jay Thompson for initial U-Pb analyses and Linda Godfrey for loaning secondary zircon standards.

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