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A Triad of Geological and Environmental ICPMS Applications

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Abstract: The isotopic compositions of the elements Sr, Nd, Hf, and Pb (among others) are commonly used to distinguish the source regions of solid sample materials, whether those are billion-year-old rocks and minerals, prehistoric stone artifacts, or anthropogenic environmental particulates. This T3 project demonstrates the versatility and viability of inductively coupled plasma mass spectrometry (ICPMS) as a method to conduct isotopic analyses of environmental and geologic specimens such as aerosols, rocks and minerals.

Laser-ablation, split-stream analysis: Application to South American detrital zircon provenance

Why LASS?

Traditional laser-ablation inductivley coupled plasma mass spectrometry (see right panel) requires analysis of different volumes (or locations on a grain) of a mineral sample in order to acquire U-Pb isotopic data for age determination and Hf isotope data to constrain rock origins. This can be problematic because zircon crystals are notoriously heterogeneous and preserve different geochemical fingerprints from different parts of their potentially long and complex history.

By splitting the gas line carrying the ablated sample between two different mass spectrometers (Fig. 1), both U-Pb and Hf isotopes can be analyzed at the same time, from the same volume of sample material. This project established the analytical protocols and provided proof-of-concept data to demonstrate the viability of the LASS method.

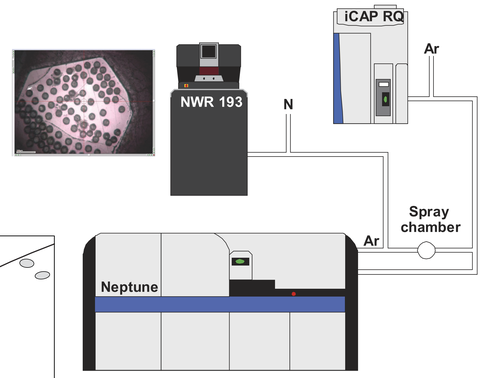


Figure 1. Schematic diagram showing laboratory setup for laser-ablation, split-stream analysis (LASS) at the Williams Radiogenic Isotope Geosciences Laboratory at Texas A&M University. This setup allows for simultaneous collection of Hf and U-Pb data for individual detrital zircon grains.

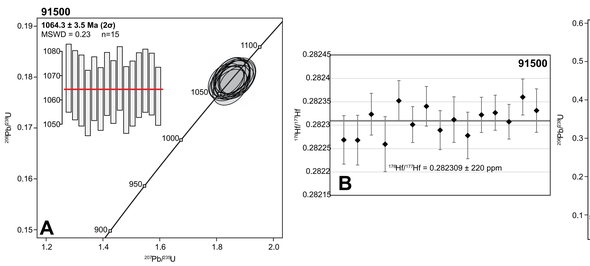


Figure 2. (A) Concordia plot and weighted mean plot of primary zircon standard 91500 analyzed during analysis of sample SAZ09. Yuan et al. (2004) report an age of 1063.1± 8.1 Ma for zircon 91500. (B) ^{176} Hf/^{177} Hf ratio calculations for 91500 zircon standard. (C) Concordia plot of detrital zircon U-Pb ages for sample SAZ09.

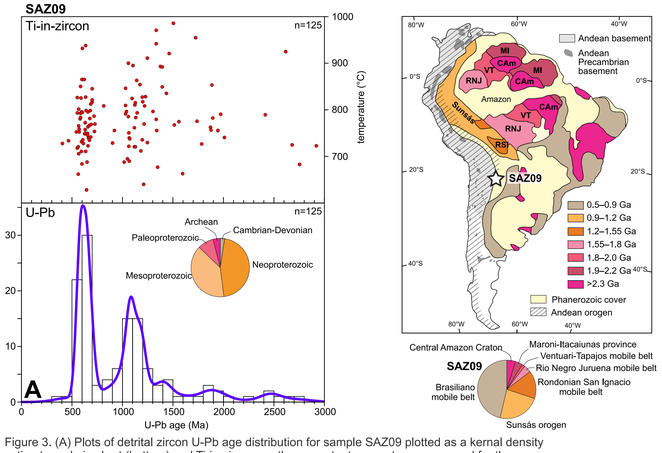


Figure 3. (A) Plots of detrital zircon U-Pb age distribution for sample SAZ09 plotted as a kernal density estimate and pie chart (bottom) and Ti-in-zircon geothermometry temperatures measured for the same zircon grains. (B) Map of South America showing sample location and potential source area age/distribution modied from Pepper et al. (2016); pie chart showing interpreted detrital zircon provenance distributions for sample SAZ09 created using the above age bins. Abbreviations: MI—Maroni-Itacaiunas province, CAm —Central Amazon Craton, VT—Ventuari-Tapajos mobile belt, RNJ—Rio Negro Juruena mobile belt, RSI—Rondonian San Ignacio mobile belt.

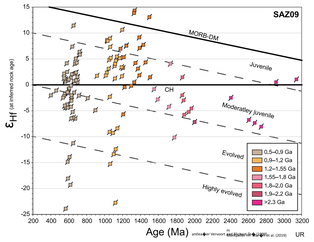
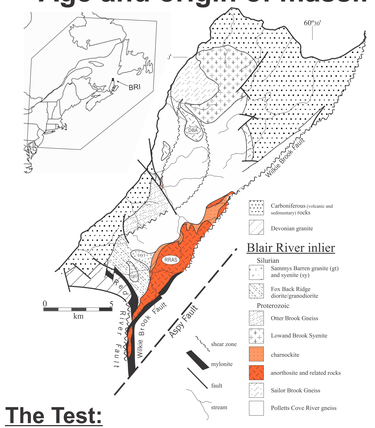


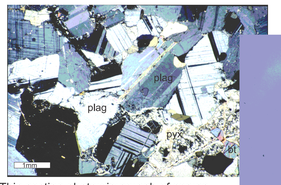
Figure 4. Combined U-Pb–Hf(t) results for Triassic strata. Abbreviations: CHUR — chondritic uniform reservoir, DM — depleted mantle.

Age and origin of massif anorthosite, Cape Breton Island, Nova Scotia Canada

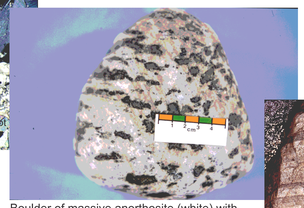


The Problem:

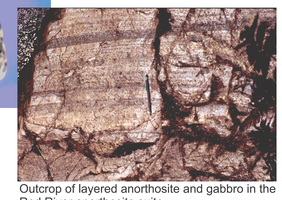
The Blair River inlier (BRI) in northern Cape Breton Island, Nova Scotia, contains a variety of distinctive rock types, including "massif-type anorthosite". These rocks are common on the Moon, but on Earth are found only in the deeply eroded roots of mountain belts more than about 1 billion years old. Recent analyses (Keppie et al., 2019, Shellnut et al., 2020) have suggested that the BRI anorthosite is the first-know example of a relatively young (ca. 435 Ma) massif-type anorthosite, contradicting previous age interpretations (Miller et al., 1993). Confirmation of this relatively young massif-type anorthosite would necessitate a re-evaluation of our current understanding of the geological conditions under which this rock type is formed.



Thin section photomicrograph of coarse plagioclase (plag), pyroxene (pyx), and biotite (bt) from the Red River anorthosite suite.



Boulder of massive anorthosite (white) with pyroxene megacrysts (black) from the Red River anorthosite suite.



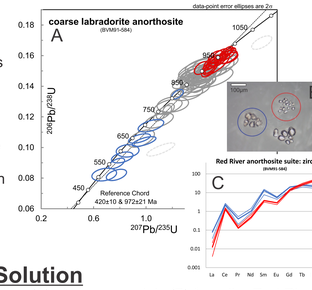
Outcrop of layered anorthosite and gabbro in the Red River anorthosite suite.

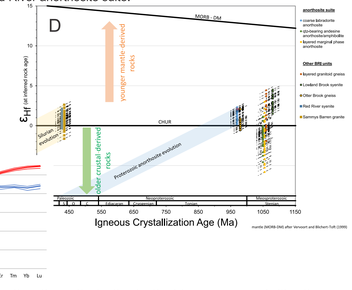
The Test:

To determine the age and origin of the anorthosite, we conducted laser-ablation, inductively coupled plasma mass spectrometry (LA-ICPMS) analysis of zircon crystals from several different rock types within the anorthosite igneous suite in order to re-evaluate their age and their Hf isotopic composition.

LA-ICPMS: so much information from so little material

Laser-ablation, inductively coupled plasma mass spectrometry (LA-ICPMS) is an analytical method that allows for precise analysis of rocks and minerals. Sampling is conducted by ablation of 30-50 µm circular spots. The ablated aerosols are carried in a gas flow to one or more mass spectrometers (see left panel) where elemental and isotopic data are collected to constrain age and characterize the geological setting of rock formation. Shown at left is a zircon crystal (150 x 50 µm) on a penny; the volume of zircon analyzed is significantly smaller than the zircon crystal.





A novel method for isotopic characterization of low-mass airborne Particulate Matter (PM) using MC-ICPMS

How is MC-ICPMS applied to airborne particulate matter?

Multi-collector inductivley coupled plasma mass spectrometry (see above left panel) is a method that combines the most desirable aspects of two, until relatively recently, different types of mass spectrometry. Multiple ion collectors allow for high-precision isotope ratio measurements and plasma ionization creates more intense ion beams for better signal/noise ratio compared to other mass spectrometry methods. The combination results in both high throughput and high precision analysis of isotope compositions of elements such as Sr, Nd, Pb, and Hf.

In the case of samples collected from airborne particulate matter (PM), where very small sample mass is common, these analyses require highly optimized sample preparation, chemical separation, and instrument protocols. This project seeks to establish the optimal methods for analysis of PM.

Methods

- Minimize any losses of sample mass in pre-analysis chemistry so as to make better measurements with the MC-ICPMS
- Design and calibrate our columns to completely separate Sr, Nd, and Hf into three different aliquot fractions
- Analyze various low level concentrations of standard samples (NIST 987) of known isotope ratio and amount of signal and noise in measurements and influence of interfering species
- Optimize the chemistry for removal of interfering species in the sample for Sr, Nd, and Hf respectively.
- Analyze ^{87}Sr/^{86}Sr, ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf for less than <1 mg sample mass

Results - Optmized chemical separation:

- Determined optimal column configuration and flow to attain minimum loss.
- Optimized elution curves and reagent volumes

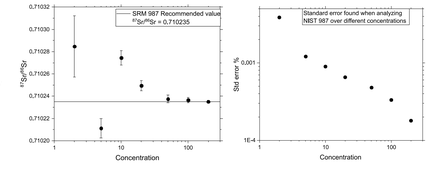


Fig. 1. ^{87}Sr/^{86}Sr at different concentrations of standard reference material, with accuracy and precision of measurement achieved with by MC-ICPMS

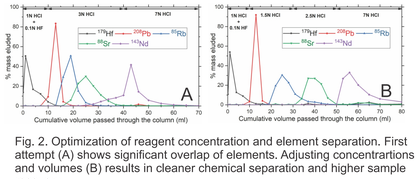


Fig. 2. Optimization of reagent concentration and element separation. First attempt (A) shows significant overlap of elements. Adjusting concentrartions and volumes (B) results in cleaner chemical separation and higher sample recovery

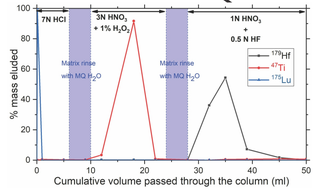


Fig. 3. Optimized separation of Hf, Ti, and Lu necessary for high-precision, interference-free analysis of Hf isotope compositions in PM

RESULTS

1) Detrital zircon U-Pb ages are consistent with provenance primarily in the Brasiliano belt and the northly Suasas orogen and the Rondonian San Ignacio belt. This provenance may indicate a north-south, axial, drainage pattern during Triassic deposition of the Ipaguazu Formation.

2) Combined U-Pb and Hf(t) results show a decrease in Hf(t) values that indicates an increase in crustal recycling from the Archean to the Devonian.

3) Detrital zircons derived from the Central Amazon Craton have moderately juvenile Hf(t) values indicating the craton formed from a recycled older crustal source.

4) The highest Hf(t) values are interpreted to be from detrital zircon grains sourced from back-arc plutons in the Rondonian San Ignacio belt, which could have provided this juvenile crustal material..

The Solution

U-Pb dating (A) of zircon crystals (B) from the Red River anorthosite suite indicate that igneous crystallization occurred between about 0.95 - 1.0 billion years ago (red analyses in A). In addition, there was significant partial resetting of these zircon grains at about 420 million years ago (blue analyses in A). The rare-earth element compositions of the two groups of zircon crystals (C) show that the reset zircons were hydrothermally altered older zircons and were not newly grown. Hf isotopic data (D) support that interpretation and also indicate that the anorthosite formed from isotopically evolved crustal sources, similar to other units in the Blair River inlier, but which would be even more isotopically evolved than other 420-435 million-year-old (Silurian) rocks. This indicates that the Red River anorthosite is not anomalously young and new mechanisms for its origin are not required. We anticipate that Hf isotopic analysis of the 435 million-year- old zircon crystals analyzed by Keppie et al., (2019) and Shellnut et al., (2020) would clarify the discrepancy between prior age interpretations and more recent ones.

References Cited:

Keppie, J. D., et al. (2019). "Silurian UPb zircon intrusive ages for the Red River anorthosite (northern Cape Breton Island): Implications for the Laurentia-Avalonia boundary in Atlantic Canada." Gondwana Research 73: 54-64.

Miller, B. V., et al. (1993). New U-Pb data from the Blair River Complex, northern Cape Breton Island, Nova Scotia, Canada, Geological Society of America, Northeastern Section, 28th annual meeting, Anonymous, Boulder, CO, United States, Geological Society of America (GSA), 25: 2: 64.

Peppers, M., Gehrels, G., Pullen, A., Ibanez-Mejia, M., Ward, K.M., and Kapp, P., 2016, Magmatic history and crustal genesis of western South America: Constraints from U-Pb ages and Hf isotopes of detrital zircons in modern rivers: Geosphere, v. 12, no. 5, p. 1532–1555.

Shellnutt, J. G., et al. (2020). "Formation of Anorthositic Rocks within the Blair River Inlier of Northern Cape Breton Island, Nova Scotia (Canada)." Lithosphere 2020(1): 1-21.

Yuan, H., Gao, S., Liu, X., Li, H., Gunther, D., Wu, F., 2004, Accurate UPb Age and Trace Element Determinations of Zircon by Laser Ablation Inductively Coupled Plasma Mass Spectrometry: Geostandards and Geoanalytical Research, v. 28, no. 3, p. 353–370.