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Mission to Very Early Earth

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Summary

The Hadean Earth is often viewed as an inhospitable and, perhaps, unlikely setting for the rise of primordial life. However, carbonaceous materials supplied by accreting meteorites and sources of chemical energy similar to those fueling life around modern deep-sea volcanic vents would have been present in abundance. More questionable are two other essential ingredients for life – liquid water and clement temperatures. Did the Hadean Earth possess a hydrosphere and temperate climate compatible with the initiation of biologic activity? If so, the popular model of an excessively hot planetary surface characterized by a basaltic crust, devoid of continental material is invalid. Similarly, establishment of an Hadean hydrosphere prior to the cessation of heavy asteroid bombardment may mean that primitive life could have evolved and then been extinguished, only to rise again. The most effective means of determining the environmental conditions on this young planet is through geochemical analysis of samples retrieved from the Early Earth. While rocks older than 4 billion years (4 Ga) have not been found, individual zircon grains, the detritus of rocks long since eroded away, have been identified with ages as old as 4.4 Ga – only ~160 million years younger than the Earth itself. If we can use the geochemical information contained in these unique samples to infer the nature of their source rocks and the processes that formed them, we can place constraints on the conditions prevailing at the Earth's surface shortly after formation. This project utilizes a combined analytical and experimental approach to gather the necessary geochemical data to determine the parameters required to relate the zircons to their parent materials. *Mission to Early Earth* involves dating, isotopic and chemical analyses of mineral and melt inclusions within zircons and of the zircons themselves. The major experimental activity at LLNL focused on the partitioning of trace elements between zircon and melt to elucidate the relationships between host zircons and mineral inclusions and between zircons and crustal fluids. *Mission to Early Earth* utilizes a broad array of new analytical facilities at LLNL supporting a variety of national security programs and has already become instrumental in developing these instrumental capabilities and a new cadre of qualified users for this and more applied programs.

Introduction/Background

The origin of life on Earth and other planetary bodies has long fascinated mankind. The question of “How life on Earth evolved” is intimately related to another, perhaps more tractable, question “When did the Earth become suitable for habitation?” The later

question is relevant regardless of whether life evolved on Earth or, if as some suggest, life “arrived” on Earth from an extraterrestrial source [Davis and McKay, 1996]. The establishment of conditions suitable for life on Earth is the end product of our planet’s earliest geologic evolution, and the differentiation of the terrestrial hydrosphere and atmosphere. Insights into the early geological evolution of the Earth can be gleaned from comparative planetology, the study of other planetary bodies whose geologic processes may have been “quenched” in antiquity, providing snapshots of the potential evolutionary paths. For instance, the lunar surface provides an impressive record of meteorite impact and planetary volcanism that dominated its (and presumably the Earth’s) early evolution. The most obvious shortcoming of this approach is the relevance of another planet’s evolution to that experienced by Earth. Alternatively, the geologic record provides a wealth of chemical information potentially related to the evolution of the atmosphere and hydrosphere. The major shortcoming of this approach is that terrestrial samples may be more accessible in space, but not necessarily in time. The dynamic nature of the Earth has erased the oldest geologic record through erosion, metamorphism and melting, and recycling of material back into the Earth’s interior by plate tectonic processes. Planetary mixing processes not only obscure the necessary chemical signatures, but also reset the isotopic clocks that enable quantitative dating. Fortunately, this recycling system is imperfect and samples of great antiquity, though rare, have been found. The oldest rocks yet found on the Earth – the Acasta Gneiss from northern Canada – are 4.0 billion years old [Bowring and Williams, 1999]. However, the discovery of ≥ 4.3 billion year old (4.3 Ga) mineral grains, detrital zircons from Jack Hills, West Australia, provides unique remnants of magmatic processes on the nascent Earth pre-dating the rock record by 400 million years. The Jack Hills zircons offer a unique opportunity to probe environmental conditions during the earliest phase of Earth evolution [Mojzsis et al., 2001; Peck et al., 2001; Wilde et al., 2001; Cavosie et al., 2004] and constitute the major focus of the Mission to Very Early Earth.

The Mission to Very Early Earth (MVEE) is a multi-institution project utilizing samples preserved from the earliest epoch of Earth’s history. The project involves elements of discovery and inversion and is analogous to a planetary sample return mission with the notable exception that MVEE is an adventure in time rather than in space. The “discovery” component involves acquisition of new, previously inaccessible, chemical, isotopic and mineralogical data from a unique suite of samples. Zircons are chemically refractory and the sedimentary grains from Jack Hills are expected to retain faithfully the chemical characteristics of the early Earth, 4.4 Ga ago [Valley et al., 2002b; Cavosie et al., 2005]. However, while providing an invaluable geologic tracer, zircons constitute only a very small portion of the Hadean lithosphere. The Jack Hills zircons are actually the sedimentary detritus derived from erosion of granitic source rocks no longer extant. As such, it is critical to relate the composition of the zircon to that of the rock from which it crystallized and, in turn, the composition of the rock to that of the early Earth’s mantle. This inversion requires new experimental data relating chemical and isotopic distribution patterns measured in old zircons to those inferred for the source rocks. The key element we bring to MVEE is the capability to garner these essential data, through the micro-scale characterization of Jack Hills zircons and synthetic materials produced at LLNL. These activities are strongly linked to activities at other institutions

and share a common set of samples, namely, a population of ~100 detrital zircons from Western Australia with ages of greater than 4000 million years.

Research Activities

The research activities and primary results of this project are summarized in three manuscripts (attached) submitted for publication. These publications describe a series of experimental activities focused on the partitioning of trace elements between fluids and crystallizing solids. These data are essential to understanding the trace element compositions of the Jack Hills zircons and the coexisting mineral inclusions and to using these data to address issues ranging from early planetary differentiation and core formation (metal–silicate interactions), to the characterization of geochemical reservoirs in the lower-mantle (solid-liquid silicate partitioning), to the trace-element characteristics of core-mantle interactions, and to the determination of the geochemical signature of lithospheric material subducted in the lower mantle and its influence on upwelling material at the source of hotspot volcanism.

Mineral-fluid partitioning of trace elements in phlogopite and clinohumite at subduction zone pressures and temperatures: implications for fluid transport in the mantle wedge [Feinmann et al, 2007; UCRL-JRNL-227472] describes measurements of mineral-fluid partition coefficients for Cs, Rb, Ba, Th, U, Nb, Ta, Pb, and Sr in phlogopite, and for Nb and Ta in clinohumite, at 800-900°C and 1.0-3.0 GPa, conditions comparable to those in subduction zones. All of the elements studied are compatible in phlogopite with the exception of U. Large ion lithophile elements (LILE; e.g. Rb, Ba, Sr, and Pb) are strongly compatible in phlogopite. LILE abundances in subduction zone volcanics are widely interpreted to be a direct signal of fluid contribution from the slab; however, as little as 1% phlogopite in the mantle wedge is sufficient to immobilize LILEs if the fluid is traveling sufficiently slowly to equilibrate with the mantle. Therefore, the observed enrichment of LILEs in arc magmas provides important constraints on modes of fluid transport in the mantle wedge. In addition, we find that clinohumite may play an important role in determining high field strength element mobility in the slab and mantle wedge.

Experimental study of radium partitioning between anorthite and melt at 1 atmosphere [Miller et al., 2007] describes the first experimental radium mineral/melt partitioning data, specifically between anorthite and a CMAS melt at atmospheric pressure. Ion microprobe measurements of coexisting anorthite and glass phases produce a molar $D_{\text{Ra}} = 0.040 \pm 0.006$ and $D_{\text{Ra}}/D_{\text{Ba}} = 0.23 \pm 0.05$ at 1400°C. Our results provide the first experimental confirmation that lattice strain partitioning models (Blundy and Wood, 1994) fit the divalent (Ca, Sr, Ba, Ra) partition coefficient data of this study well and support previous work on crustal melting and magma chamber dynamics that has relied on models to approximate radium partitioning behavior in the absence of experimentally determined values. The dominant mantle reservoir of radium below the plagioclase-peridotite field is likely clinopyroxene, except possibly in hydrous environments, where

phases such as phlogopite may play a significant role in radium storage at depth (Feineman and DePaolo, 2003). Given that Ra^{2+} has been shown here to be a well-behaved ion whose partitioning behavior is closely approximated by a lattice strain partitioning model (Blundy and Wood, 1994), this study lends further confidence to clinopyroxene/melt D_{Ra} estimates, typically on the order of 10^{-7} (Cooper et al., 2003), calculated from such models.

Chemical Imaging with NanoSIMS: A Window into Deep-Earth Geochemistry [Badro et al., 2007] describes novel chemical imaging using a combination of analytical transmission electron microscopy (ATEM) and nanometer-resolution secondary ion mass spectrometry (NanoSIMS) of material transformed in a laser-heated diamond anvil cell, in the pressure and temperature range of Earth's lower mantle. MORB (mid-ocean ridge basalt), one of the components of subducted oceanic lithosphere, was transformed to an assemblage of Mg-perovskite, Ca-perovskite, stishovite and a calcium ferrite-structure phase at 55 GPa and 2100 °C in a laser-heated diamond anvil cell (LH-DAC). Elemental imaging spanning the entire range of concentrations, from major elements such as silicon (49.5 wt% SiO_2), to minor elements such as titanium (1.8 wt% TiO_2), to trace elements such as strontium (118 ppm), scandium, and yttrium (both at 40 ppm) was obtained with the LLNL NanoSIMS. We observe preferential partitioning of scandium, yttrium and strontium in the calcium silicate perovskite phase and compare this behavior to recently measured solid-liquid partition coefficients and fractionation at lower pressures. This type of measurement demonstrates that even the most complex mineral assemblages can be probed using this combination of techniques and opens new pathways towards the characterization and quantification of geochemical interactions and processes occurring in the deep Earth. These experiments extend the pressure and temperature range where chemical analysis can be accomplished, making the laser-heated diamond anvil cell an experimental petrology tool, and opening up a new field of research in deep-Earth geochemistry.

Summary

The *Mission to Very Early Earth* makes use of a broad array of unique, microanalytical techniques at LLNL to evaluate the partitioning of trace elements between melts and crystals relevant to crustal recycling and the genesis of the Jack Hills zircons. The essential role of these facilities for this study is clearly evident. What should not be overlooked is their relevance to national security applications. In this sense, The *Mission to Very Early Earth* has much in common with strongly program-oriented applications in nuclear and chem/bio forensics. In each case investigators are challenged to determine the origin of samples with unknown provenance and then infer process information, either environmental or industrial, based upon chemical and isotopic signatures. The relationship between process and signature maybe only partially understood, requiring new experimental data. The same statement applies to investigations of meteorites, interplanetary dust and samples returned from planetary missions, all of which share the same analytical methods and expertise. As such, *The Mission to Very Early Earth* provides an opportunity to pursue an exciting research area, while building a cadre of

trained analysts available for more program-oriented applications and positioning LLNL for participation in future sample return missions.

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