EXPERIMENTAL MEASUREMENTS OF ZIRCON/MELT TRACE ELEMENT PARTITION COEFFICIENTS: KEY ISSUES AND POSSIBLE SOLUTIONS WITH Nano-SIMS.

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Introduction: Zircon is a chemically inert mineral that can survive the processes of weathering, transportation, diagenesis, metamorphism and even crustal melting. Magmatic zircons incorporate minor and trace amounts of geochemically important lithophile elements such as Sc, Y, the rare earth elements (REE), Ti, Hf, Th, U, Nb, Ta, V, and P [1, 2]. Therefore, zircon/melt partition coefficients (D values) of these elements can be used to estimate the trace element composition of the magma from which zircon crystallized. Such information is of particular interest to geochemist and petrologist who study the chemical composition and evolution of the Earth's crust [2]. For example, D values have been applied to Eoarchean detrital zircons to determine whether the trace element composition of the coexisting magma was tonalitic, granitic or mafic [3-6].

Experimental studies attempting to determine D values of zircon/melt are few because growing zircon crystals that are large enough on laboratory timescales to allow accurate in situ measurements of their trace element contents has remained extremely challenging [7]. In a pioneering study, Watson [8] measured D values for La, Sm, Ho and Lu at 0.2 GPa and 800°C for peralkaline melt. He used an electron microprobe to analyze synthetic zircons and then estimated trace element concentrations in run product glasses using a mass balance method. However, D values of REE peak at Ho rather than Lu, disagreeing with predictions made using the lattice strain crystal-melt partitioning model of Blundy and Wood [9]. Dickinson et al. [10] obtained partition coefficients of REE for zircon and coexisting high-SiO_2 and low-SiO_2 immiscible liquids using microprobe analyses, and their D values are much lower than those of Watson [8]. Subsequently, Okano et al. [11] synthesized zircon from melts with andesitic and pelitic compositions. They used isotope dilution mass spectrometry to measure concentrations of REE and Hf in separated zircon and matrix phases, and their D values were also lower than those of Watson [8]. Recently, Rubatto and Hermann [12] experimentally measured D (zircon/granite) values at 2 G Pa and 800-1000°C for P, Y, rare earths, Zr, Hf and Th and U. Because run product zircon crystals were very small (generally < 5 um), they estimated

concentrations using mixed analyses containing variable proportions of run product zircon and glass, and obtained D values again lower than those of Watson [8]. D values acquired by analysis of natural zircon/matrix pairs range over 4 orders of magnitude for Light REE and 2 orders of magnitude for heavy REE [7], the discrepancy is far more serious than the experimental studies highlighted above. Therefore, more precise experimental measurements are required to develop a clear understanding of such large variation of D values. Most recently, Luo and Ayers [13] have undertaken a series of experimental study designed to measure quantitatively and systematically the effects of temperature (800-1300°C), pressure (0.2-1.5 GPa) and oxygen fugacity upon the partitioning of a comprehensive set of trace elements between zircon and peralkaline melt. Compared to Watson [8] and Rubatto and Hermann [12], the progress of [13] is their success in growing bigger zircons, with the largest one up to 50 micron. This allows trace element concentrations measured in completely separated zircon and melt phases using electron microprobe and LA-ICP-MS, respectively.

Key issues: The outstanding problem remains: all the experimental studies including [13] show less fractionated HREE/LREE pattern compared to D values measured from natural phenocryst/matrix pairs by Sano et al. [14] that is able to reproduce known melt compositions. For example, when combined with compositions of "out-of-context" zircons such as the Eoarchean detrital zircons from Jack Hills, Australia and zircon xenocrysts in the Acasta gneisses, using D values from [14] yields LREE-enriched source rocks while the use of experimentally determined D values from [13] yields LREE-depleted source rocks (Fig. 1) [13]. It is likely that all experimentally measured D values underestimate the amount of fractionation because sub-micron scale diffusive boundary layers (Fig. 2) develop as a result of rapid zircon growth during the short timescale experiments. As the rate of zircon growth is greater than the rate of diffusive supply of REE in the melt to the zircon/melt interface [13], we hypothesize that incompatible elements concentrate and compatible elements become depleted near the surface of the growing zircon crystal [15]

according to [16, 17]. This effect increases concentrations of incompatible elements in the boundary-layer melt and thus in the zircon, while decreasing concentrations of compatible elements in the boundary layer melt and therefore in the zircon [15].
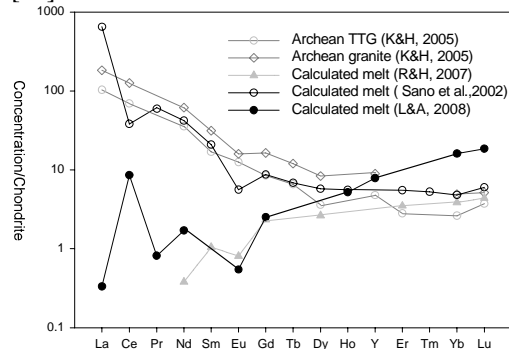
Fig. 1: Comparison of calculated melt composition in equilibrium with Hadean zircons using D values measured by granitic melt at 800°C reported in [13] (labeled "L&A"), in [12] (labeled "R&H"), in [14] (labeled Sano et al.) and average concentrations of REE in Archean TTG and granite [18] (labeled "K&H").
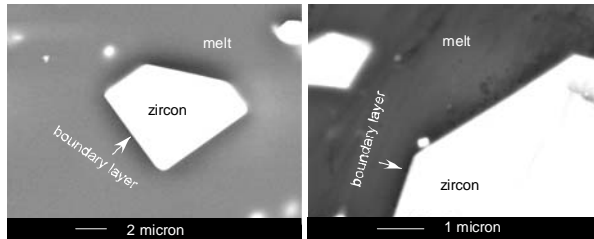
Fig. 2: Two backscattered electron images of compositional boundary layer (<1 micron) evident in glass near the interface of zircon/melt from experiment run at 0.2 GPa and 800°C.

In [13], electron microprobe analysis is not sensitive enough to measure the trace elements of run product melts. Although LA-ICP-MS is sensitive, the relatively low spatial resolution (>10 micron) requires melt concentrations be measured far from the crystal-melt interface. Equilibrium concentrations of zircon and melt, however, are likely present only at the crystal-melt interface, which is generally less than 1 micron wide. Thus, novel nano-scale analytical methods with spatial resolutions of < 1 um are required to accurately determine D (zircon/melt) values in experimental zircon growth studies.

Proposed Solutions: We therefore propose to use Nano-SIMS to analyze the interface of zircon rims and diffusive boundary layers with sub-micron resolution. This state-of-the-art *in situ* analytical technique has the ability to extend the *in-situ* analysis to extremely small areas or volumes (~50 nm size with a cesium primary beam, ~150 nm with an oxygen primary bean) while maintaining high sensitivity at high mass resolution with detection limits at levels below 100 ppmw [19]. Such analytical advantages would be particularly attractive to solve the key issues of the current experimental study.

Significance: The scarcity of accurate, systematic experiments, plus the large discrepancy in D values for zircons limit our ability to calculate melt compositions, especially for detrital zircons to which the source-rock composition is missing [7]. Using Nano-SIMS for *in-situ* analysis at zircon/melt interface holds the promise to obtain more accurate zircon/melt D values in experimental studies. High quality D values would have major implications for the use of detrital zircon grains from the Jack Hills, Australia, the oldest known terrestrial mineral [20] to calculate parent magma compositions and hence the trace element composition of 4400 Ma old crust [7]. Combined with previously determined zircon REE composition [3, 21], oxygen isotope ratios [3, 6, 22, 23, 24], Ti thermometry [6, 24, 25] and Hf isotope composition of Hadean zircons [24, 26], inferred trace element composition of Hadean magma using accurate D (zircon/melt) values would place important constraints on the evolutionary history of the Hadean Earth.

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