

**PARTITION COEFFICIENTS FOR REE AND Hf BETWEEN ZIRCON AND LIQUID: INFERENCES FOR LUNAR GRANITE PETROGENESIS;** Osamu Okano,<sup>1</sup> E. Bruce Watson,<sup>2</sup> and Mitsunobu Tatsumoto,<sup>1</sup> <sup>1</sup>U.S. Geological Survey, Federal Center, Denver, CO 80225, <sup>2</sup>Department of Geology, Rensselaer Polytechnic Institute, Troy, NY 12180-3590.

**INTRODUCTION.** Knowledge of zircon/liquid partition coefficients for trace elements such as REE, Y, Hf, U, and Th is important to detailed trace element models of lunar felsic magma production and evolution [e.g. 1,2]. In order to place better constraints on models for lunar petrogenesis using REE and Hf isotopes, we have previously determined REE, Hf and Zr partitioning in apatite and zircon [3,4] using naturally-occurring andesites and granite. The zircon/groundmass partition coefficients obtained for REE are similar to those of Nagasawa [5], which were also obtained from naturally-occurring zircon. The coefficients for LREE are 1 to 7 but those for HREE are larger than 100 (Fig.1). The partition coefficients for Lu and Hf are about 300 and 700, respectively. However, the coefficient pattern for REE was markedly different from that of Watson [6], which was obtained from zircon grown in the laboratory from a peralkaline, felsic melt. The partition coefficients for REE obtained by Watson are: La, 1.4-2.1; Sm, 26-40; Ho 340+; Lu, 72-126 and the heavy REE end of the pattern is concave downward (Fig.1). The partition coefficients obtained also from synthesized zircon using a KREEP basalt by Dickinson et al. [7] are even smaller than Watson's (Fig. 1). Thus, more consistent measurements for zircon /liquid partition coefficients for REE, Hf, U, Th, and Pb are needed. We report preliminary results on the partition coefficients for REE and Hf.

**EXPERIMENTS.** Zircon was synthesized from two synthetic composition, one a siliceous "andesite" (AA,  $\approx 60\% \text{SiO}_2$ ), the other a typical pelite (BTC,  $\approx 65\% \text{SiO}_2$ ). The compositions were previously used for a zircon saturation study [8]. The starting materials were each doped with 100 ppm for six REE and 300 ppm for Hf. The runs were made in sealed gold capsules initially containing 160 mg of glass powder and 8.3 wt%  $\text{H}_2\text{O}$  for a duration of 9 days at 1000°C in a piston-cylinder apparatus at approximately 10 kbar. The runs yielded about 2 % zircon in the charge. The zircon crystallized from composition AA ranged from 1 to 10  $\mu\text{m}$  in diameter and from BTC was 5-15  $\mu\text{m}$ . The run products were crushed and sieved below 50  $\mu\text{m}$ . Zircon fractions were concentrated using a Frantz isodynamic separator equipped with an alcohol filled chute. Zircons were treated with HF for dissolution of matrix material. Only 0.2 mg of AA zircons were recovered. The zircons on the bottom of BTC gold capsule were accidentally lost and only very fine zircon crystals floating in the glass were recovered. Pure matrix was also obtained from the isodynamic separation. Sub-micron zircon crystals which may have existed in the matrix may not have been dissolved by the usual HF dissolution procedure for silicates. Zircon was dissolved with isotope-spikes using HF in a Krogh [9] type Teflon bomb for two weeks at 210°C. Concentrations of REE and Hf in the zircons and matrices were determined by isotope dilution mass spectrometry.

**RESULTS and DISCUSSION.** The results for partition coefficients of zircon/liquid for REE and Hf are shown in Fig. 1. The partition coefficients obtained for AA increase smoothly from Ce  $\approx 2$  to Lu  $\approx 29$  for REE, but not to several hundreds for Lu as reported for naturally occurring zircon. However, the partition coefficient for Hf obtained for AA is  $\approx 190$  and slightly lower than that for natural zircon. The partition coefficients for Ce and Lu obtained for AA are similar to those of Watson's [6] which were obtained with glass + ZrN +  $\text{AgNO}_3$ . However, the coefficients for the middle REE do not increase to form a concave downward partition coefficient pattern. The partition coefficients obtained from BTC floating zircon are even smaller for LREE (0.25 for Ce and 28 for Lu) and similar to those of Dickinson et al. [7]. At present, we have not any explanation for the difference in results between these two experiments, except difference in glass compositions.

Two viable processes regarding petrogenesis of lunar granite have been proposed; fractional crystallization [e.g. 10] and liquid immiscibility [e.g. 11]. The lunar felsites ("lunar granite") and gray breccias have peculiar bowl-shaped REE patterns which are quite different from those of LREE-enriched, black, basaltic breccia or KREEP. If partition coefficients for HREE are as large as those of natural zircon, zircon crystallization cannot account for the bowl-shaped REE pattern

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unless apatite and/or whitlockite dominates the fractionation [1,3]. If newly obtained partition coefficients for REE and Hf from AA composition are reliable, there is a possibility that zircon crystallization played a role in the late stage evolution of lunar magmas. However, if those from BTC are appropriate values at lunar conditions then zircon crystallization is precluded from playing a major role in the evolution [1].

Lunar felsites and gray breccias have higher Lu/Hf values and are less enriched in Hf than black, basaltic breccia and KREEP [2]. Fractional crystallization of zircon may also help to explain the Lu-Hf features of lunar granites.

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Fig. 1. Zircon/liquid partition coefficients for REE and Hf compared with data of [4], [5], [6], and [7].

