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Th and U partitioning between monazite and felsic melt

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ABSTRACT

We present experimental measurements of monazite/melt partition coefficients ($K^{monz/melt}$) for thorium (Th) and uranium (U) in haplogranitic Na_2O–Al_2O_3–SiO_2 melts (with 6–10 wt.% H_2O) at 900 °C–1100 °C and 1 GPa pressure. Our results show the following trends: (1) K_{Th} and K_U in felsic melts are strongly dependent on melt Al/Na. Both partition coefficients reach maxima in mildly peraluminous region and decrease toward strongly peraluminous ($Al/Na > 1$) and peralkaline ($Al/Na < 1$) melt compositions. K_{Th} and K_U vary by 2 orders of magnitude for Al/Na in the range of 0.4 to ~2. (2) For identical melt compositions, the effect of temperature on K_U is pronounced: A 200 °C increase in temperature results in a 6-fold decrease in K_U. In contrast, the same temperature change results in only 50% decrease of the less temperature-sensitive K_{Th}. (3) One experiment with 10 wt.% H_2O added does not change K, which may suggest little dependence of K upon water content from 6 to 10 wt.%. (4) K_{Th} is much larger than 1 at all natural magmatic temperature, so the removal of monazite during fractionation crystallization or its retention as a residual phase during partial melting has a significant effect on the content of Th in the coexisting melt phase. (5) U is much less compatible than Th, and could even behave incompatibly at high temperatures (e.g., at 1000 °C, K_U is 0.01 for melts containing 75 wt.% SiO_2 and Al/Na ~ 0.4).

1. Introduction

Granitic rocks contain as much as 40 wt.% of the Th and U in the continental crust (Van Schmus, 1995), and monazite is one of the main hosts for these elements (Miller and Mittlefehldt, 1982; Bea, 1996). Gavrilova and Turanskaya (1958) showed that up to 90% of the bulk-rock Th and U content in monazite-bearing felsic rocks is contained in monazite. Moreover, because of the ubiquitous distribution of this mineral and its notable resistance to radiation damage (Meldrum et al., 1998), Th and U in monazite may retain geochronological and tectonic information through metamorphism and partial melting. Trace element partitioning between mineral and melt is an important parameter for deciphering trace element behavior in petrogological processes. Skora and Blundy (2010) and Stephov et al. (2012), for example, explored the temperature, pressure and water effect on monazite-melt partition coefficients, but neither of these studies provides systematic information on the effect of melt structure on partitioning. Complete understanding of the factors that control Th and U partitioning between monazite and coexisting melt will further our ability to model and interpret the behavior of these elements during crustal magma production and differentiation.

Our experiments focused on evaluation of the effects of melt composition and temperature (900–1100 °C) on Th and U distribution between monazite and hydrous sodium aluminosilicate melts at 1 GPa. Because 90 wt.% of common felsic melts are alkali aluminosilicate components, we used simple Na_2O–Al_2O_3–SiO_2 (NAS) melts as analogs for more complex natural melt compositions in order to simplify the analyses of the experimental run products and the interpretation of our results. The significance of the experimental results to models of Th–U distribution during generation and evolution of felsic magmas is discussed. The dependence of Th and U partitioning on liquid composition is explained in terms of silicate melt structure.

2. Experimental system and methods

2.1. Starting materials

All experiments described in this paper were performed at the same pressure (1 GPa), so the observed difference in partitioning behavior could be attributed solely to differences in starting melt composition and temperature. The starting materials are chosen based on two considerations: 1) the experiments should start with a simple system rather than natural compositions, because relatively little is known about the molecular structure of natural melts. In addition, potassium should be avoided because of X-ray interferences between the uranium Mβ and potassium Kα lines, and the large uncertainty associated with measurement of trace amounts of UO_2 in the glass by microprobe. 2) Felsic melt compositions are preferred because monazite is very common in granites, especially in S-type granite, but rare in mafic systems. Sequestration of Th and U in melting residues and fractional crystallization of monazite are potentially important for the trace element evolution of felsic magmas (Miller and Mittlefehldt, 1983; Watt and Harley, 1993). For these reasons, we used felsic melts in the Na_2O–Al_2O_3–SiO_2 system as the starting glasses. Homogenous glasses were prepared by

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Table 1
Summary of run information, starting materials and monazite/melt partition coefficients. All experiments were conducted at 1 GPa.

Run	T (°C)	Run duration (hours)	H_2O (wt.%)	Al/Na (atomic ratio)	SiO_2 (wt.%)	K (Th)	K (U)	Phases in addition to Mz & glass
MON21_L	1000	48	6	1.92	75	118	0.47	Corundum
MON21_R	1000	48	6	1.94	75	92	0.4	Corundum
MON22_2	1000	48	6	1.60	75	72	1.91	
MON22_L	1000	48	6	1.12	75	169	2.87	ThO_2 and UO_2
MON22_R	1000	48	6	1.53	75	158	7.05	
MON24_1	1000	48	6	1.33	75	235	6.91	
MON24_2	1000	48	6	1.32	75	271	3.66	
MON24_3	1000	48	6	1.28	75	306	3.29	
MON26_L	1000	48	6	1.16	75	127	5.89	Corundum
MON26_R	1000	48	6	0.73	75	13	0.5	
MON29_2	1000	48	6	1.07	75	224	1.76	
MON30_1	1000	48	6	0.92	75	121	1.23	
MON30_2	1000	48	6	0.4	75	5	0.1	
MON33_L	1100	12	6	1.67	75	129	3.87	Corundum
MON33_R	1100	48	6	1.11	75	152	1.89	
MON34_1	1100	48	6	1.67	75	141	4.26	Corundum
MON34_2	1100	48	6	1.43	75	172	2.62	
MON34_4	1100	48	6	1.25	75	218	1.89	Corundum
MON37	900	192	6	1.25	75	87	26.82	Corundum
MON41_1	900	192	6	1.11	75	225	13.61	ThO_2 and UO_2
MON41_2	900	192	6	1	75	312	36.32	ThO_2 and UO_2
MON31_1	1000	48	6	0.77	70	24	0.3	
MON31_2	1000	48	6	0.79	70	27	0.4	
MON31_3	1000	48	6	0.81	70	32	0.32	
MON35_3	1000	48	6	0.83	70	244	3.01	
MON35_4	1000	48	6	1.25	70	31	0.17	Corundum

Fig. 2. BSE image of monazite crystals in experiment no. MON30_2 at 1000 °C with Al/Na = 0.4. Note that crystals are euhedral and free of discernible zoning.

decarbonation of 2 g of pre-weighed mixtures of Na_2CO_3, Al_2O_3 and SiO_2 in a Pt crucible at 850 °C for 12 h, followed by cooling the sintered mixes in air and grinding into powder. The powders were then fused for 6 h at 1200 °C. The quenched glass was coarsely crushed and ground to a powder, then mixed with the desired amounts of $CePO_4$ (~3 wt.%), ThO_2 (~0.1 wt.%) and UO_2 (~0.1 wt.%). In some cases, additional Al_2O_3 was added at this stage to adjust the Al/Na ratio. Starting glass compositions are shown in Table 1.

Twenty-six experiments producing monazite crystals and glass were conducted in an end-loaded piston-cylinder apparatus. Experiments above 1000 °C were run in Pt-lined oxidized Ni cylinders (Watson and Cherniak, 1997); experiments at 900 °C were run in silver capsules. Before each experiment, 6–10 wt.% of double distilled H_2O was added to the starting material using a syringe. This level of water was chosen as appropriate for H_2O-saturated crustal felsic melts, and also served the purpose of speeding up reaction kinetics and suppressing crystallization of silicate phases. The runs in Pt capsules consisted of two steps: 1. To help ensure homogeneity, the experiments were programmed to run up to 1300 °C (above the monazite solubility) for 2 h, then cooled to the final run temperature (1000 °C or 1100 °C) and held for an additional 48 h. This homogenization procedure was found to especially important for the strongly peraluminous starting materials. 2. Because of the low growth rate of monazite at 900 °C, seed crystals were added to the starting materials in these runs, and experimental conditions were maintained for 8 days in order to obtain a wide enough overgrowth rim for analysis. Run conditions of the 26 experiments are summarized in Table 1.

2.2. Analytical techniques

2.2.1. Electron microprobe analysis

The charges were sectioned and polished and carbon coated. At least 8 analysis spots were selected at random from monazite-free regions of the glass of each charge. Analyses of monazite with diameters as small as ~1 µm were conducted using a CAMECA-SX100 electron microprobe (EMPA) at RPI. All crystals were analyzed at 15 kV and a specimen current of 30 nA using a focused beam. For the H_2O-bearing glasses, however, a two-step protocol was required because of the dual challenge of limiting Na loss while at the same time collecting enough X-ray counts on U and Th. A low current-density beam (5 nA, 30 µm diameter) was used to reduce Na migration during analysis for major elements, but trace-element analyses (Ce, P, Th, U) required a higher

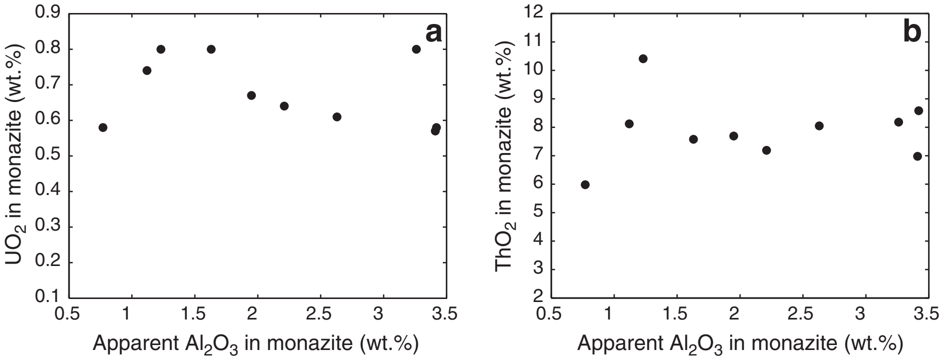

Fig. 1. ThO_2 (a) and UO_2 (b) dependence on the melt contribution in different analysis spots of MON24_2.