Contrib Mineral Petrol (1986) 94:42–45

Contributions to
Mineralogy and
Petrology

Partition coefficients of Hf, Zr, and REE between zircon, apatite, and liquid

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Abstract. Concentration ratios of Hf, Zr, and REE between zircon, apatite, and liquid were determined for three igneous compositions: two andesites and a diorite. The concentration ratios of these elements between zircon and corresponding liquid can approximate the partition coefficient. Although the concentration ratios between apatite and andesite groundmass can be considered as partition coefficients, those for the apatite in the diorite may deviate from the partition coefficients. The HREE partition coefficients between zircon and liquid are very large (100 for Er to 500 for Lu), and the Hf partition coefficient is even larger. The REE partition coefficients between apatite and liquid are convex upward, and large ($D=10$–100), whereas the Hf and Zr partition coefficients are less than 1. The large differences between partition coefficients of Lu and Hf for zircon-liquid and for apatite-liquid are confirmed. These partition coefficients are useful for petrogenetic models involving zircon and apatite.

Introduction

Patchett (1983) emphasized the importance of the Lu-Hf method not only for chronological study, but for petrogenetic implications as well and urged that more partition coefficient data be acquired. Fujimaki et al. (1984) reported the self-consistent sets of partition coefficients of Hf and REE between phenocrysts and liquids, and further demonstrated the usefulness of the Lu-Hf method in the discussion of lunar basalts (Fujimaki and Tatsumoto 1984). However, the self-consistent partition coefficients of Hf and Lu between zircon, apatite, and liquid had not yet been obtained. Those minor minerals, with which REE are compatible, have been thought to play significant roles in extreme cases of crystallization differentiation. Hafnium should be compatible with REE in zircon but incompatible in apatite; however, the partition coefficients have not been determined and the incompatibility/compatibility relationship not determined. In this paper, I report analytical results for Hf and REE in zircon, apatite, and coexisting liquids.

Samples and analytical method

Three samples were selected for the experiments, two augite-hypersthene andesites, and a biotite-hornblende quartz-diorite. The analytical results for the major elements are shown in Table 1. Before zircon and apatite were separated, the samples were analyzed by XRF for Zr and P_2O_5.

The andesite samples are essential lenses in welded tuffs, both consisting of plagioclase, hypersthene, augite, and magnetite phenocrysts and cryptocrystalline groundmass with minor amounts of plagioclase, pyroxenes, opaque minerals, apatite, and zircon in order of decreasing abundance. In the groundmass, some apatites are slightly larger than the other minerals, indicating that they are microphenocrysts. Some hypersthene phenocrysts include apatite. The cryptocrystalline minerals exceed 95% of the groundmass. Modal zircon is 0.012 (andesite 1) and 0.015% (andesite 2) of the groundmasses, and apatite 0.13% (andesite 1).

The diorite sample consists mainly of plagioclase, K-feldspar, quartz, hornblende, biotite, and magnetite with accessory of sphene, apatite, allanite, and zircon. The modal abundances of zircon and apatite are 0.003% and 0.12%, respectively. Most of the zircons are included in biotite or hornblende; the apatite gener-

Table 1. Analytical results of samples

wt% (Zr in ppm)	1[a]	2[b]	3[c]
SiO_2	64.86	63.21	65.52
TiO_2	0.78	0.79	0.68
Al_2O_3	17.14	17.60	15.76
Fe_2O_3	3.95	4.33	0.28
FeO	0.66	0.59	3.44
MnO	0.10	0.06	0.08
MgO	0.32	0.48	1.38
CaO	2.91	2.38	4.02
Na_2O	3.71	2.90	3.69
K_2O	2.40	2.34	2.94
P_2O_5	0.19	0.20	0.24
$H_2O(+)$	2.10	2.94	1.08
$H_2O(-)$	1.32	2.53	1.04
Total	100.44	100.35	100.15
Zr[a]	224	271	196
P_2O_5[d]	0.28	0.27	0.34
M[e]	1.29	1.04	1.65

Analyst: K. Aoki

[a] Groundmass of augite-hypersthene andesite from Kumamoto, southern Kyushu, Japan

[b] groundmass of augite-hypersthene andesite from Kagoshima, southern Kyushu, Japan

[c] Biotite-hornblende-quartz diorite from Kagoshima, southern Kyushu, Japan

[d] The Zr and P_2O_5 abundances were determined with an XRF before zircon and apatite were removed

[e] M value is cation ratio $(Na+K+2Ca)/(Al\times Si)$ (Watson and Harrison 1983)

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ally occurs along grain boundaries, although some are included in minerals.

Zircon was separated by hand-picking, washed in 2N HF in an ultrasonic cleaner, and rinsed in distilled water. Apatite was also handpicked, then washed in cold 1 N HCl for a few minutes and rinsed twice in distilled water in an ultrasonic cleaner. Although this process might have caused slight dissolution of the apatites, indication of leaching of the grain surfaces was not apparent. The zircon separates, I believe, are to be at least 99% pure. The apatite separates may be less pure (97%).

The groundmass portions of the andesitic rocks, from which zircon and apatite were removed, may contain fragmental phenocrysts. For the dioritic rock, the whole-rock split, after removal of zircon and apatite was used as an approximation to the coexisting liquid. I attempted to retain sphene and allanite in the whole-rock fraction, but some may have been lost.

The Hf, Zr, and REE abundances were determined by the isotope dilution method. The chemical procedures to separate the elements have been described previously, and the accuracy and precision of the results are the same as those reported by Fujimaki et al. (1984).

The homogeneity of the minerals was checked with an electron probe microanalyzer using the separated minerals as well as the thin sections. The minerals are almost homogeneous with respect to major elements. A synthetic glass (Ce_2O_3 15.2%, HfO_2 15.1%, SiO_2 69.7%) was used as a standard to check the trace element distributions in the minerals. The operating conditions were 20 kV and 0.025 μA in a Faraday cup. Although special care was taken during analysis, the counting statistics indicated an error of 12%–25% (1σ). The trace element distributions (grain-to-grain, and core-to-rim) are as follows: cerium contents in the apatites range from 0.07 ± 0.01 (core) to 0.09 ± 0.02 (rim) wt% (andesite 1), and from 0.09 ± 0.01 (core) to 0.22 ± 0.03 (rim) wt% (diorite); hafnium abundances in the zircons vary from 0.39 ± 0.02 (core) to 0.42 ± 0.04 (rim) wt% (andesite 1), 0.49 ± 0.02 (core) to 0.52 ± 0.03 (rim) wt% (andesite 2), and 1.0 ± 0.53 (core) to 1.3 ± 0.23 (rim) wt% (diorite).

Results and discussion

The Hf, Zr, and REE concentrations in the samples are presented in Table 2 with the calculated concentration ratios. On the assumption that these ratios approximate partition coefficients, the patterns are plotted in Figs. 1 and 2. In the following, I discuss whether thay can approximate the partition coefficient patterns. Although the concentration ratios of phenocryst/groundmass coefficients are generally accepted as the partition coefficient and used for petrogenetic modelling, the partition coefficients for minor phases such as zircon and apatite should be treated with caution as pointed out by Haskin and Korotev (1977). This is because the minor phases may grow from late differentiated liquid (mesostasis) and be considerably zoned in incompatible elements (Gromet and Silver 1983). Although the microprobe analyses demonstrated that the zircons and apatites in the andesites are not significantly zoned, those in the diorite are zoned, and large differences among the grains are noticed. Therefore, close attention should be given to the treatment of the minerals in the diorite.

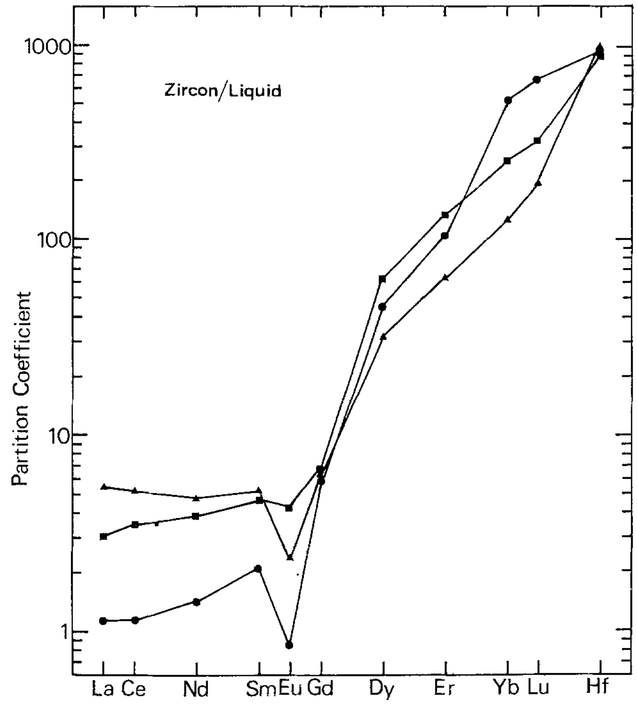

Fig. 1. Hf and REE concentration ratios, presumably partition coefficients, between zircon and liquid. Solid squares: zircon in andesite 1, Solid triangles: zircon in andesite 2, solid circles: zircon in diorite

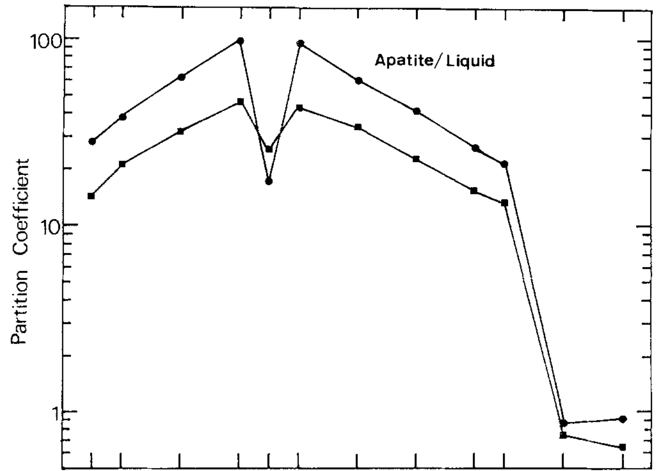

Fig. 2. Hf, Zr, and REE concentration ratios, presumably partition coefficients, between apatite and liquid. Solid squares: apatite in andesite 1. Solid circles: apatite in diorite

Watson (1979a) demonstrated, on the basis of experimental results, that non-peralkaline felsic silicate melt is saturated with zircon at Zr concentrations as low as 100 ppm. Recently, Watson and Harrison (1983) revised the Zr saturation value to that for a normal peraluminous granite; the value ranges from ~100 ppm at 750° C to 1,330 ppm at 1,020° C. According to their treatment of the melt, I have calculated M values for my specimens and presented them in Table 1. The pyroxene thermometry (Wells 1977) indicates that the pyroxene phenocryst equilibration temperatures (CPX rim to OPX rim) were 850° C for andesite 1 and 870° C for andesite 2. The groundmass liquidus temperatures should be lower than these temperatures. Since they have low M values and their Zr concentrations (before zircon and apatite separation) are 224 and 271 ppm (Table 1), respectively, zircon can be a liquidus phase of the groundmasses. The zircons, uniformly distributed in the andesite groundmasses, are independent grains of euhedral to subhedral shape; this should be a strong indication that zircon is a groundmass liquidus phase, and

Table 2. REE, Hf, and Zr concentrations and concentration ratios

Sample[a]	1			2		3		
	Gm	Ap	Zr	Gm	Zr	Gm	Ap	Zr
ppm								
La	19.3	280	60.0	27.6	145	22.2	626	25.3
Ce	36.7	774	128	49.0	252	47.5	1,777	55.6
Nd	14.7	482	55.9	18.1	86.3	23.9	1,463	33.0
Sm	2.52	116	11.9	3.04	15.7	5.38	530	10.9
Eu	0.518	13.2	2.19	0.756	1.81	1.47	25.1	1.25
Gd	3.19	140	21.6	4.32	27.7	5.71	546	34.3
Dy	3.85	134	244	4.17	131	5.40	329	242
Er	2.35	53.3	317	2.09	135	2.24	93.2	240
Yb	2.27	35.0	576	1.86	238	1.48	40.8	764
Lu	0.348	4.80	116	0.268	52.5	0.190	4.09	131
Hf	4.26	3.11	4,081	5.16	5,145	11.45	10.1	11,167
Zr	96.6	62.4		152		170	154	
Concentration ratios								
La		14.5	3.11		5.25		28.2	1.14
Ce		21.1	3.49		5.14		37.4	1.17
Nd		32.8	3.80		4.77		61.2	1.38
Sm		46.0	4.72		5.16		98.5	2.03
Eu		25.5	4.23		2.39		17.1	0.850
Gd		43.9	6.77		6.41		95.6	6.01
Dy		34.8	63.4		31.4		61.0	44.9
Er		22.7	135		64.6		41.6	107
Yb		15.4	254		128		27.6	516
Lu		13.8	333		196		21.5	689
Hf		0.730	958		997		0.878	971
Zr		0.636					0.906	

[a] Sample numbers are the same as those in Table 1. Gm: groundmass or whole-rock split with zircon and apatite removed; Ap: apatite; Zr: zircon

not a mesostasis phase. Therefore the obtained concentration ratios of Hf and REE of zircons in the andesite groundmasses can represent partition coefficients between zircon and liquid.

The zircons in the diorite are mostly included in biotite and hornblende, demonstrating that they started crystallizing at a relatively early stage of solidification. Applying two-feldspar geothermometer (Stormer 1975; Powell and Powell 1977), seven sets of plagioclases and their inclusions of non-exsolved alkali-feldspars provide the equilibration temperature of 600° C–720° C under 1–10 kb. Although the thermometer will not provide correct liquidus temperature (Brown and Parsons 1981), the obtained range qualitatively demonstrates that the liquidus temperature should be very low. Therefore, even though the M value is 1.65, zircon can crystallize as a liquidus phase in the diorite whole rock system which has 196 ppm Zr. Nevertheless, the concentration ratios between zircon and the dioritic whole-rock split seem slightly different from the partition coefficients obtained from the andesite samples (Fig. 1). Watson's experimental results (1979a) also indicate that Zr solubility increases with molar Na_2O+K_2O/Al_2O_3 ratio in the liquid. In a peralkaline liquid, a large amount of Zr is required to precipitate zircon. I consider that the zircon started crystallizing in an early stage of solidification of the diorite magma, but enrichment in Na_2O and K_2O in the residual system might have slowed its growth. Therefore, the result obtained should be regarded as integrated over the entire stage of solidication.

The HREE partition coefficients between zircon and liquid are extremely large (more than 100), whereas the LREE partition coefficients are small (less than 10). Similar features were described by Nagasawa (1970). As Patchett et al. (1981) estimated, the Hf partition coefficients between zircon and liquid are two to five times larger than D_{Lu}, suggesting that zircon fractionation will effectively fractionate Hf from Lu. The D_{HREE} and D_{Hf} are so large, and so influential, that even if zircon comprises only 1% of the fractionating phases, the residual liquid will be more depleted in HREE and Hf than the parental liquid.

The experimental results indicate that apatite saturation is dependent on temperature, SiO_2 and P_2O_5 contents in the melt (Watson 1979b), and in general, the more silicic the melt is, the less P_2O_5 will be required to reach saturation in apatite. In a basaltic magma, more than 4% P_2O_5 is needed (Watson 1979b), but in an intermediate peralkaline magma only 1–1.5% P_2O_5 is required to precipitate apatite (Carmichael 1967) and 0.2% P_2O_5 is enough to precipitate apatite in a felsic melt (Watson and Capobianco 1981). Although the groundmass separate (andesite 1) is less silicic than Watson and Capobianco's (1981) experimental materials, it contains 0.28% P_2O_5, and the possibility that apatite is a near-liquidus phase of the groundmass cannot be ignored. The occurrences of apatite of microphenocryst as well as as inclusions in phenocryst hypersthene also imply that they can be a near-liquidus phase of the andesite groundmass system. Consequently, the obtained concentration ratios can be taken as an approximation of the partition coefficients.

However, as for the apatite in the diorite sample, the obtained concentration ratios may not be partition coefficients. Large and euhedral apatites mostly appear at grain boundaries, and some grains are included in feldspars, hornblende, and biotite. The occurrence implies that they started crystallizing with these minerals, and continued until all the residual liquid was consolidated, but the amount of crystallizing apatite was small in an early stage of solidification, then increased at the latest stage. It is possible that only feldspars, quartz and zircon grew during the early crystallization stage; if so there would have been a parallel increase in incompatible elements in the residual liquid, without significant changes in REE pattern (except Eu) and relative abundances of Hf and Zr, because of the negligible amount of zircon present. If this is the case, the obtained concentration ratios are probably higher than the true partition coefficient between apatite and liquid because modal quartz and feldspar amount to 78.7%. Assuming that all feldspars and quartz crystallized before apatite started crystallizing, and that no REE, Hf and Zr were contained in them, the elemental abundances of REE, Hf and Zr in the liquid coexisting with apatite should be four times higher than the measured values. The concentration ratios are, accordingly, smaller than one fourth of the calculated ones. The reduced values are within the range of the partition coefficients determined experimentally (Watson and Green 1981). Therefore, the measured concentration ratios for apatite-diorite pair should be regarded as qualitative approximations of the partition coefficients.

The REE partition coefficients between apatite and the andesite groundmass are essentially the same as those reported by Nagasawa (1970) and Watson and Green (1981). Apatite is not believed to contain significant amount of quadrivalent cations such as Hf and Zr. Therefore, even though the Hf and Zr partition coefficients are 0.01 to 0.2 times those of the REE, they are unexpectedly large. Although this might be due to possible impurities in the mineral separates, the obtained partition coefficients for the apatite-groundmass pair may be useful for petrogenetic modelling until more plausible data become available. Apatite fractionation, if dominant, effectively decreases middle REE concentrations, whereas Hf and Zr abundances will be increased.

Concluding remarks

The obtained concentration ratios of Hf, REE for the zircon can approximate the partition coefficients, and so can those of Hf, Zr, and REE for the apatite in andesite. However, the concentration ratios for apatite in diorite may less accurately represent the partition coefficients and should be regarded with suspicion.

The REE, Hf and Zr partition coefficients reported in this paper should be used with caution not only because the crystallization sequence of these minerals can cause an immense and rapid change in elemental abundances in the liquid, but because many factors, such as temperature, SiO_2 content, and alkalinity should have serious effect on the partition coefficients as well (Watson and Green 1981). An inadequate treatment involving apatite and zircon will result in disastrous deviations from the natural behavior of Hf, Zr and REE.

Acknowledgements. The author is grateful to M. Tatsumoto for use of his laboratory and his encouragement throughout this study, and K. Aoki for the chemical analyses of the samples. The author thanks Z.E. Peterman, D.M. Unruh, T.K. Hinkley and G.A. McKay, who provided invaluable comments that improved the manuscript. The author also thanks M. Henneck for typing the manuscript. This work is supported by NASA Interagency Transfer Order T-783-H.

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Received September 4, 1985 / Accepted April 4, 1986