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Direct laboratory measurements of distribution coefficients for trace elements are impractical because of the difficulty in separating for analysis fine-grained minerals from their surrounding parent glass in quenched furnace charges. Therefore, we have studied the partition of Gd^{3+} between an aqueous phase and several silicate minerals and between an aqueous phase and silicate melts, and have obtained crystal-melt distribution coefficients as ratios of results of the two types of measurement. This technique is somewhat similar to that used by Iiyama (4), except that we measured the partition between the aqueous and silicate phases, instead of using water as a transferring agent for the trace element between two silicate phases. Also, the crystal-silicate melt distribution coefficients we obtained are between phases which are not in equilibrium with respect to their major constituents under the conditions of measurement.

We used conventional hydrothermal apparatus (5) to study forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$) at $900 \pm 5^\circ C$ and 500 ± 10 bars water pressure, and diopside ($CaMgSi_2O_6$) at $800 \pm 5^\circ C$ and 1000 ± 10 bars. The minerals were synthesized from mixtures of the constituent elements as oxides in sealed gold capsules in the presence of water or of dilute $GdCl_3$ solutions containing ^{153}Gd as a tracer (6). Samples were left in the furnaces for 1 to 2 weeks. The establishment of equilibrium was demonstrated by reversals in which previously synthesized pure crystals were equilibrated with $GdCl_3$ solutions and by reversals in which Gd -bearing crystals were equilibrated with pure H_2O . In addition, the ratio of fluid to silicate phase was varied by nearly a factor of 10 with no observable effect on the values of the distribution coefficients.

After their removal from the furnaces, the gold capsules were cut open and placed in 20 ml of 0.01M aqueous $GdCl_3$ to bring into solution by exchange any ^{153}Gd tracer adsorbed on the mineral crystals or walls of the capsule. The ^{153}Gd contents of the crystals and the solutions were then separately assayed by scintillation counting. The aqueous and solid phases recovered in this way contained over 95 percent of the initial ^{153}Gd . The remaining ^{153}Gd was found to be mechanically trapped in folds in the

Table 1. Distribution coefficients for Gd^{3+} .

Mineral	Phenocryst-host matrix (4)	Ultramafics-gabbros (5)	Skaergaard intrusion	Mineral-aqueous phase	Mineral-silicate melt
Olivine	0.012	0.04	0.007	2.4 ± 0.9	0.015 ± 0.006
Orthopyroxene	0.04-0.17	0.03		7.7 ± 2.9	0.048 ± 0.009
Clinopyroxene	0.1-1.4	0.46	0.35	55 ± 23	0.34 ± 0.16
Plagioclase (An_{65})	0.017-0.21		0.02	8.5 ± 2.0	0.053 ± 0.018
Silicate melt (Hawaii)				165 ± 35	
(Lipari)				153 ± 31	

distorted capsules. The identity of the solid phases was checked by microscopic examination in immersion oils and by x-ray diffractometry; the solids were homogeneous, except for small amounts (less than 5 percent) of forsterite or quartz in a few of the enstatite samples.

Distribution coefficients (D) for Gd^{3+} between aqueous fluid and three magnesian minerals are listed in Table 1, and the data from which they were obtained are illustrated in Fig. 1. Within the precision of the measurements (standard deviation, ± 40 percent) the values of D for each of the three minerals are constant over a concentration range from 0.6 part per billion to 4 parts per thousand in the solid phases, a factor of more than 10^6 . Such would not be the case if an unobserved, insoluble phase containing Gd as an essential component were being formed; instead, a constant concentration for Gd^{3+} in the aqueous phase would be expected (7).

In view of the high values for D (crystal-aqueous fluid) and because of the tendency for highly charged ions such as Gd^{3+} to adhere to surfaces, it must be demonstrated that the Gd^{3+} in our experiments has been actually incorporated into the silicate structures, rather than merely adsorbed or occluded. When dilute aqueous $GdCl_3$ is placed in contact with crystals of forsterite, enstatite, or diopside, most of the Gd^{3+} is quickly adsorbed onto the surfaces of those minerals. This Gd^{3+} can be quantitatively removed from those surfaces in less than 30 minutes by exchange with 10 ml of 0.01M $GdCl_3$ (dashed line, Fig. 2). Crystals of enstatite equilibrated with Gd^{3+} at high temperatures do not relinquish that ion readily at room temperature; after more than 5000 hours, less than half of the Gd^{3+} has been exchanged from these crystals (solid line, Fig. 2). Similar experiments for olivine and diopside gave

similar results. Since the crystals of all these minerals are so small (10 to 200 μm), this rate of loss can probably be attributed to diffusion. Boiling of Gd -impregnated enstatite crystals for 1 hour in concentrated HCl removed less than one-fourth of the Gd^{3+} , even though enstatite dissolves slowly in that acid (dotted line, Fig. 2). Also, different values were found for D for each of the three minerals. Taken all together, these measurements suggest, but do not prove, that Gd^{3+} was actually in solid solution instead of being on crystal surfaces or along cracks and grain boundaries.

In these experiments it is not clear just how ionic charge is compensated in the presumed substitution of Gd^{3+} for Mg^{2+} and Ca^{2+} . Values for D were not measurably changed when the aqueous phase was made 0.1M in NaF (crosses, Fig. 1). The constancy of the distribution coefficients over such a wide range of concentrations is a strong indication that the assumptions leading to Eq. 1 were not violated. Linear least-squares analysis of the logarithms of the equilibrium concentrations of Gd in the aqueous and mineral phases gives slopes equal to unity (to within 5 percent) as required for a constant value for D for each mineral over the range of concentrations studied.

Distribution measurements for Gd^{3+} between aqueous fluid and two obsidians (8) were made at $900 \pm 5^\circ C$ and 500 ± 10 bars; results are included in Table 1. Rhyolitic obsidians were used in order that the obsidians would be essentially completely molten; under the experimental conditions less than 5 percent of either crystallized (as plagioclase). At room temperature, exchange of ^{153}Gd between 0.1M aqueous solutions and these quenched silicate melts proceeds at a rate similar to that shown for enstatite (Fig. 2). Room temperature measurements of adsorption and desorption of Gd^{3+}