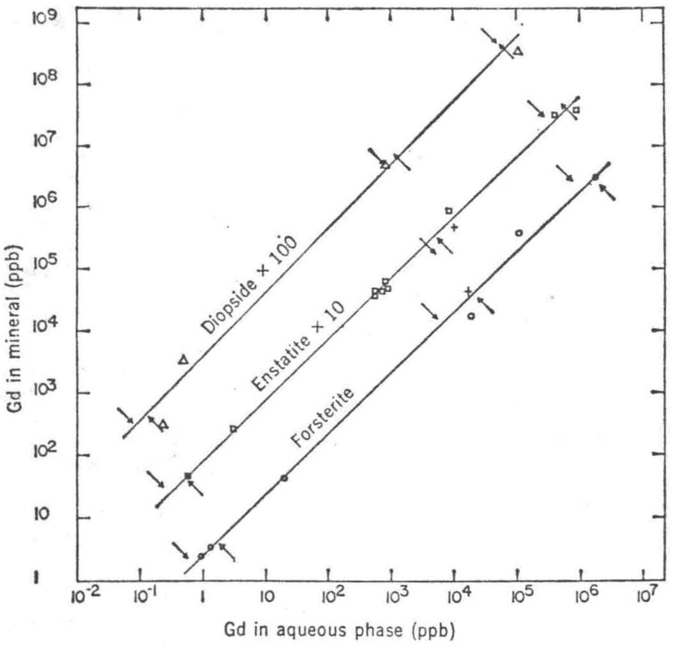

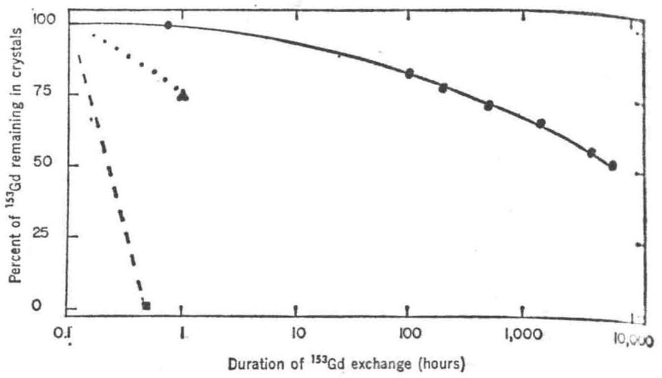

Fig. 1 (left). Concentrations of Gd^{3+} in equilibrium mineral-aqueous phase pairs are shown for forsterite (lowest line), enstatite (middle line, displaced upward by a factor of 10 for display), and diopside (upper line, displaced upward by a factor of 100). Open symbols indicate experiments in which the minerals were synthesized from their constituent oxides in the presence of aqueous $GdCl_3$; pluses indicate similar conditions, except that the aqueous phase was 0.1*M* in NaF. Arrows pointing to the left indicate equilibration of previously synthesized minerals with aqueous $GdCl_3$; arrows pointing to the right indicate equilibration of pure H_2O with minerals containing Gd^{3+}. Points of arrows represent equilibrium concentrations. Fig. 2 (right). Rates of removal of ^{153}Gd tracer from crystals of enstatite under different conditions are shown: (dashed line) room temperature adsorption of $^{153}Gd^{3+}$, exchange with 0.01*M* $GdCl_3$; (dotted line) $^{153}Gd^{3+}$ synthesized into crystals, crystals boiled in concentrated HCl; (solid line) $^{153}Gd^{3+}$ synthesized into crystals, exchanged at room temperature with 0.01*M* $GdCl_3$. The abscissa scale is logarithmic.

also gave results similar to those for enstatite. Apparently, the Gd^{3+} is dissolved in the silicate melts.

Several measurements of the distribution coefficient for plagioclase feldspar were made by equilibrating natural crystals of that mineral with aqueous $GdCl_3$ at 900°C and 500 bars. The average and standard deviation from the average for these measurements are included in Table 1.

We tentatively assume that the distribution coefficients for Gd^{3+} are not strongly dependent on temperature or pressure. In fact, *D* values measured for one sample each of forsterite and diopside at temperatures 100°C lower than those used to obtain the data for Fig. 1 were the same, within experimental error, as the values at the higher temperatures. We also assume that the accommodation of Gd^{3+} by common silicate melts is not greatly affected by variations in the chemistry of the major elements. The *D* values for Gd in minerals of the Skaergaard intrusion did not change measurably with large changes in the composition of the residual liquid (*3*). On the basis of these assumptions, ratios of *D* (aqueous fluid–mineral) to *D* (aqueous fluid–melt) (Table 1) should approximate the values found for natural systems. The close correspondence between the *D* values in natural and experimental systems supports the above assumptions and gives confidence that the *D* values can be used to describe natural processes.

Concentrations of Gd in olivine, orthopyroxene, and clinopyroxene from rocks of gabbroic composition range from 0.02 to 0.15, 0.1 to 2, and 0.3 to 9 parts per million, respectively (*1–3*). Concentrations of Gd exceeding 4000 ppm were reached in all three minerals in our experiments. We interpret this, along with the high distribution coefficients for silicate mineral–aqueous phase partition, as compared with those for silicate mineral–silicate melt partition, to mean that olivine, orthopyroxene, and clinopyroxene are capable of readily accommodating much higher concentrations of the rare earths than have been found in them in nature. The concentrations in nature do not, therefore, appear to be limited by low capacities of these minerals for the rare earths such that when the minerals crystallize from a silicate liquid their crystallochemical character excludes the incorporation of rare earth ions. Instead, the low concentrations of rare earths found in natural crystals appear to result principally from the inability of those crystals to compete successfully with silicate melts in providing favorable sites for those elements. The minerals do compete very successfully with water. (In part, of course, the low rare earth concentrations in natural minerals result from rather low concentrations of those elements in silicate melts. Plagioclase, diopside, and amphibole from some pegmatites, whose parent liquids may be presumed to have had higher concentrations of rare earths than those giving rise to basalts or gabbros, contain rare earth concentrations 10 to 40 times greater than the usual gabbroic contents of those minerals.)

The exact properties of silicate liquids that make them more suitable hosts than water or silicate minerals for rare earth ions are not known. Possibly chains of silicate polymer wrap themselves around the ions, thus effectively complexing them in a manner similar to a multidentate ligand in aqueous solution. Perhaps a silicate liquid, because of its irregular structure, merely provides an abundance of cation sites of ideal size and coordination number for the rare earths. (Perhaps these two concepts are equivalent.)

The constancy (within experimental uncertainties) of the distribution coefficients measured in these experiments indicates that the ratio $\gamma(Gd^{3+}, \text{mineral})/\gamma(Gd^{3+}, \text{water})$ is constant (Eq. 2). It is unlikely that the activity coefficients for these several phases would all vary independently in exactly the same way with changes in the concentration of Gd^{3+}. Thus, the individual activity coefficients are probably constant over the range of concentrations studied and appear to have reached the values corresponding to

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