Pacific. Few storms have the intensity to penetrate as far as San Diego; thus the annual rainfall averages only 10 inches per year. We have collected rainfall at the La Jolla station and analyzed it for lead during the past 3 years. Lead concentrations range from 3 to over 300 μg per liter of rainwater, and there is an inverse relationship between the amounts of rainfall and the lead concentration. The average lead contents in La Jolla rainwater is about 40 μg/liter. Lazrus *et al.* (*12*) reported an average of 36 μg of lead per liter for a U.S. nationwide sampling network. They concluded that the lead content in rainwater at various cities is correlated with the gasoline consumption there. According to the U.S. Public Health Service drinking water standard, the "grounds for rejection" limit for drinking water is 50 μg of lead per liter (*13*).

In the San Diego region the amount of dust falling was 72 and 113 mg/m^2 per day for the fourth quarter of 1969 for our La Jolla and downtown San Diego stations, respectively. About two-thirds of the La Jolla dust consists of water-soluble matter primarily composed of sea salts. The gross lead content of the La Jolla dust is 0.09 percent, which corresponds to a lead precipitate of 65 μg/m^2 per day. San Diego dust, about one-third of which consists of soluble matter, contained 0.84 percent lead, equivalent to 950 μg/m^2 per day. On the basis of a comparison of the lead contents in the La Jolla and downtown San Diego dust (0.09 and 0.84 percent, respectively) with those of the lead aerosols in the suspended matter (0.68 and 4.62 percent, as given in Table 1), it is clear that only a fraction of the lead aerosols precipitate out near the source of emissions. The remainder of the lead aerosols are carried in the air currents and spread around the globe (*14*).

A portion of these lead pollutants have undoubtedly been incorporated into plants and animals (*15*). Long-term increases in atmospheric lead concentration will result in predictably higher concentrations of lead in the blood of the exposed populations (*16*). Because of the well-known toxicity of lead, the health hazard of increasing lead pollutants in the environment cannot be ignored.

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Gadolinium: Distribution between Aqueous and Silicate Phases

Abstract. *Studies of the partition of trivalent gadolinium between aqueous and silicate phases have been made at temperatures from 800° to 900°C and at pressures from 500 to 1000 bars. Constant values for the distribution coefficients for forsterite, enstatite, and diopside were obtained over a concentration range from 0.6 part per billion to 4 parts per thousand in the solid phases. Ratios of silicate crystal–aqueous phase distribution coefficients to silicate melt–aqueous phase distribution cofficients are close to the values for silicate crystal–silicate melt distribution coefficients estimated from natural systems. The free ion activity of trivalent gadolinium in the silicate melts appears to be less than one-hundredth of its value for aqueous phases of the same concentration.*

The number of thermodynamic parameters that would have to be evaluated in order to predict the behavior of a trace element during solidification of a natural silicate liquid is prohibitive. A promising approach is to measure distribution coefficients for trace elements in the hope that they will be constant over a useful variety of silicate compositions. Such seems to be the case for the rare earth elements since estimates of their distribution coefficients lie within a narrow range. These estimates are derived from studies of several natural systems which include phenocrysts and host matrices treated as equilibrium solid-liquid pairs (*1*), ultramafic rocks and basalts treated as partial melt–residue pairs (*2*), and minerals and estimated residual liquids from the Skaergaard intrusion (*3*). We have obtained laboratory values for distribution coefficients of Gd that are similar to those found for natural systems. Our measurements also show a strong affinity of silicate liquids for that element.

Most of the cations that are essential components of common silicate minerals are mono- or divalent. Entry of Gd^{3+} into one of the silicate structural sites, therefore, requires charge compensation. In natural silicate melts the concentrations of both major cations and possible compensating anions presumably exceed that of Gd by several orders of magnitude. If so, no conceivable distribution of the Gd between the solid phase and its parent liquid will significantly affect the activities of those ions in either phase. The equilibrium distribution of Gd will then be given by the ratio of the activities of that element for the two phases according to Eq. 1

$$K = \frac{A(\mathrm{Gd^{3+}}, \text{solid solution})}{A(\mathrm{Gd^{3+}}, \text{liquid})} \qquad (1)$$

where K is a constant.

In this paper we define a distribution coefficient D as the ratio at equilibrium of the bulk concentration of the trace element in the solid to its bulk concentration in the liquid. This distribution coefficient is related to the constant K as follows, where γ represents the activity coefficient of Gd^{3+}

$$K = \frac{\gamma(\mathrm{Gd^{3+}}, \text{solid solution})}{\gamma(\mathrm{Gd^{3+}}, \text{liquid})} D \qquad (2)$$

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.

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

Mineral	Phenocryst–host matrix (*4*)	Ultra-mafics-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_{66})	0.017–0.21		0.02	8.5 ± 2.0	0.053 ± 0.018
Silicate melt					
(Hawaii)				165 ± 35	
(Lipari)				153 ± 31	

We used conventional hydrothermal apparatus (*5*) to study forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$) at 900° ± 5°C and 500 ± 10 bars water pressure, and diopside ($CaMgSi_2O_6$) at 800° ± 5°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.

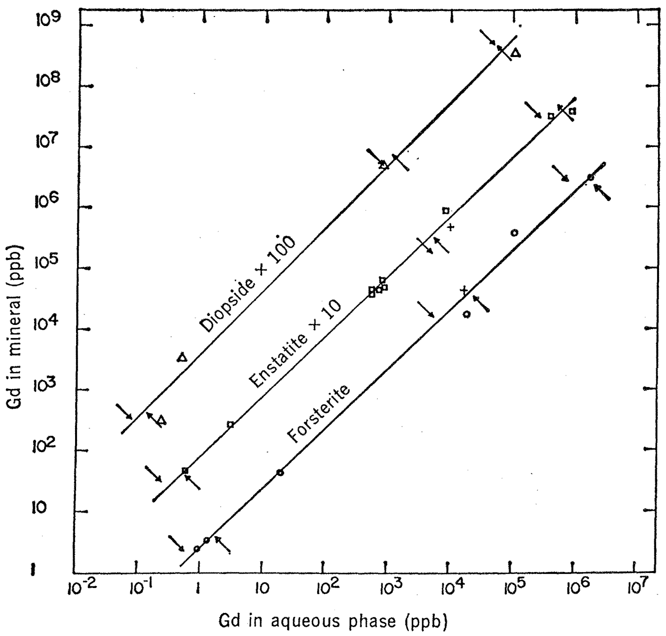
After their removal from the furnaces, the gold capsules were cut open and placed in 20 ml of 0.01*M* aqueous $GdCl_3$ to bring into solution by exchange any ^{153}Gd tracer adsorbed on the mineral crystals or walls of the capsule. The ^{153}Gd contents of the crystals and the solutions were then separately 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 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 $GdGl_3$ 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 0.01*M* $GdCl_3$ (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 0.1*M* 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° ± 5°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 0.1*M* 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+}



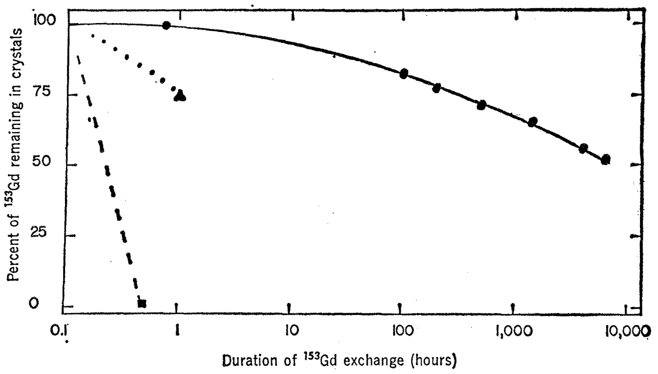


Fig. 1 (left). Concentrations of Gd^{3+} in equilibrium mineral-aqueous phase pairs are shown for forsterite (lowest line), enstatite (middle line, displaced upward by a factor of 10 for display), and diopside (upper line, displaced upward by a factor of 100). Open symbols indicate experiments in which 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 infinite dilution. This is certainly reasonable for the aqueous phase, in which the values of the activity coefficients depend on the ionic strength, and in which the ionic strength will barely be affected by changes in the low concentrations of Gd^{3+}. If the same standard state for Gd^{3+} is chosen for all phases, then relative to its value in the aqueous phase, the free ion activity coefficient for Gd^{3+} in the silicate liquids is only about 0.006. On that basis, the assumption which is sometimes made that cations present in trace quantities in a silicate liquid behave as they do in aqueous solution would appear to be a very poor one, at least for the rare earths.

The reaction between a complexing agent (L^{-x}) and Gd^{3+} in a silicate liquid might be represented by the following equation:

$$\mathrm{Gd}^{3+} + nL^{-x} \rightleftharpoons \mathrm{Gd}L_n^{3-nx} \qquad (4)$$

From the equilibrium constant for this reaction, it is seen that the free ion activity of Gd^{3+} would be proportional to the total concentration of Gd in the solution and would vary as the reciprocal of the concentration of the complexing agent to the *n*th power. Since the effect in nature and in our experiments of the composition of the silicate liquids on the distribution coefficients appears to be small, it is inferred that the entity responsible for lowering the free ion activity of Gd^{3+} is present in copious and approximately constant concentrations in common silicate liquids. If so, as long as the assumptions leading to Eq. 1 are valid, knowledge of distribution coefficients for rare earths is of as much practical use as knowledge of the appropriate activity coefficients for predicting equilibrium concentrations.

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6. Starting mixes were prepared from oxides supplied by Spex Industries Metuchen, N.J. Upper limits of < 1 ppb Gd in these oxides and < 1 ppb Gd in the deionized water were set by neutron activation analysis. Capsules were not buffered with respect to oxygen fugacity because of the stability of the Gd ion in the +3 state.
7. No measurements of the solubility of $\mathrm{GdCl_3}$ in water above its critical temperature (647°K) have been made, but water at the pressure and temperature of these experiments is known to be an excellent solvent for NaCl [S. Sourirajan and G. C. Kennedy, *Univ. Calif. Radiat. Lab. Rep. No. 6175* (1960); *Amer. J. Sci.* **260**, 115 (1962)].
8. These obsidians are from Hawaii and Lipari, Italy, and their respective compositions in percentage (by weight), as obtained by electron microprobe measurements, are: $\mathrm{SiO_2}$, 77.1, 75.0; $\mathrm{Al_2O_3}$, 12.1; 12.9; Fe as FeO, 1.08, 1.60; MgO, 0.00, 0.05; CaO, 0.37, 0.71; $\mathrm{Na_2O}$, 3.67, 4.03; $\mathrm{K_2O}$, 5.23, 5.32; $\mathrm{TiO_2}$, 0.09, 0.09; MnO, 0.02, 0.07; $\mathrm{H_2O}$, 0.45, 0.36 (by difference). Their Gd concentrations are < 10 ppm.
9. We thank Drs. P. R. Bender and C. D. Cornwell for helpful suggestions. Supported in part through funds administered by the Research Committee of the Graduate School of the University of Wisconsin and by NSF grants GA-1655 and GA-14070.

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Microwave Noise from Rainstorms

Abstract. *Observations of microwave noise due to rainstorms have been made at 1415 Mhz. The observed effect may well be due to electrical discharge between water droplets.*

It has been suggested that electric discharges occur between charged water droplets during rainstorms, and further that these discharges will produce broadband noise extending into the microwave region (*1*). The intensity of this noise is predicted to be between 20°K and 100°K equivalent noise temperature. Since such an effect would be easily detectable with standard techniques of radio astronomy, we looked for it during the spring and summer of 1969 (*2*).

The observations were made at 1415 Mhz with a 20-foot horn-reflector antenna (2° beam width). This frequency is appropriate, because it is sufficiently low that rain attenuation and associated thermal radiation are very small. Yet this frequency is high enough to insure that galactic radiation is negligible, except near the galactic disk.

The radiometer used a transistor preamplifier and had a bandwidth of 1.5 Mhz centered at 1415 Mhz. The rectified output was recorded on a chart recorder, with the response time of the system determined by the settling time of the pen, ~ 0.5 second. The antenna was pointed at an elevation of 32° and an azimuth of 226°, because a continuously operated 16-Ghz radiometer system oriented in this direction is located approximately 200 m north of our antenna. The 16-Ghz device is part of a system that monitors antenna temperature to obtain atmospheric attenuation statistics at that wavelength.

Observations were made on ten occasions for periods ranging from 24 to 100 hours, during rainy weather. The data included some two dozen heavy rainstorms as well as a number of extended periods of light rain. In no case did the antenna temperature increase during a rainstorm exceed 5°K (*3*), a value an order of magnitude below the predictions mentioned above. Small increases, typically 1°K to 2°K, were observed, however. When these features were compared with the attenuation at 16 Ghz derived from the noise data, good correspondence of features was obtained. The ratio of the equivalent attenuation at 1415 Mhz (that is, the observed increase in antenna temperature divided by 280°K) to the attenuation at 16 Ghz, was typically 2×10^{-3} for heavy rainstorms (Fig. 1).

The sharp spikes on the 1415-Mhz

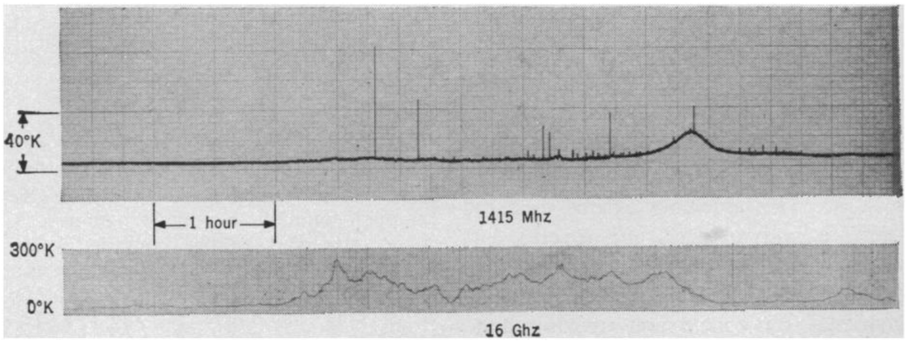

Fig. 1. Radiometer records at 1415 Mhz and 16 Ghz. Small but definite increases in the upper trace coincide with peaks in the lower record.