

LIMITS OF SOLUTION OF TRACE ELEMENTS IN MINERALS ACCORDING TO HENRY'S LAW:
REVIEW OF EXPERIMENTAL DATA

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ABSTRACT

Results of a survey of experimental data on trace element partitioning between crystals and coexisting liquid and between crystals and coexisting aqueous fluid are reported. These studies involve combinations of elements such as Cs, Rb, K, Na, Li, Ba, Sr, Ni, and Sm dissolved in minerals such as feldspars, micas, feldspathoids, garnets, pyroxenes, amphibole, and olivine. It is shown that the concentration ranges of these elements in minerals with solution behavior according to Henry's law appear to extend to less than 1 wt.% and often to less than 100 ppm of the element in the crystalline phase.

The available data indicate that the concentration ranges of solution in minerals according to Henry's law can be positively correlated with the difference of ionic radii between trace element and the host element for which the tracer is assumed to substitute. Furthermore, studies involving crystals and coexisting aqueous fluid have been used to determine whether Henry's law or Raoult's law adequately describes the solution. Based on the assumption that the aqueous fluid solution can be considered ideal, models have been proposed stating that if the difference between the ionic radii of the tracer and the host element in the crystalline phase is less than about 10% (relative to the host element), the solution is ideal (Raoult's law). With larger differences between the ionic radii, there is an excess free energy of mixing, although Henry's law is still obeyed in the concentration ranges where crystal-liquid or crystal-fluid partition coefficients are independent of element concentration.

INTRODUCTION

Elements that occur in trace amounts in rocks have been used extensively to model the formation and evolution of igneous rocks (e.g., GAST, 1968; PHILPOTS *et al.*, 1972; MINSTER *et al.*, 1977). Such elements are considered particularly useful because they tend to discriminate strongly between individual minerals and coexisting partial melts, and between melts and potential liquidus and near-liquidus minerals during the evolution of igneous rocks. Furthermore, because of the assumption that the thermodynamic laws of dilute solution (NERNST, 1891) may apply to the solution of these elements in the phases involved (MCINTIRE, 1963), the partition coefficients may be considered independent of the trace element concentration for a given bulk composition, temperature, and pressure. These considerations may be tested experimentally, provided experimental and analytical tools are available to determine elements in the concentration ranges of their natural abundance.

Experiments to determine partition coefficients of trace elements and to determine the concentration ranges of constant partition coefficients have been carried out at pressures corresponding to the upper portions of the crust ($P < 2$ kbar) during the past 23 years (e.g., EUGSTER, 1954, 1955; IYAMA, 1968). Under such pressure conditions, separation of the individual phases in an experimental charge could be obtained after quenching of the experiment. The pressure range has recently been extended to that of the mantle ($P > 10$ kb). Thus, evaluation of trace element partitioning between minerals and melts during partial melting and fractional crystallization in the upper mantle has become possible.

DATA

Trace element partition coefficients (D) are usually defined as $D(i)_{a/b} = C(i)_a/C(i)_b$, where a and b are the two phases, i is a given element and C is concentration in weight percent. Sometimes, a modification of this partition coefficient, $K(i)_{a/b} = C(i)_a/C(\text{host})_a/C(i)_b/C(\text{host})_b$, is used, where i is the trace element and host is the element for which i is supposed to substitute. In the latter case it is assumed that the trace element i substitutes for a given element or group of elements in the phases under consideration. Thus, the concentration ratio, $C(i)_a/C(\text{host})_a$, is proportional to an atomic fraction of the element i on a given crystallographic site. This notation is therefore useful for thermodynamic considerations. The weight ratio of concentrations, $D(i)_{a/b}$, on the other hand, is often more convenient for geochemical calculations. Both ratios will be used in this review.

Exchange of alkali metals and alkaline earths between feldspars and an aqueous fluid phase has been extensively studied (e.g., EUGSTER, 1954, 1955; IIYAMA, 1968; LAGACHE and SABATIER, 1973; IIYAMA and VOLFINGER, 1976). Exchange of two elements (tracer and host in this case) between feldspars and an aqueous fluid is useful from both a theoretical and an experimental point of view because (1) the two phases can easily be physically separated before analysis, (2) the aqueous fluid may be considered an ideal solution with the ionic strengths used in the experiments (ORVILLE, 1963; IIYAMA, 1964; DELBOVE, 1971), and (3) there is only one crystallographic site in the feldspars where the tracer under consideration can substitute. Feldspars are also petrologically important, as they constitute more than 50% of all crustal rocks.

The first results of such exchange experiments were reported by EUGSTER (1954). He used radiometric methods to determine Cs partitioning between K-feldspar and an H_2O -rich fluid at 1000 and 2000 bars in the temperature range 500° - 800°C with Cs/K (wt ratio) in the fluid varying from 2×10^{-4} to 10^{-2} . EUGSTER (1954) found that the partition coefficient, $K(i)_{K\text{-feldspar}/\text{fluid}}$, began to deviate from a constant value at Cs/K in the vapor near 10^{-2} . An accurate value of the Cs-K ratio of the vapor was not determined, however. The value of the partition coefficient ranged from 0.48 at 500°C to 1.2 at 800°C in the concentration region of thermodynamically dilute solution of Cs in K-feldspar. In the light of the large difference of ionic radii of Cs and K (1.67 and 1.33 Å, respectively), it is likely that the activity coefficient (γ) of the Cs component in the K-feldspar differs from unity (LAGACHE and SABATIER, 1973). Thus, the (K,Cs)-feldspar is a nonideal solution, but may be described with Henry's law in the Cs concentration range of constant crystal-fluid partition coefficient. With a crystal-fluid partition coefficient between 0.48 and 1.2, the data of EUGSTER (1954) indicate that less than about 1500 ppm Cs can dissolve in K-feldspar according to Henry's law if it is assumed that the ratio of activity coefficients in the fluid, $(\gamma_{\text{Cs}}/\gamma_{\text{K}})_{\text{fluid}}$, remains constant to greater Cs concentrations than about 1500 ppm in the fluid.

The work of EUGSTER (1954) was modified and extended by LAGACHE (1971) and LAGACHE and SABATIER (1973). They studied the partitioning of Cs, Rb, and K between albite and chloride solution and the partitioning of Cs, Rb, and Na between K-feldspar and chloride solution at pressures and temperatures near 1 kbar and 600°C , respectively. For the K-feldspar and coexisting fluid, the partition coefficient, $K(i)_{K\text{-feldspar}/\text{fluid}}$, remained constant until the value of $(\text{Cs}/\text{K})_{\text{fluid}}$ was near 10^{-2} , in apparent agreement with the data of EUGSTER (1954). The fluid phase in the experiments by LAGACHE (1971) and LAGACHE and SABATIER (1973) differed from that of EUGSTER (1954), however, in that it was a slightly acidic (0.5 N) chloride solution whereas EUGSTER (1954) used a hydrous vapor. The value of the partition coefficient, $K(i)_{K\text{-feldspar}/\text{fluid}}$, was given by LAGACHE (1971) as 0.025 at 600°C and 800 bars. This value is about 4% of that reported by EUGSTER (1954), suggesting that addition of KCl to the fluid enhances the solubility of Cs in the fluid. With a value of the partition coefficient near 0.025 and a concentration of Cs equivalent to $\text{Cs}/\text{K} = 10^{-2}$ in the fluid, the data of LAGACHE (1971) lead to the conclusion that about 60 ppm Cs can dissolve in K-feldspar without affecting the crystal-fluid partition coefficient. LAGACHE and SABATIER (1973) considered albite as well as K-feldspar. They determined upper bounds of concentration limits of Henry's law for Na, K, Rb and Cs in several feldspars. Accurate values were not reported. In a few cases, no upper limit was found in the concentration range considered by LAGACHE and SABATIER (1973). These bounds are shown in Table 1.

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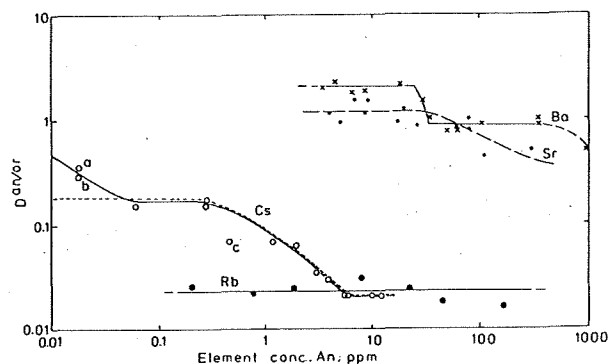
Table 1. Concentration limits (ppm) of dilute solution Na, Rb, K and Cs in alkali feldspars at 600°C and 800 bar*

Element	Mineral	Limit
K	albite	150
Rb	albite	1,600
Cs	albite	500
Na	K-feldspar	8,500
Rb	K-feldspar	10,000
Cs	K-feldspar	480
Na	Rb-feldspar	4,000
K	Rb-feldspar	12,000
Cs	Rb-feldspar	400

* Data from compilation of LAGACHE and SABATIER (1973).

The experimental technique of exchange of elements between an aqueous fluid and a crystalline phase may be extended to include two crystalline phases and an aqueous fluid to measure partition coefficients between the two minerals directly. No information on the mixing properties of the fluid is necessary for such experiments. This technique was used by IYAMA (1968) to study the partitioning of Cs, Rb, Ba, and Sr between coexisting alkali feldspar and plagioclase at 1 kbar and 600°C. It was found that the concentration ranges of constant $D(i)_{\text{alkali feldspar/plagioclase}}$ depended on both the feldspar composition and the trace element involved. The data for pure K-feldspar (or) and anorthite (an) are reproduced in Fig. 1. It can be seen that there is a

Figure 1. Partition coefficient, $D(i)_{\text{an/or}}$, versus element content of anorthite at 600°C and 1 kbar (from IYAMA, 1968). Run durations, 7-30 days. IYAMA (1968) reported that 4 days was sufficient to attain equilibrium, but no description of the method used to ascertain equilibrium was provided. Element analysis by radiometric method using ^{86}Rb , ^{134}Cs , ^{85}Sr , and ^{133}Ba as source of beta and gamma activity. Quoted relative uncertainty of individual analysis is 10%. Short dashed line is the partition coefficient for Cs with uncertainty of points a, b and c greater than 10%.



definite upper limit to the Ba content (20-30 ppm in an; 40-60 ppm in or) above which the value of $D(\text{Ba})_{\text{an/or}}$ decreases in an apparently stepwise fashion as a function of the Ba content of the system. There also appears to be an upper limit of Sr concentration that occurs in the range 50-100 ppm Sr in anorthite. The cesium partition coefficient appears to pass through several steps of decreasing $D(\text{Cs})_{\text{an/or}}$ with increasing Cs content. IYAMA (1968) claimed 10% relative uncertainty in the data with the radiometric technique used in these experiments. With that uncertainty, the two steps in the $D(\text{Cs})_{\text{an/or}}$ versus concentration of Cs in anorthite, $C(\text{Cs})_{\text{an}}$, are real variations even though IYAMA (1968) suggested only one step. An alternative curve to accommodate the latter suggestion leads to the conclusion that the data points marked a, b, and c (Fig. 1) are somewhat more uncertain than 10% (relative). In view of this uncertainty, the data reproduced in Fig. 1 lead to the conclusion that

between 0.5 and 5 ppm Cs can dissolve in anorthite coexisting with orthoclase before $D(\text{Cs})_{\text{an/or}}$ becomes dependent on the Cs content of the anorthite or the orthoclase, or both.

According to the data reproduced in Fig. 1, more than 150 ppm Rb can dissolve in anorthite (corresponding to nearly 10,000 ppm Rb in orthoclase) without affecting $D(\text{Rb})_{\text{an/or}}$.

It appears from the data of IYAMA (1968) that as albite is dissolved in both anorthite and K-feldspar the concentration ranges of Cs, Rb, Ba, and Sr in the low concentration plateaus in the coexisting feldspars of constant D values increase. There is no clear relation between Na content of the system and the value of the partition coefficient within the concentration ranges of constant partition coefficient (Table 2).

Table 2. Partition coefficients, $D(i)_{\text{plag/K-feldspar}}$, of Cs, Rb, Ba, and Sr at 600°C and 1 kbar as a function of albite content of coexisting phases*

Composition	Cs	Rb	Ba	Sr
$\text{An}_{30}\text{Ab}_{70}/\text{Or}_{75}\text{Ab}_{25}$	0.239	0.104	1.28	1.25
$\text{An}_{50}\text{Ab}_{50}/\text{Or}_{85}\text{Ab}_{15}$	0.333	0.040	1.25	1.18
$\text{An}_{100}/\text{Or}_{100}$	0.213	0.025	1.92	1.18

* Data from IYAMA (1968).

In the data discussed above, variations of the partition coefficient of an element between two crystalline phases as a function of element concentration indicate deviation of solution behavior from Henry's law in at least one of the coexisting phases. The data of IYAMA (1968) cannot be used to determine whether plagioclase or alkali feldspar first shows deviation from Henry's law with increasing element concentration, however. It may be inferred, by combining the data summarized in Fig. 1 and Table 2 with those of LAGACHE and SABATIER (1973), that less Cs, Rb, Sr, and Ba can dissolve in anorthite than in orthoclase to form a solution that behaves according to Henry's law. The concentration ranges of solution according to Henry's law become extended with solution of an albite component in both feldspars. Data summarized by ROUX (1971) indicate, however, that the concentration range of solution of these four elements in albite is even narrower than in K-feldspar as indicated by the data summarized in Fig. 2. Thus, this extension of the concentration ranges of solution according to Henry's law in plagioclase and alkali feldspar is due to the properties of the feldspar solid solutions, not those of the individual feldspar components.

By using a technique similar to that for the feldspar-aqueous fluid exchange experiments described above, VOLFINGER (1969, 1970, 1975, 1976) determined exchange equilibria involving Cs, Rb, and Na between aqueous fluid and muscovite at 1 kbar in the temperature range 400°-600°. He found that both the Cs and Na isotherms pass through an inflection in the concentration range 40-60 ppm Cs and 100-200 ppm Na in the muscovite (Fig. 3). The data shown in this figure have been recalculated to weight proportions of the trace element in muscovite. IYAMA and VOLFINGER (1976), in replottting these data as $(\text{Cs/K})_{\text{fluid}}$ versus $(\text{Cs/K})_{\text{muscovite}}$, suggested that the curves may have an S-shape such as reproduced in Fig. 4. It seems questionable, however, that such an S-shaped curve is warranted by the data.

Exchange of Cs, Rb, and K between nepheline and aqueous fluid was studied by ROUX (1971, 1974) at 1 kbar and 600°C. A summary of his data is shown in Fig. 5. The concentration range of constant partition coefficient extends to 1000-2000 ppm K and Rb and 40-60 ppm Cs. ROUX (1974) argued that the exchange behavior seen for these elements can be explained in terms of a two-site model because of the two distinct sites in the nepheline structure (BUERGER et al., 1954). Rubidium, cesium, and to a great extent potassium filled the larger of

Figure 2. Comparison of Cs contents of albite and orthoclase as a function of compound partition coefficient (crystal-vapor) at 600°C and 1 kbar. Data from ROUX *et al.*, (1971). Analysis by radiometric technique using ^{134}Cs as radioactive source.

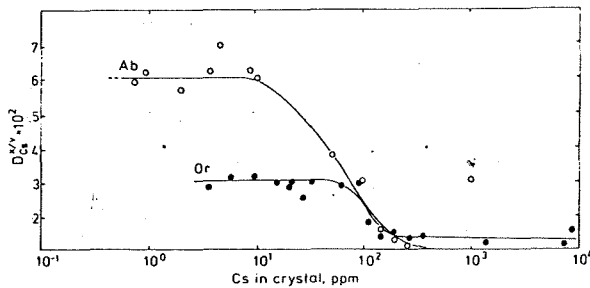


Figure 3. Comparison of Cs, Rb, and Na contents of muscovite as a function of compound partition coefficient (crystal-vapor) at 500°C and 1 kbar. Data from VOLFFINGER (1969, 1970, 1975, 1976). Analysis by radiometric technique. Other aspects of technique as discussed by ROUX *et al.*, (1971).

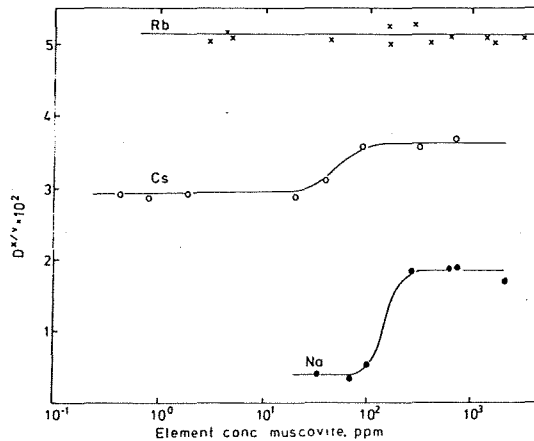
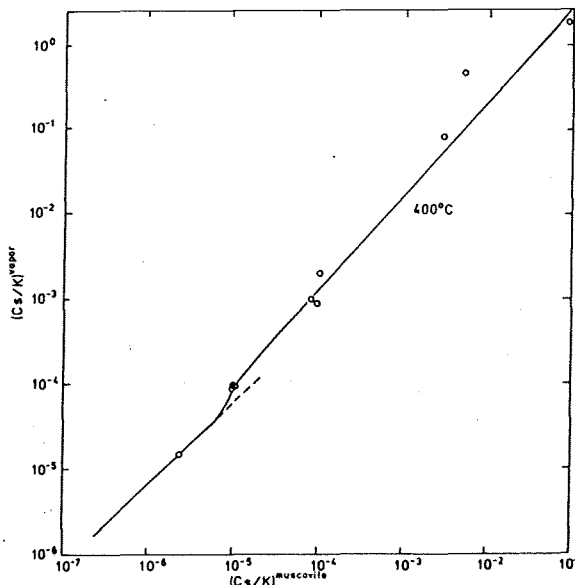


Figure 4. Cs/K of coexisting muscovite and hydrothermal fluid at 400°C and 1 kbar. Solid curve and data points after IIYAMA and VOLFFINGER (1976). Experimental technique as discussed by IIYAMA (1968) and briefly summarized in Fig. 1.



partition coefficients are extended as the temperature is increased. It should also be remembered that the compositions of the feldspars were different in the two systems. The data of IYAMA (1968) indicate that the concentration ranges of Henry's law solution behavior in feldspars depend on the composition of the feldspars. Final conclusions cannot be made, however, until experiments are carried out in the same element concentration ranges using the same bulk compositions of the feldspars.

Except for the data of DRAKE (1972) and DRAKE and WEILL (1975), the data summarized thus far have been acquired by exchanging trace elements between an aqueous fluid and crystals using run durations of up to several weeks. IYAMA (1968), in describing the technique of cation exchange between crystals and aqueous solution, commented, without supplying data, that a run duration of about 4 days was necessary to obtain equilibrium. IYAMA (1974) expanded on the experimental technique by commenting that data reported by IYAMA (1968), VOLFINGER (1969, 1970), LAGACHE (1971), and LAGACHE and SABATIER (1973) were internally consistent. The data of VOLFINGER (1975, 1976) and IYAMA and VOLFINGER (1976) are also consistent with the earlier work. Thus, it was argued that the exchange isotherms were determined under equilibrium conditions. In addition to this argument, IYAMA (1974) reported that reversal experiments had been conducted at 600°C and 1 kbar. In these experiments, crystals were first grown from a gel coexisting with an aqueous fluid that contained the radioactive tracer. These crystals, containing the radioactive tracer, were then subjected to the same pressure and temperature conditions together with the same aqueous solution but without the radioactive tracer. In these experiments, a run duration of 10 days was necessary to attain the same values of partition coefficients involving Na, K, Rb, Cs, Sr and Ba as in the original experiments. Because all the experiments reported by IYAMA and coworkers were for 10 days or more, it would seem that equilibrium partitioning of elements between the fluid and the crystals was attained.

CULLERS et al. (1973) and ZIELINSKI and FREY (1974) studied partitioning of rare earth elements between aqueous vapor and clinopyroxene, orthopyroxene, and olivine under pressure and temperature conditions that were similar to those used by IYAMA and coworkers. These experiments were conducted by reacting the aqueous vapor containing a tracer with materials that were already crystalline. The experiments were then reversed by reacting such crystals with an aqueous vapor that did not contain the trace element at the beginning of the experiment. These studies indicated that a run duration of several months was necessary to attain equilibrium compared with only 10 days in the experiments of Iiyama and coworkers. This difference in time reported for equilibration may be because of different grain size of the minerals (an important variable, as pointed out by ZIELINSKI and FREY, 1974) and on different diffusivity of the various elements in the minerals involved. Lack of information on diffusion coefficients and on the grain size of the run products (with the exception of ZIELINSKI and FREY, 1974) make quantitative assessment of these possibilities unfeasible, however.

Except in the experiments of DRAKE (1972) and DRAKE and WEILL (1975), none of the analytical techniques used in the experiments reported above provides a means of studying the element distribution within the individual phases. Furthermore, physical separation of the phases involved was necessary. Confidence in the experimental results may be greatly increased if these two aspects of the analysis can be evaluated. Autoradiography has recently been employed for this purpose (SEITZ, 1974; MYSEN and SEITZ, 1975; BENJAMIN et al., 1976). With this technique, variations of element concentrations within individual phases greater than about 5% can be detected over an area of about 5 μm . Furthermore, no physical separation of the phases prior to analysis is necessary.

WOOD (1976) used this technique (also called beta-track mapping) to determine samarium partitioning between pyrope (py) and a water-undersaturated liquid of the same composition at 30 kbar as a function of Sm concentration and water content of the melt. The water content was increased from 3.31 wt % at 1500°C to 24.2 wt % at 1200°C. WOOD (1976) argued that at constant pressure and temperature (30 kbar and 1500°C) the partition coefficient, $D(\text{Sm})_{\text{py/liq}}$, decreased as a function of increasing Sm content until about 10 ppm Sm had dissolved in the garnet. With higher Sm content, $D(\text{Sm})_{\text{py/liq}}$ remained constant. This observation contrasts with those summarized above and those of MYSEN (1976a,b, 1977a,b) in which the partition coefficient remained constant until a certain element concentration in the crystals was reached. Then, the partition coefficient began to decrease. As can be seen from the results of WOOD (1976),

summarized in Fig. 6, data were reported from about 0.2 ppm Sm to about 5000 ppm. WOOD (1976) chose to draw a curve showing continuous decrease of the partition coefficient through the data points with less than 10 ppm Sm (curve A). Curve B in Fig. 6 is an alternative suggested by the present author. With such a curve, the data on Sm partitioning summarized by WOOD (1976) would be in agreement with those discussed above and those of MYSEN (1976a,b, 1977a,b), as discussed below.

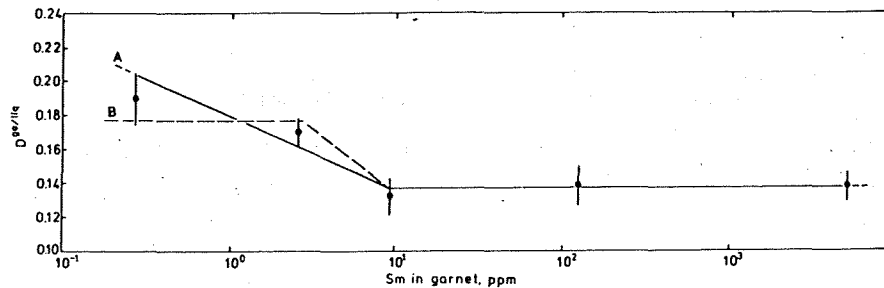


Figure 6. Partition coefficient $D(\text{Sm})_{\text{py/lig}}$, as a function of Sm content of pyrope at 30 kbar and 1500°C from WOOD (1976). Length of error bars equal $\pm 1\sigma$. Curve A (solid line) is that of WOOD (1976). Curve B (dashed line) is an alternative curve suggested by the present author.

WOOD (1976) also found that if more than 5-10 ppm Dy was dissolved in the garnet, the value of $D(\text{Sm})_{\text{py/lig}}$ became similar to that at $C(\text{Sm})_{\text{py}} > 10$ ppm even with less Sm than that dissolved in the garnet. Thus, solution of Dy in garnet affects the partitioning of Sm between pyrope and hydrous liquid of pyrope composition in the same manner as Sm itself! This observation marks the first documentation of a dependence of trace element partitioning on the presence of another trace element.

Beta-track mapping was also used by MYSEN (1976a,b, 1977a,b) to measure Ce, Sm, Tm, and Ni partitioning between hydrous silicate liquid and garnet peridotite minerals and between hydrous silicate liquid and amphibole at high temperatures and pressures. For REE partitioning, studies of chemical homogeneity of individual phases, time studies, and reversals were utilized to ascertain that equilibrium was reached. The studies of nickel partitioning were conducted similarly to those of the rare earth elements, except that because of the technique used to overcome problems with Ni loss to the (Au, Pt) sample containers, rigorous reversal experiments could not be carried out. A summary of the nickel partitioning data is given in Figs. 7 and 8. There is a limited concentration range starting from the lowest nickel concentrations within which the D-values are independent of the nickel contents of the system. At higher concentrations, the partition coefficients decrease rapidly with increasing nickel content and sometimes approach a new and lower value. The magnitude of the decrease is less than at the higher temperature.

It may be argued that the deviations from constant D-values are because of lack of isotopic equilibrium or because of nickel-loss to the (Pt, Au) containers used in the experiments. Data and discussion of MYSEN (1977a) appear to negate such arguments, however. For a detailed discussion of these effects, the reader is encouraged to consult MYSEN (1977a).

After discussing the possible role of a water-saturated liquid in controlling variations of crystal-liquid partition coefficients, MYSEN (1977a) argued that the cause of the deviations from constant $D(\text{Ni})_{\text{crystal/liq}}$ was to be found in the solution behavior of Ni in the crystalline phases. Therefore, the experiments of MYSEN (1976a, 1977a) are analogous to those reported by Iiyama and coworkers. Nickel partitioning data for coexisting olivine and liquid are shown in Fig. 7. More than 500 ppm Ni can dissolve in olivine under all physical conditions studied before the olivine-liquid partition coefficient became dependent on the nickel content of the olivine. Increasing temperature appears

to result in less abrupt deviations from constancy of $D(\text{Ni})_{\text{ol/liq}}$. Similar observations were made by VOLFINGER (1969, 1970, 1975, 1976) on Na-K and Cs-K exchange between muscovite and an aqueous fluid. Increasing pressure appears

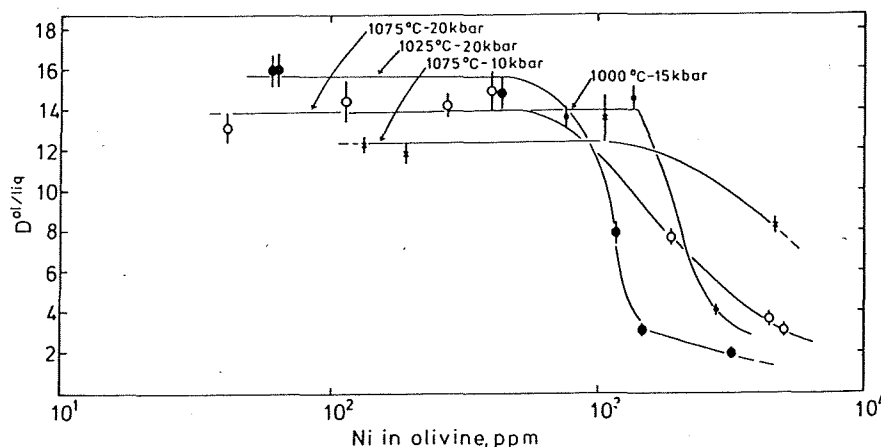


Figure 7. $D(\text{Ni})_{\text{ol/liq}}$ as a function of nickel content of crystal under various pressure and temperature conditions. Data from MYSEN (1967a). Length of error bars equals $\pm 1\sigma$.

to cause a reduction of the range of nickel concentration in olivine with constant $D(\text{Ni})_{\text{ol/liq}}$. Plots similar to Fig. 7 are presented in Fig. 8 for coexisting clinopyroxene and liquid, garnet and liquid, amphibole and liquid, and orthopyroxene and liquid. It can be inferred from the data in these figures that in all the phases considered by MYSEN (1976a, 1977a) nickel behaves in a qualitatively similar way but that the concentration ranges of constant partition coefficient depend on the mineral.

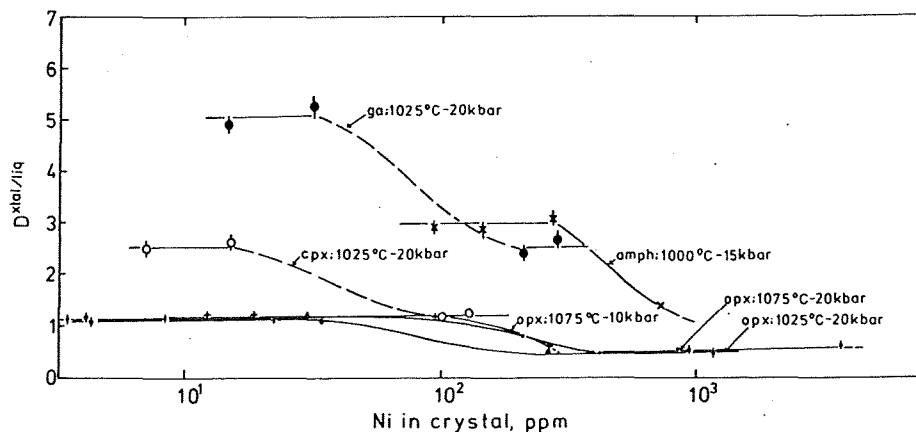


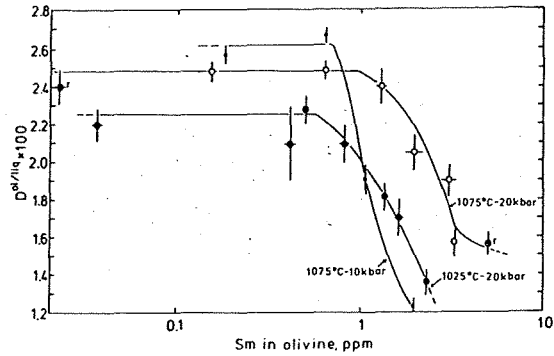
Figure 8. $D(\text{Ni})_{\text{crystal/liq}}$ as a function of nickel content of the system. Data from MYSEN (1976a, 1977a). Length of error bars equals $\pm 1\sigma$.

LINDSTROM and WEILL (1978) studied nickel partitioning between diopside and liquid under conditions similar to those of DRAKE and WEILL (1975). They did not observe a low nickel concentration range of constant partition coefficient, in apparent conflict with the data of MYSEN (1976a, 1977a). The experimental conditions and bulk compositions of the experiments of LINDSTROM and WEILL (1978) were quite different from those of MYSEN (1976a, 1977a), making a direct comparison between the two sets of data difficult.

MYSEN (1977b), in studying Ce, Sm, and Tm partitioning among hydrous silicate liquid and the same crystalline phases as reported by MYSEN (1977a) for nickel partitioning, again found limited concentration ranges of constant partition

coefficients (Figs. 9 and 10). In fact, only several parts per million Sm dissolves in orthopyroxene, olivine, and pargasite according to Henry's law, whereas perhaps a few tens of parts per million Sm dissolves in garnet and

Figure 9. Same as Fig. 7 but with Sm instead of Ni. Data from MYSEN (1976b, 1977b).



clinopyroxene with constant $D(\text{Sm})_{\text{crystal/liq}}$. By comparison with the results of MYSEN (1977a), it can be seen that whereas the concentration range of constant $D(\text{Ni})_{\text{crystal/liq}}$ decreases in the order $\text{ol} > \text{amph} > \text{cpx} \approx \text{ga} > \text{opx}$, the order for Sm is $\text{ga} \approx \text{cpx} > \text{amph} > \text{opx} > \text{ol}$. As was the case for nickel, it was found that the concentration range of constant D value is extended with increasing temperature. MYSEN (1976b) also noted that the rate of change of partition coefficients with increasing Sm content is more rapid the smaller the crystal-liquid partition coefficient and the narrower the Sm concentration range of constant partition coefficient.

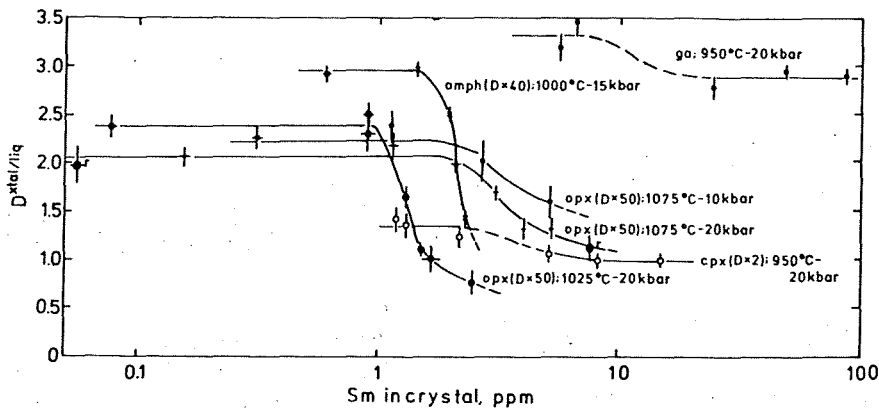


Figure 10. Same as Fig. 8, but with Sm instead of Ni. Data from MYSEN (1977b).

DISCUSSION

LAGACHE and SABATIER (1973) attempted to evaluate which of the thermodynamic laws of dilute solution (Henry's law or Raoult's law) best describes the element solubility within the concentration ranges of constant partition coefficients involving crystals and an aqueous fluid. It was assumed that the trace element substituted for a specific major element in the mineral. Furthermore, it had to be assumed that the ratio of activity coefficients of tracer and host element in the aqueous fluid was unity. Experimental support for the latter assumption was found in ORVILLE (1963), IYAMA (1964), and DELBOVE (1971). The elements considered by LAGACHE and SABATIER (1973) were Cs, Rb, K, and Na, which were exchanged between aqueous solution and alkali feldspars.

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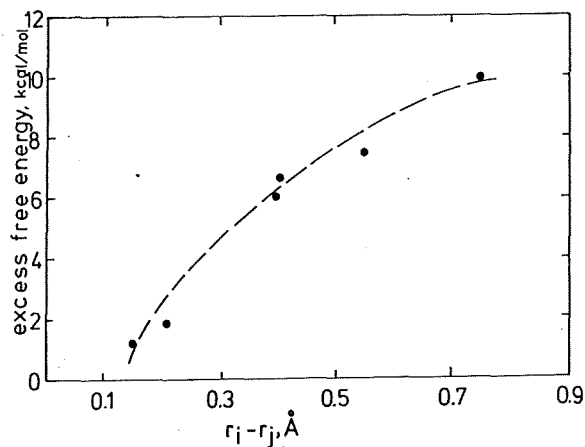
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The experimental data thus obtained were used to calculate excess free energy functions (LAGACHE and SABATIER, 1973) for the solid solutions. When such functions differed from zero, they would indicate deviation from ideality in the solid solution. LAGACHE and SABATIER (1973) concluded that a critical parameter that determines whether the thermodynamically dilute solution range could be described as that of an ideal solid solution was the difference of ionic radii between the trace element and the host for which the tracer supposedly substituted (see Fig. 11). If this difference exceeded about 10%, the solution would be nonideal (but could obey Henry's law) at low concentrations.

Figure 11. Excess free energy (kcal/mol) of solution of Cs, Rb, K and Na in alkali feldspars of different ionic radii (after LAGACHE and SABATIER, 1973).



Even though thermodynamic formulations can be used to describe the solubility behavior of trace elements in minerals such as reviewed here, such formulations do not provide information pertinent to the substitution mechanisms either inside the ranges of solution according to the thermodynamic laws of dilute solution or at higher element concentrations.

Before these alternatives are considered, possible effects of experimental design on the crystal-liquid and crystal-fluid equilibria should be discussed. Minerals may contain metastable defects. WRIEDT and DARKEN (1965) found, for example, that nitrogen solubility in cold-pressed steel containing well-described defects depended on the defect concentrations. The nitrogen solubility curves published by WRIEDT and DARKEN (1965) have certain similarities to the solubility curves discussed here. If these similarities are due to the presence of defects in the crystal structure, possible means of generating defects need to be discussed. WEI and WUENSCH (1977) suggested that point defects could be created in ionic crystals by decay of radioactive isotopes that emitted charged particles. These authors argued that there is a correlation between specific activity of the isotope and the defect concentration in the crystal structure. In the light of this argument, it could be suggested that because all the experimental studies on partitioning of trace elements in their natural abundance range were conducted by means of radioactive tracers, the apparent changes of partition coefficients as a function of element concentration could be related to artificially generated defects in the crystal structures. Data from MYSEN (1977a) covering a specific activity range of about a factor of 10 for nickel-63 are reproduced in Table 3. The olivine-liquid partition coefficients determined with this nickel-63 method, however, do not change within this specific activity range. Thus, it is argued that possible defect generation by radioactive transmutation is not the cause of the concentration dependence of the crystal-liquid and crystal-fluid partition coefficients.

Table 3. Partition coefficient, $D(\text{Ni})_{\text{ol/liq}}$, at 20 kbar and 1075°C (data from MYSEN, 1977a)

Nickel concentration in olivine (ppm)	Specific activity of ^{63}Ni in olivine (mCi/mg)	$D(\text{Ni})_{\text{ol/liq}}$
41	5.4×10^{-4}	$13.1 \pm 0.8^*$
115	1.5×10^{-3}	14.9 ± 0.9
273	3.6×10^{-3}	14.2 ± 0.7
399	5.3×10^{-3}	15.0 ± 0.8

*Uncertainties are $\pm 1\sigma$

Defects in the crystal structure could also be formed as a result of the mechanism of growth during an experiment. Under such circumstances, the type and number of defects in a crystal formed at a given temperature and pressure would depend on the run duration. The time studies of crystal-liquid partitioning of nickel and samarium (MYSEN, 1977a,b) indicate that this process is not responsible for the solubility behavior because the value of the partition coefficients is independent of the run length.

It is concluded, therefore, that the deviations of solution behavior from Henry's law at low element concentrations (ppm range) are not caused by experimental design. Conclusive data as to the site occupancies of trace elements in their natural abundance ranges in minerals are scarce. X-ray techniques are insensitive in these low concentration ranges. Therefore, doping techniques to attain higher element concentrations have been utilized. Extrapolation of such structural data to the ppm concentration range is uncertain for two reasons. First, site assignments rely on accurate chemical analysis of the phase involved. The uncertainty of such analysis is on the order of, or greater than, the natural abundance of the trace elements in the phase. Second, it is assumed that only regular crystallographic sites are occupied by the trace element (thus excluding interstitial sites and defects). Also, as pointed out by BURNS (1973), for example, conventional X-ray techniques provide only average structural parameters even though it is known that the majority of the sites in rock-forming minerals are deformed to varying degrees in individual crystals and have varying metal-oxygen distances (e.g., MEGAW *et al.*, 1962; CLARK *et al.*, 1969; WENK and RAYMOND, 1971).

Electron paramagnetic resonance measurements are sensitive to element distribution within crystals in the ppm concentration range, and may therefore be useful to study site occupancies of trace elements in minerals and glasses. Unfortunately, only a few measurements are available on systems relevant to rock-forming processes. These include Mn^{2+} in Mg_2SiO_4 (MICHOUILLER *et al.*, 1969) Fe^{3+} in Mg_2SiO_4 (CHATELAIN and WEEKS, 1973) and Eu^{2+} and Gd^{3+} in feldspars and ferromagnesian minerals (MORRIS, 1975). Although there are, sometimes, ambiguities in the interpretations, the possibility exists that Fe^{3+} on the ppm level may enter both octahedral and tetrahedral sites in forsterite, for example (CHATELAIN and WEEKS, 1973). MORRIS (1975) commented that REE may enter enstatite and forsterite structures in interstitial sites, and that clusters of elements are sometimes observed, whereas Ca-bearing minerals (e.g., diopside) may accept REE on the Ca-site or sites.

All available data with exception of those of WOOD (1976) and HARRISON (1977) indicate the existence of a low-concentration range where the activity coefficient of the trace element is independent of element concentration. Thus, no interaction between the individual trace element atoms in the structure is indicated. The rapid decrease of the partition coefficient at higher element concentration indicates that either the element begins to fill another site or sites in the structure at this concentration level, or the presence of the element at such a concentration causes sufficient distortion of the structure around the atoms so that the activity coefficient of the trace element is affected. The former possibility is consistent with a multi-site model involving crystallographic sites with low concentration substitution occurring in

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unexpected sites such as indicated by the studies of CHATELAIN and WEEKS (1973) and by MORRIS (1975). Alternatively, the trace element at low concentration enters dispersed defects in structure as suggested by MYSEN (1977b) and WOOD (1976). The other possibility is suggested by IYAMA and VOLFINGER (1976) in their "Local Lattice Deformation Model". Neither model is tested with independent measurements. It is suggested, however, that careful high-resolution electron microscopy such as indicated by BUSECK (1977) may help disprove or prove the validity of the suggested mechanism.

BETA-TRACK VERSUS ELECTRON MICROPROBE MEASUREMENTS

Direct comparison between partition coefficients obtained at the concentration levels of the natural abundance of trace elements with those measured at high element concentrations (doped to utilize the electron microprobe) is difficult at present because the physical conditions of the experiments and the bulk compositions used are quite different. The only elements where such comparison could be made at present are Ce, Sm, Tm and Ni. It should be remembered, however, that WATSON (1976) showed, for example, that REE crystal-liquid partition coefficients could vary by at least a factor of five depending on whether the coexisting liquid was basaltic or dacitic. Similarly, ARNDT (1977) showed that olivine-liquid partition coefficients decrease by nearly a factor of ten by changing the liquid composition from tholeiite to komatiite, a feature also demonstrated by WATSON (1977) for Mn partitioning between forsterite and liquid. The effect of pressure on transition metal crystal-liquid partition coefficients is to lower the coefficient by more than a factor of 2 as the result of pressure-induced liquid structural changes (KUSHIRO and MYSEN, in preparation). MYSEN (1977c) speculated that volatiles dissolved in silicate melts at high pressure would affect the partition coefficients. For example, it was suggested that transition metal partition coefficients would decrease and those of REE would increase by dissolving H₂O in the liquid. Solution of CO₂ in the melt may cause partition coefficients to change in the opposite direction.

In view of the fact that all the work done with electron microprobe analysis has been conducted at low pressure, and with different bulk compositions than the work carried out with beta-track mapping, and that the beta-track mapping results have been carried out at high pressure and often with volatiles in solution in the silicate melt, a comparison of the results obtained with different techniques seems unjustified at this time. IRVING (this Volume) has summarized available data determined with different analytical techniques and with different extensive and intensive variables.

At present, there appear to be several arguments against doping experimental charges with trace elements to concentration levels where electron microprobe analysis can be carried out. Some of these arguments are summarized in the discussion above of possible site occupancy of trace elements. On the other hand, it should also be remembered that the partitioning data obtained in the concentration range of natural abundance (using radioactive tracer techniques) were conducted in synthetic systems. These systems, with the exception of some data by WOOD (1976), only contained the trace element to be determined. The possibility of several different trace elements filling the same site exists. Thus, the low concentration range of constant partition coefficient seen in the synthetic systems may disappear if several trace elements were added simultaneously. If so, one must determine which element in which phase and under what physical conditions may be affected. Careful evaluation of experimental techniques are also needed. Only then can experimentally determined trace element partition coefficients be applied quantitatively to rocks.

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