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Partitioning of trace elements between crystals and melts

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Abstract

Advances in analytical geochemistry have made it possible to determine precisely the concentration of many trace elements and their isotopes in rocks. These data provide the cornerstone for geochemical models of the Earth and terrestrial planets. However, our understanding of how trace elements behave has not kept pace with the analytical advances. As a result, geochemists are often hampered in their interpretation of geochemical data by an incomplete knowledge of trace element partitioning under the conditions of interest. Through advances in trace element microbeam analysis it is now possible to determine partition coefficients experimentally under important conditions, such as during melting of the crust and mantle. This large body of experimental data can be used to investigate the fundamental controls on element partitioning. Simple continuum theories of elastic strain and point charges in crystal lattices, that account, respectively, for mismatch in ionic radius and ionic charge between the substituent trace ion and the lattice site on which it is accommodated, provide a very useful theoretical framework. This approach can be used as the basis for quantitative models of trace element partitioning, in terms of pressure, temperature, redox state and composition, and as a means of predicting partition coefficients for elements not routinely analysed. Experimental studies of partitioning are supported by atomistic computer simulations at zero K. Developments in computational techniques that enable direct simulation of high temperature and pressure mineral-melt partitioning will revolutionise the field in the near future. Use of novel, spectroscopic techniques to probe the structural environment of trace elements in crystals and glasses will provide valuable new data for computational and theoretical models. Extension of high temperature partitioning theory to ambient conditions is an essential step in understanding current climate change proxies, and tackling a host of environmental problems.

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1. Introduction

Most of what we know about the origin and subsequent differentiation of Earth and terrestrial

planets comes from chemical analyses of trace elements and their isotopes in rocks. Rapid advances in analytical technology, particularly the advent of plasma mass spectrometry, allow geochemists to measure sub-femtogram ($< 10^{-15}$ g) amounts of trace element isotopes. These data have revolutionised our knowledge of issues as diverse as the age of formation of Earth's core [1] and atmosphere [2], the depth and rate of

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melt extraction beneath mid-ocean ridges [3], and the extent of crustal recycling into Earth's mantle [4]. In all cases, interpretation of the chemical data relies on knowledge of the high temperature behaviour of the trace elements of interest, especially how they distribute themselves (or *partition*) between coexisting phases, such as crystals, metals and liquids. Some geochemical problems require only a crude understanding of trace element partitioning. In most cases, however, a better knowledge of partitioning is required to model or interpret the data. Yet our understanding of how trace elements behave lags far behind our ability to measure them, so compromising our ability to get the most from our data. Here, firstly, we make a case for using the best possible partitioning data, and, secondly, highlight recent experimental and theoretical advances that can be used to understand and extrapolate those data.

2. Why use trace elements?

The value of trace elements, generally taken to be those present at concentrations of less than 0.1 wt%, lies in their low abundance and chemical diversity. Low concentration ensures, in most cases, that they are entirely passive, having negligible influence on the outcome of a particular process, while chemical diversity ensures that different elements behave in different ways in certain situations. The preference of an element for a given phase is measured by its *partition coefficient* (D ; Fig. 1). It is customary to use trace elements whose partition coefficients are sensitive to the presence or absence of particular phases. For example, the lanthanides (or rare earth elements) exhibit distinctive partitioning behaviour between garnet and melt and can therefore be useful in determining whether melt generation took place in the presence of that mineral, which in turn has implications for the depth of melting. Trace elements with radioactive isotopes add a valuable time dimension. For example, short-lived radioisotopes in the uranium and thorium decay series are now routinely used to study magmatic processes occurring on timescales of less than 10^5 years [3].

Partition coefficients defined

(a) Nernst partition coefficient:	${}^{\alpha/\beta}D_i$	$\frac{\text{weight fraction } [i] \text{ in phase } \alpha}{\text{weight fraction } [i] \text{ in phase } \beta}$
(b) Molar partition coefficient:	${}^{\alpha/\beta}D_i^*$	$\frac{\text{molar fraction } [i] \text{ in phase } \alpha}{\text{molar fraction } [i] \text{ in phase } \beta}$
(c) Equilibrium constant:	$K_i^{\alpha/\beta}$	$\frac{\text{activity of } i \text{ in phase } \alpha}{\text{activity of } i \text{ in phase } \beta}$
(d) Strain-compensated partition coefficient:		${}^{\alpha/\beta}D_{0(M)}^{n+}$
(e) Doubly-compensated partition coefficient:		${}^{\alpha/\beta}D_{00(M)}$

Fig. 1. There are various ways of describing the partitioning of trace element i between coexisting phases α and β , such as mineral and melt. The *Nernst partition coefficient* (a) is most useful in geochemical modelling, while its molar equivalent (b) takes account of differences in gram formula weight between the phases, and therefore has greater thermodynamic value. In modelling melting or crystallisation processes the *bulk partition coefficient* is calculated as the weighted mean of the mineral phases in the proportions in which they participate. The ultimate objective in any thermodynamic model is the *equilibrium constant* (c) for a particular partitioning reaction, which takes full account of activity-composition relations in both phases. A useful parameter is the *strain-compensated partition coefficient* (d) for ions of valence $n+$ entering lattice site M, which describes the partitioning of a (fictive) ion that enters the crystal lattice without causing any elastic strain (see text). By further correcting for the effects of ionic charge, we can derive the *doubly-compensated partition coefficient* (e) for all ions entering M.

An interesting new application of trace element partitioning, which also provides temporal information, is *diffusive chemical fractionation* [5]. Experimental determinations of solid state diffusivity show that some trace elements diffuse much more slowly than the rates of melting and melt extraction. Consequently, these elements will be unable to equilibrate fully with the melt. The extent to which partitioning deviates from equilibrium is then a measure of the rates of melting and melt extraction. In order to assess deviation from equilibrium, it is necessary to know what equilibrium partitioning itself looks like at the conditions of interest.

3. Trace element partitioning – the conventional approach

Most of the mathematical expressions used to

model chemical differentiation processes (melting, crystallisation, etc.) assume, for convenience, that partition coefficients remain constant throughout the process. This raises two issues for the discerning geochemist: (1) to obtain the best possible partition coefficients for the process of interest, and (2) to evaluate the extent to which these partition coefficients vary in the course of the process and how to incorporate this variability into a model (numerically or analytically, e.g. [6]). The conventional approach is to select appropriate partition coefficients from the available compilations [7–9], normally on the basis of silica content of the melt (basalt, rhyolite, etc.) and/or physical conditions (pressure, temperature, etc.). Advances in microbeam trace element analysis [10,11] have lead to a proliferation of new and precise experimentally-determined partition coefficients, making selection rather difficult. Furthermore, few geochemists perform sensitivity analyses to assess to what extent their conclusions are predicated on their choice of partition coefficients. Undoubtedly in some cases it does not matter; but in many others it does.

The trace element content of a liquid (or melt) is very sensitive to partition coefficients. This sensitivity varies with the absolute magnitude of the partition coefficient and with the style of melting or crystallisation (fractional, batch, etc.). For example, highly incompatible elements ($D \ll 1$) are very useful for determining the extent of melting or crystallisation, although their concentrations in the source are in turn extremely sensitive to the effects of any prior fractionation. By focussing on concentration ratios of chemically similar elements (e.g. zirconium/hafnium, niobium/tantalum, etc.), or the activity ratios of highly incompatible short-lived radioisotopes (e.g. thorium-230, radium-226), the sensitivity of models to partition coefficients and source compositions is reduced. Nonetheless, small changes in partition coefficient ratios can be manifest as measurable changes in the equivalent concentration ratios in melts (Fig. 2) and residues. This problem is particularly acute where the melt fraction is of the same order of magnitude as the partition coefficient, and in the expanding field of melt inclusion analysis (Fig. 2) (e.g. [12,13]).

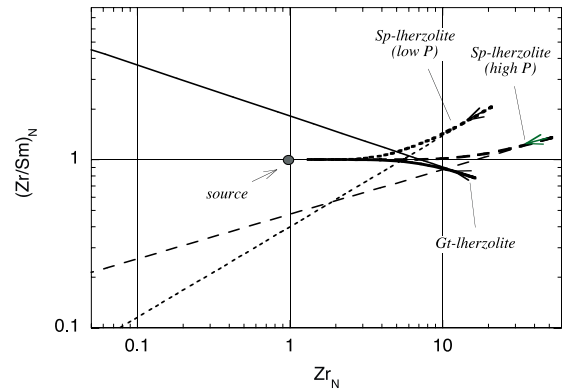


Fig. 2. Trace element ratios in melts are sensitive to both the magnitude of the partition coefficients and the style of melting. We illustrate this by reference to the Zr/Sm ratios of aggregated and instantaneous melts produced by dynamic (or 'critical') melting of the mantle. Dynamic melting assumes that a critical threshold porosity must be attained before melt can be extracted from a partially molten rock, and is widely acknowledged to be the most physically plausible mechanism for melt generation in the mantle. In performing the calculations we assume that a trapped melt fraction of 0.01 is retained in the source throughout melting. Ratios and concentrations are calculated relative to those in the source, as denoted by subscript N . The bulk values of D_{Zr} and D_{Sm} we have used are [14,18]: 0.052 and 0.038, respectively, for fertile garnet lherzolite at 3 GPa; 0.0092 and 0.016, respectively, for fertile spinel lherzolite at 2.8 GPa; and 0.038 and 0.089, respectively, for fertile spinel lherzolite at 1.5 GPa. The difference between spinel and garnet lherzolites is clearly a consequence of different mineralogies; the difference between low and high pressure spinel lherzolites is due only to changes in phase composition and physical conditions. Our simple models contrast the behaviour of aggregated dynamic melts (such as those erupted on the ocean floor), shown with bold lines, and instantaneous melts from throughout the melting column (often trapped as melt inclusions in mantle minerals), shown with thin lines. The arrows on the lines denote the direction of increasing melt fraction starting at 10^{-4} . The $(Zr/Sm)_N$ ratio of aggregated melts produced from these different sources differ within analytical resolution at low melt fraction (F), but converge as F approaches D . For instantaneous melts the differences between sources are much more marked. Clearly, by careful consideration of changes in partition coefficients, it is possible to use melt inclusion compositions as a sensitive probe of melting dynamics.

4. Getting the right partition coefficients

There are two parallel approaches to getting the partition coefficients right. The first involves experimental determination of the partition coefficients for all elements of interest under the exact

conditions of pressure, temperature and composition for the process of interest. The second approach involves the development of predictive models of partitioning that can be applied over a wide range of conditions for a large number of elements. The first approach is time-consuming and challenging, and ultimately accurate only for processes that are isobaric and isothermal. The second approach is thermodynamic and requires both a theoretical underpinning and an experimental calibration dataset.

The principal technical difficulty with experimentally determining partition coefficients specific to each and every magmatic process is that it is rarely possible both to recreate the conditions of interest and to grow crystals large enough for microbeam trace element analysis. For example, mantle melting involves partitioning at the peridotite solidus where the melt fractions are a few per cent or less and invariably too small to analyse. The best alternative is to obtain by iteration the appropriate solidus phases and compositions, but in different proportions such that the melt is sufficiently voluminous to analyse. By this means we are slowly arriving at a consensual set of partition coefficients for processes such as partial melting of mantle lherzolite [14–19], subducted oceanic crust [20,21] and lower crustal metamorphic rocks [22,23], with and without water.

The most prudent approach is to harness specific partitioning experiments to a theoretical model so as to account for changes in partitioning as conditions deviate from those in the experiments. As most processes of chemical differentiation are polythermal and often polybaric it is improbable that one set of partition coefficients, however carefully determined, will suffice for all permutations of a process. For example, even in the relatively straightforward case of plagioclase fractionation from basalt it has been shown [24] that the partition coefficients for strontium are so sensitive to plagioclase composition that no single value of D_{Sr} can adequately model the process (Fig. 3). By performing partitioning experiments over an unnaturally wide range of pressure, temperature and composition it is possible to calibrate the theoretical models to cover almost every eventuality.

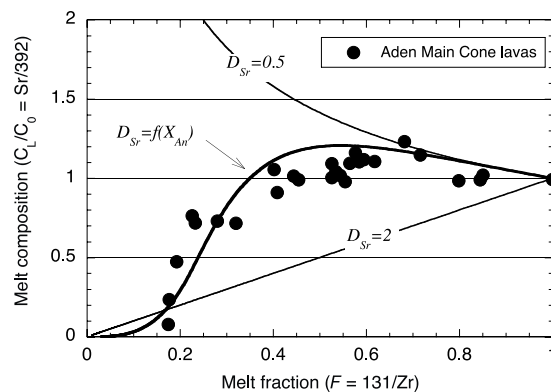


Fig. 3. Trace element partition coefficients are often sensitive to crystal composition, and can vary even for a single phase in the course of crystallisation. This is illustrated here for the case of plagioclase fractionation from lavas of the Aden Main Cone, Yemen [24]. Sr partitioning between plagioclase and melt depends on the molar anorthite content of the plagioclase (X_{An}) according to the expression: $R T \ln D_{Sr}^{plag/melt} = 26.8 - 26.7 X_{An}$ where T is temperature (in K) and R is the universal gas constant, $0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}$. As X_{An} typically decreases during crystallisation this results in non-linear variation in the Sr content of melts produced by crystal fractionation (thick line) in a way that cannot be modelled by any single constant value of D_{Sr} (thin lines). In performing the calculations, for a starting composition with 392 ppm Sr and 131 ppm Zr, the composition of plagioclase was varied during crystallisation, but its proportion (40%) was not. D_{Zr} was taken to be zero. The variable D_{Sr} trend provides a close match to the data from Aden Main Cone lavas in a way that no single value partition coefficient can.

5. Lattice strain – size matters

V.M. Goldschmidt [25] laid the theoretical foundation for trace element partitioning. Recognising that trace element ions enter specific lattice sites in minerals, Goldschmidt proposed that the key variables controlling partitioning are the charge and size of the trace ion relative to the charge and size of the lattice site, which itself varies with mineral composition. There is an energy penalty for size and charge mismatch that is reflected in lower partition coefficients for ions that do not fit well onto lattice sites compared to ions that do.

Goldschmidt's 'rules' have since proven to be an oversimplification (see below). Still, his first 'rule', namely that ions of the same charge and radius will enter a crystal lattice with equal ease,

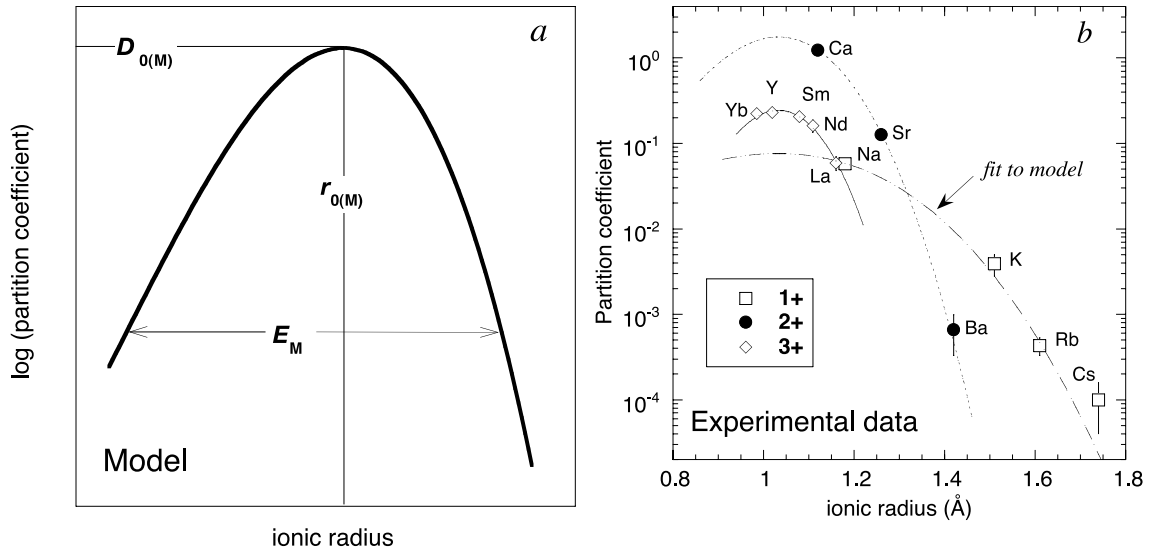


Fig. 4. Ionic radius has a strong influence on partition coefficients. (a) Cartoon illustrating the *lattice strain model* of trace element partitioning. For an isoivalent series of ions with charge $n+$ and radius r_i entering crystal lattice site M, the partition coefficient, $D_{i(M)}$, can be described in terms of three parameters: $r_{0(M)}^{n+}$, the radius of that site; E_M^{n+} , the elastic response of that site (as measured by Young's Modulus) to lattice strain caused by ions that are larger or smaller than $r_{0(M)}^{n+}$; and $D_{0(M)}^{n+}$, the strain-compensated partition coefficient for a (fictive) ion with radius $r_{0(M)}^{n+}$, according to the expression [30]:

$$D_i = D_{0(M)}^{n+} \times \exp \left\{ \frac{-4\pi N_A E_M^{n+} \left[\frac{1}{2} r_{0(M)}^{n+} (r_i - r_{0(M)}^{n+})^2 + \frac{1}{3} (r_i - r_{0(M)}^{n+})^3 \right]}{RT} \right\}$$

where N_A is Avogadro's Number. (b) Fits of experimental clinopyroxene-melt partitioning data [41] for isoivalent cations to the lattice strain model (curves). Only cations entering the VIII-coordinate M2-site are plotted (ionic radii from [35]). Note that the curves become tighter (E_M^{n+} increases) and displaced to lower $r_{0(M)}^{n+}$ as charge increases from +1 to +3. Error bars denote 1 s.d. analytical uncertainty.

provided the basis for a theoretical treatment of the problem, which came with the advent of atomistic models of crystal lattices. These 'lattice strain' models were based on the simple premise of trace ions as charged point defects in a dielectric, elastic continuum. Consequent disruption of the lattice around the defect is minimised by re-locating (or *relaxing*) the neighbouring ions and distributing the surplus elastic or electrostatic energy through the lattice [26,27]. The elastic strain energy is roughly symmetrical about an optimum ionic size. In other words, the energy penalty for accommodating an ion that is fractionally too large for a site is about the same as that for ion that is too small by the same amount. The elastic strain energy is inversely correlated with the logarithm of the partition coefficient, which, for a

specific lattice site, should vary near-parabolically with ionic radius (Fig. 4a). The maximum partition coefficient is obtained for the ion that fits the lattice with the least strain. These theoretical developments arose in the absence of experimental partitioning data on which to be tested. However, partition coefficients obtained from coexisting phenocrysts and groundmass in lavas [28], when plotted against ionic radius (the so-called 'Onuma diagram'), showed one or more humps each corresponding in size to a site in the mineral. The lattice strain models adequately explained this behaviour, but in the absence of systematic experimental studies, the field lay fallow for several decades, until the advent of trace element microbeam techniques revolutionised the experimental determination of partition coefficients.

A reawakening of lattice strain theory came about in 1994 with the publication of two experimental partitioning studies, one on olivine [29], the other on clinopyroxene and plagioclase [30]. Both studies showed that not only was the partitioning of isovalent series of cations in keeping with lattice strain theory (Fig. 4b), but the elastic response of the strained lattices was consistent with the known elastic properties of minerals and their constituent oxides (Fig. 5). Indeed, it could be argued that armed only with a set of partition coefficients one could determine the bulk elastic modulus of the host crystal! It was further shown that the optimum size of a crystal site, as deduced from partitioning data, correlates with the metal–oxygen bond lengths as determined by structure refinement of the same crystal [31,32]. Application of atomistic computer models of trace defect incorporation [33] to the analogous

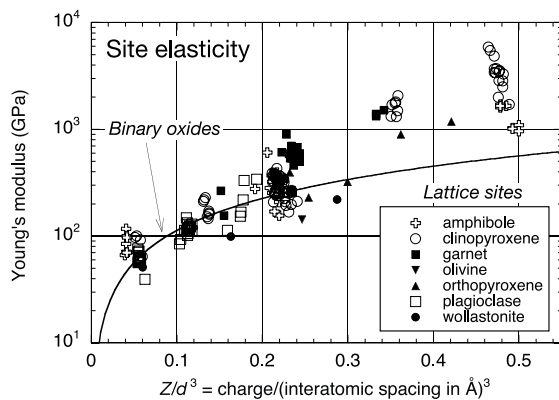


Fig. 5. Variation in lattice strain parameter (E_M^{n+}) that describes the apparent Young's modulus of a lattice site, as obtained from partitioning experiments. E_M^{n+} increases with the ratio Z/d^3 , where Z is the ionic charge and d is the metal–oxygen bond length at the site of interest, given as $r_{0(M)}^{n+} +$ the radius of IV-coordinate O^{2-} ions ($=1.38 \text{ \AA}$ [35]). Data are presented for non-tetrahedral cation sites only. The solid line shows the variation in bulk E with Z/d^3 for binary oxides [71], assuming that $E \equiv 1.5 \times$ bulk modulus. Oxides and lattice sites agree well at values of Z/d^3 less than 0.3, but at higher values lattice sites appear to be considerably stiffer. Evidently small lattice sites are very resistant to the accommodation of misfit highly charged cations, which has implications for the incorporation of, for example, Zr^{4+} and Nb^{5+} onto M1 in clinopyroxene. Extrapolation of the lattice site trend to zero charge shows that E_M^{0+} will be very low, suggesting very little discrimination between the noble gases on the basis of their atomic radii.

problem of solid–solid partitioning have shown surprisingly good agreement between theory and experiment. Together these developments herald a happy union of experimental geochemistry and mineral physics in just the way anticipated by Goldschmidt 70 years earlier.

A great virtue of the lattice strain approach is that it allows partition coefficients to be predicted for elements for which there are presently no partitioning data (e.g. cadmium, indium), based only a knowledge of their valence and ionic radius. As plasma spectrometry provides more and more data on unusual elements [34], a means to interpret these data will become increasingly in demand. The same is also true of several short-lived uranium-series elements, such as radium and protactinium, the radioactivity of which precludes conventional experimental studies of their partitioning behaviour.

The lattice strain approach is also able to account for some of the subtle variations in partitioning behaviour observed experimentally. This is because small changes in crystal chemistry lead to small changes in optimum site radius (sometimes less than 0.01 \AA), which can lead to surprisingly large fractionation between elements of similar ionic radius (Fig. 7). One such example is the fractionation between niobium and tantalum produced by amphibole. Tiepolo et al. [32] showed that the ratio of Nb and Ta partition coefficients in amphibole is correlated with the size of the M1-site into which these elements substitute. Changes in amphibole M1-site size result from variations in mineral chemistry, especially the magnesium number ($mg\# = \text{molar Mg}/[\text{Mg} + \text{Fe}]$). Nb and Ta are conventionally viewed as having identical ionic radii (0.64 \AA in octahedral co-ordination [35]). However, the sensitivity of D_{Nb}/D_{Ta} to amphibole $mg\#$ is consistent with Ta^{5+} having a radius some $0.01\text{--}0.02 \text{ \AA}$ smaller than Nb^{5+} [32], such that Ta is favoured by amphiboles with smaller M1-sites, i.e. higher $mg\#$. This finding has potential implications for the origin of low Nb/Ta ratios of early continental crust [36].

Another example is fractionation between uranium and thorium caused by clinopyroxene [37,38]. In diopside-rich clinopyroxenes the M2-

site into which U and Th are incorporated is similar in size to Ca^{2+} , such that the Th^{4+} ion (1.05 Å in VIII-fold co-ordination) is more readily incorporated than U^{4+} (1.00 Å; Fig. 6). In contrast, diopside-poor clinopyroxenes, characteristic of the mantle solidus, have a smaller M2-site, which preferentially incorporates U rather than Th. The sense of U–Th fractionation during melting of spinel lherzolites is therefore sensitive to clinopyroxene composition, which in turn varies with pressure. This finding has important ramifications for the observed radioactive disequilibrium between ^{230}Th and ^{238}U in mid-ocean ridge basalts, and the depth at which melting begins [37,38].

Finally, Van Westrenen et al. [39] have shown that the fractionation of Zr and Hf by garnet is very sensitive to garnet composition, because the larger Zr^{4+} ion can enter both the X- and Y-sites in some garnets, whereas smaller Hf^{4+} is largely confined to the Y-site in all garnets. The distribution of Zr between the two sites is a sensitive function of X-site size, which in turn is related to the calcium content of the garnet. This finding has potential implications for the fractionation of these two elements during melting of recycled ocean crust in the mantle.

It is worth noting that both of these examples invalidate Goldschmidt’s second ‘rule’, namely that when two ions have similar radii and the same charge, it is always the smaller ion that is more readily incorporated. Of critical importance is the size of the ions *relative to the site of interest*: no simple generalisation is possible.

6. Electrostatics – charge matters too

The observation that partition coefficients vary near-parabolically with ionic radius is not, in itself, enough to explain all variability in partition coefficients. Electrostatic work is done when the ions of interest have a different charge to that of the cation normally resident at a lattice site, and this cannot be ignored. It has been observed that the optimum size of the lattice site varies inversely with cation charge [40,41], suggesting that polarisation of the co-ordinating oxygen ions around a lattice site is a key process. A good example is the

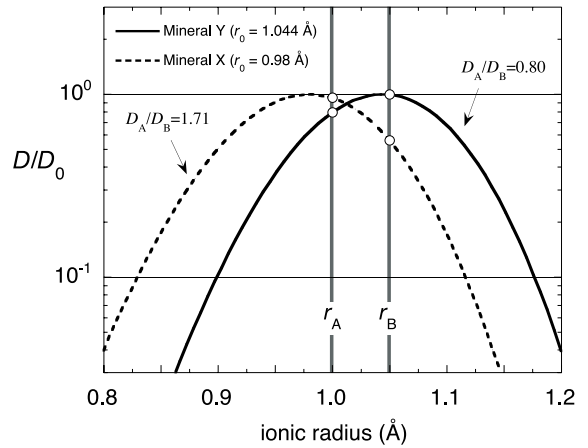


Fig. 6. Changes in composition along a solid solution series lead to small changes in the dimensions of a lattice site. These small changes lead in turn to changes in the relative fractionation between ions with the same charge and similar ionic radius. Here we show schematically the effect of changes in site size on fractionation of isoivalent ions (A^{n+} and B^{n+}) with similar ionic radii ($r_A = 1.00 \text{ \AA}$; $r_B = 1.05 \text{ \AA}$). At a given pressure and temperature, mineral X (broken curve) has an optimum site radius ($r_{0(M)}^{n+} = 0.98 \text{ \AA}$) closer to r_A than r_B , such that $D_A/D_B = 1.71$. Isomorphous mineral Y (solid curve) has $r_{0(M)}^{n+} = 1.044 \text{ \AA}$, closer to r_B than r_A , such that $D_A/D_B = 0.80$. The effect is most pronounced at large values of Z/d^3 (Fig. 5). Natural examples of fractionation caused by small change in crystal composition include Nb–Ta incorporation on the M1-site of amphibole [32], or U–Th incorporation on the M2-site of clinopyroxene [37,38].

incorporation of trivalent lanthanide (Ln^{3+}) ions at the large M2-site in clinopyroxene, normally occupied by Ca^{2+} or Mg^{2+} . Such *heterovalent* substitution requires the presence of a charge-compensating defect (cation or anion) elsewhere in the lattice (e.g. $\text{Ln}^{3+} + \text{Na}^{1+} = 2\text{Ca}^{2+}$), which will also entail some degree of lattice strain. At high temperatures there is likely to be considerable disorder between the trace ion and its compensating defect [42]: the two need not sit on adjacent sites and the total lattice strain need not be a simple sum of the contributions from the two isolated defects.

One way to address the charge problem is to use the composition of the host mineral to calculate the proportion of sites that have just the right charge for the cations of interest [43]. For example, in clinopyroxene, though most M2-sites contain Ca^{2+} there is usually sufficient tetrahedral

aluminium (Al^{T}) replacing silicon, or sodium replacing calcium, to create a statistical proportion of M2-sites the local charge of which is 3+ rather than 2+. This leads to a dependence of lanthanide partition coefficients on Al^{T} , as observed [44–46]. However, the exact relationship between lanthanide partitioning and Al^{T} suggests that some 3+ cations can enter sites with a charge other than 3+, provided an electrostatic energy penalty is paid. This penalty can be quantified [43] by assuming that the electrostatic work required to dissipate the excess (or deficit) charge is controlled by the size of the charged region and the dielectric

constant of the lattice (Fig. 7a). In other words, this is a continuum approach directly analogous to the elastic strain approach, wherein excess charge and deficit charge are penalised equally. Consequently, strain-compensated partition coefficients (D_0) for a series of cations entering a given lattice site without strain vary parabolically with charge [40,43] (Fig. 7b). The magnitude of the energy penalty is consistent with a charged region of $\sim 200 \text{ \AA}^3$ and a dielectric constant in the range of those measured for silicate minerals [43]. Once again, there is a happy fusion of experimental geochemistry and mineral physics. There is also violation of Goldschmidt's third 'rule' which proposes that when two ions have the same radius but different charge, the higher charged ion will be more readily incorporated. Evidently the critical factor is the charge of the ions *relative to the charge of the site* and it is difficult to generalise.

One useful consequence of the electrostatic approach is its ability to predict the partition coefficients for species of zero charge, such as the

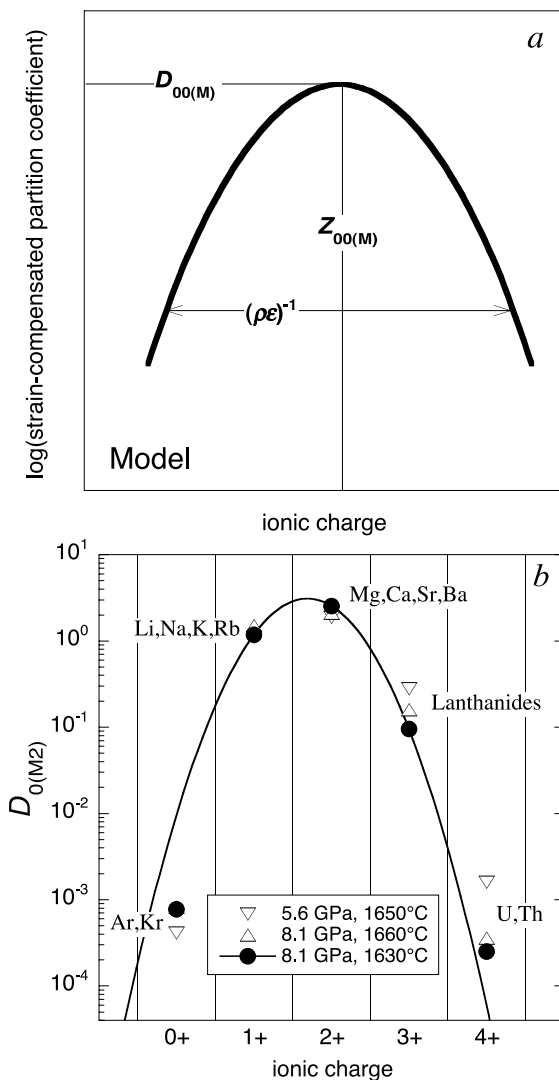


Fig. 7. Ionic charge has a strong influence on partition coefficients. (a) Cartoon illustrating the *electrostatic model* of trace element partitioning. For a series of ions with the optimum ionic radius at site M ($r_{0(M)}^{n+}$), partitioning is controlled by the ionic charge (Z_n) relative to the optimum charge at the site of interest, $Z_{0(M)}$. The larger the charge mismatch, the smaller the partition coefficient. The variation in $\log D_{0(M)}^{n+}$ with Z_n is parabolic and can be described by the expression [43]:

$$D_{0(M)}^{n+} = D_{00(M)} \times \exp \left\{ \frac{-N_A e_0^2 (Z_n - Z_{0(M)})^2}{2\epsilon \rho R T} \right\}$$

where e is the charge on the electron. The tightness of the parabola is inversely proportional to the radius (ρ) of the region over which the excess charge is distributed, and the dielectric constant (ϵ) of that region. The partition coefficient for a (fictive) ion that can enter a lattice site without causing elastic strain or electrostatic charging is denoted $D_{00(M)}$. (b) Fit of experimental clinopyroxene-melt [48] partitioning data to the electrostatic model. Three experiments, at slightly different pressures and temperatures are shown. Only species entering the large M2-site are plotted. For each isoivalent group (noble gas, alkaline-earths, lanthanides, etc.) $D_{0(M)}^{n+}$, derived as shown in Fig. 4b, is plotted against charge. The solid circles can be fit to a parabola with $Z_{0(M)}$ of +1.69 and ρe of 21.6 \AA . Note that the larger noble gases (Ar–Kr), with effective charge of approximately -2 , have similar partition coefficients to U^{4+} and Th^{4+} with effective charge $+2$.

noble gases. Although often viewed as rogue species trapped in extended defects or at interstitial sites, recent experimental studies [47,48] show that clinopyroxene-melt partitioning of neon, argon, krypton and xenon is consistent with them entering the M2-site, where they incur roughly the same electrostatic penalty as 4+ ions (e.g. U, Th). Computer simulation studies of noble gas incorporation in clinopyroxene [48,49] support this contention, showing that the energy penalty for inserting the heavier noble gases at lattice sites, charge balanced by other species elsewhere in the lattice, is much lower than that for inserting them interstitially or at grain boundaries. Evidently, if noble gases enter lattice sites in minerals then they are subject to the same partitioning constraints as conventional trace elements and the common assumption that noble gases are perfectly incompatible ($D \approx 0$) during mantle melting no longer holds.

7. The vexing question of melt chemistry

It has been known since the early 1970s that partition coefficients in silica-rich systems tend to be higher than in silica-poor systems. This could be a result of the lower temperatures of evolved systems, the more iron- or sodium-rich compositions of their minerals, or the more polymerised structure of silica-rich melts. The elastic strain approach accords relatively little significance to the melt phase for the simple reason that the negligible shear moduli of liquids preclude development of significant elastic strains. In other words, melts, with their largely disordered arrangements of ions, are much more tolerant of mismatches in ionic radius than are crystals. The corollary is that trace elements can exercise a much greater influence on their local environment in melts than they can in crystals. Consequently, we should expect melt-chemical effects on partitioning, as is apparent from the experimental observations that: (1) trace elements are not equipartitioned between coexisting silicate liquids (e.g. [50,51]), and (2) oxide activities in silicate melts are sensitive to melt composition [52]. Melt-chemical effects can be investigated by

performing isobaric, isothermal partitioning experiments in simple systems and correcting the partition coefficients for the effects of size and charge as described above. Any resultant compositional dependence in D_0 is then due to the melt, both via entropy of mixing and through variations in the partial molar free energy of solution of the host mineral with melt composition.

One simple way to quantify the effects of melt chemistry has been to treat the melts as ideal mixtures of hypothetical components with six- or twelve-oxygen stoichiometry (e.g. $\text{CaMgSi}_2\text{O}_6$, LnMgAlSiO_6 , etc.), in much the same way as in Burnham's classic model of water solubility in silicate melts [53]. Of course, melts are not really physical mixtures of equal-oxygen units, but this simple entropic device is surprisingly effective [54–56]. Certainly, the issue of melt chemistry would benefit from a more sophisticated treatment, ideally through further experimental studies of two-liquid partitioning, or of mineral solubilities as a function of melt composition. This is particularly needed in the case of crustal melting, where the budget of some trace elements is controlled almost entirely by accessory phases, such as zircon or apatite, which show little or no solid solution. In this case melt compositional effects are likely to be very important [57]. In the mantle, however, where mineral solid solution is ubiquitous it seems likely that melt compositional effects will be subordinate to those due to crystal chemistry, as evinced by the examples above.

8. Pressure and temperature

Composition, pressure and temperature are inextricably linked in high-variance natural magmatic systems. All three variables affect partition coefficients. Without careful experimentation in low-variance synthetic systems it is very difficult to assess which has the controlling influence. The approaches described above allow for systematic elimination of compositional effects, and create the basis for isolating the effects of pressure and temperature. A particular advantage of compensating for charge and size is that it allows the partition coefficients for a large number of trace

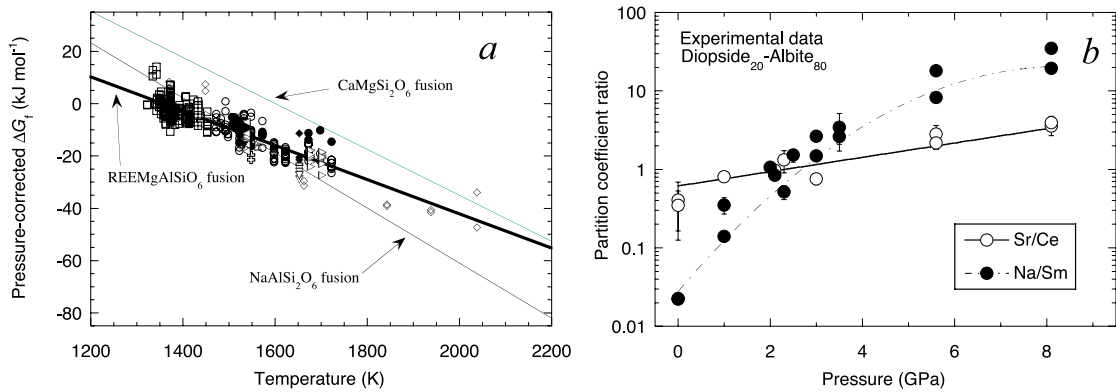


Fig. 8. Pressure and temperature have a profound effect on mineral-melt partitioning. This can be parameterised in terms of the melting (or fusion) reaction of a trace element component with the same stoichiometry as the host mineral, e.g. LnMgAlSiO_6 in the case of lanthanide incorporation into clinopyroxene. A model is derived by first correcting all partition coefficients for lattice strain. Second, simple assumptions are made about activity-composition relationships in crystal and melt to derive an equilibrium constant (e.g. K_{Ln}) for the melting reaction that has minimal compositional dependence. Finally, the set of equilibrium constants is regressed against pressure and temperature. In (a) the variation in free energy of fusion ($\Delta G_f = RT \ln K_{\text{Ln}}$), corrected for pressure, is plotted against temperature for a large number of experimental determinations, shown by different symbols [54]. The slope of the trend gives the entropy of fusion of (fictive) LnMgAlSiO_6 , the intercept is the enthalpy of fusion. The entropy of fusion of LnMgAlSiO_6 (slope) is different to that for diopside ($\text{CaMgSi}_2\text{O}_6$) and jadeite ($\text{NaAlSi}_2\text{O}_6$), indicating that fractionation between lanthanides, alkaline earths and alkali metals by clinopyroxene will be sensitive to temperature. As the volumes of fusion of these three components are also different, pressure-induced fractionation will also occur. (b) Illustration of pressure-induced fractionation between alkali metals (Na), alkaline earths (Sr) and lanthanides (Ce, Sm) as a function of pressure for near-liquidus clinopyroxene–melt partition coefficients in the system 20% diopside–80% albite. The ratios of partition coefficients $D_{\text{Na}}/D_{\text{Sm}}$ and $D_{\text{Sr}}/D_{\text{Ce}}$ increase, respectively, by a factor 2000 and 10 over the pressure range 0–8 GPa. These effects may be obscured in aggregated melts formed over a considerable depth range, but will be manifest as Sr/Ce or Na/Sm anomalies in melt inclusions or residual minerals. Experimental details can be found in references [38,47,56]; partition coefficients are from unpublished data on the same experiments. Error bars are 1 s.d.

elements to be parameterised in terms of relatively few variables (Fig. 4). This is clearly preferable to, say, deriving individual pressure–temperature expressions for all 13 lanthanides. For example, if we know how clinopyroxene–melt $D_{0(M2)}^{3+}$ (see Fig. 1 for a definition) varies with pressure and temperature we can use lattice strain theory to derive partition coefficients for each individual lanthanide.

The challenge in deriving expressions for the pressure–temperature dependence of partition coefficients lies in selecting a suitable partitioning equilibrium. Ideally this is a reaction for which the thermodynamic activity on both sides can be adequately modelled. The strain and electrostatic compensations described above are, in essence, simple activity-composition models for the crystal phase. What is needed is an equivalently robust means of estimating variations in the partial mo-

lar free energy of solution of the host mineral with melt composition. In the absence of such a model, the simplistic equal-oxygen approach, described above, provides a useful means of modelling trace element partitioning in terms of a melting (or fusion) reaction [54–56] (Fig. 8a). It is testament to the success of this approach that the derived parameters for temperature and pressure dependence resemble the known enthalpies, entropies and volumes of fusion for natural crystal components with the same stoichiometry. An interesting feature of these models is that they predict different pressure–temperature sensitivities for different valences (Fig. 8b). In the course of a natural polybaric, polythermal process one valence group will fractionate from another in a way that would be completely overlooked using the conventional constant partition coefficient approach (Figs. 2 and 8b).

A special case of melt compositional effects is that of water. There is a growing recognition that water is present in almost all geological situations, including those conventionally thought of as bone-dry, such as mantle melting [58]. In other settings, such as subduction zones, water has an overwhelming influence on magma generation and magma chemistry. Clearly, we must consider what effect water has on mineral-melt partitioning over a wide range of water content.

Even at very low concentrations water has a profound effect on phase equilibria, notably lowering melting temperatures. Water's greatest effect is on the activities of trace element components in the melt rather than the crystal. One can envisage two possibilities (Fig. 9): (1) water reduces component activities in melts, so decreasing partition coefficients, and (2) wet processes occur at lower temperature, so increasing partition coefficients. A useful approach [59] is to start with the known effect of water on the depression of melting points, which is a function of the mixing between water and other components in the melt. If it is assumed that water mixes similarly in all melts of a similar cation:anion ratio, then water should reduce the partition coefficients of all such components equally. However, the concomitant effect of temperature is a function of the enthalpy of fusion (or solution), which is not constant for all mineral components (Fig. 8a). The larger the enthalpy of fusion (or solution) of a component, the greater the temperature effect, and the less it will be offset by the effect of water. The smaller the enthalpy of fusion, the less the effect of temperature and the more it will be offset by water. In this way we can explain why water lowers clinopyroxene-melt partition coefficients for the lanthanides, but has negligible effect on garnet-melt partition coefficients [60]. Water, like temperature and pressure, also has the effect of fractionating one valence group from another.

9. Future developments

We identify three important new future developments in trace element partitioning. The first is in the field of computer simulation. Lattice statics

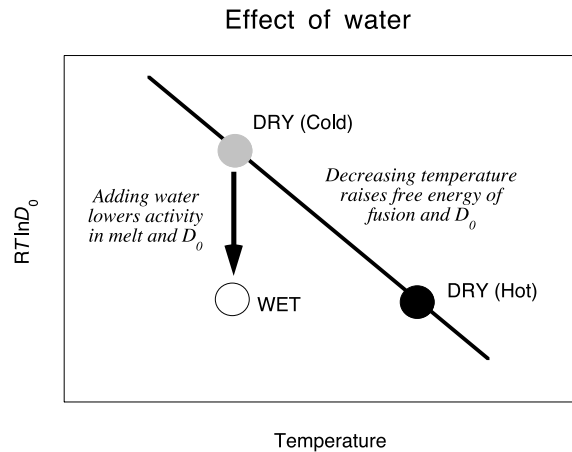


Fig. 9. Cartoon illustrating the effect of water on trace element partitioning [59]. Processes involving water occur at lower temperature than dry processes. Because most mineral phases have positive enthalpy and entropy of fusion, partition coefficients increase with decreasing temperature. This *temperature effect* is offset by the fact that water dissolves non-ideally in silicate melts, so reducing component activities more than by simple dilution. This *water effect* is related to the activity coefficient of water ($\gamma_{\text{H}_2\text{O}}$) in the silicate melt of interest, which in turn can be estimated from the depression of melting point of minerals. If the temperature effect is greater than the water effect, partition coefficients will go up with addition of water; if the temperature effect is less than the water effect, then partition coefficients will go down. By assuming that $\gamma_{\text{H}_2\text{O}}$ is the same for all components with similar cation:anion ratios (e.g. REEMgAlSiO₆, CaMgSi₂O₆, NaAlSi₂O₆) and estimating the enthalpy and entropy of fusion of fictive trace element components using partitioning data (cf. Fig. 8a), it is possible to quantify the effect of water on partitioning for any cation in any phase. Water also has the effect of fractionating one valence group from another, in an analogous fashion to pressure and temperature (Fig. 8b).

calculations, using two-body potentials to describe the energies of atoms in the lattice, provide a valuable atomistic adjunct to experimental studies [33,42]. Simulated enthalpies of trace element-doped lattices faithfully reproduce many experimental observations, and uphold the general validity of the lattice strain and electrostatic models. The simulations, however, have two big limitations. First, they are performed at zero K, and therefore take no account of vibrational energies. Second, it is prohibitively difficult to simulate silicate melts. Advances in the field of free energy calculations (including ab initio techniques) will

greatly improve the utility of the calculations [49]. A key theoretical breakthrough will be the direct simulation of silicate melts, preferably without recourse to interatomic potentials. The ability to calculate accurate mineral-melt partition coefficients (e.g. [61,62]), rather than determine them experimentally, will be of immense benefit, especially at experimentally inaccessible extreme pressures.

Spectroscopic studies of trace species in silicate minerals and glasses, such as are now possible using high energy X-rays [63,64], can provide considerable insights into the local environment of trace ions. These will be extremely important for the issue of coupling between trace elements and their charge-compensating species and the formulation of realistic activity-composition relations. Similarly, X-ray and neutron diffraction studies of synthetic crystals [65,66] are providing increasingly detailed information on the dimensions of lattice sites and on inter-site ordering of ions. Such studies provide an invaluable cross-check on inferences about lattice site sizes derived from partitioning studies alone.

A final challenge is trace element partitioning between minerals and aqueous fluids over a wide range of conditions. A number of experimental breakthroughs (e.g. [67]) has greatly increased the accessibility of mineral-fluid partitioning at high pressure and temperature. To date, however, there are insufficient data to establish whether crystal chemical controls are similar to those in mineral-melt partitioning. At much lower temperature trace element ratios in biogenic and abiogenic minerals are increasingly used as proxies for climate change [68]. Despite the proliferation of data, there is no underlying theoretical basis for the observed fractionations and there is no consensus as to whether low temperature partitioning is subject to crystal-chemical controls (e.g. [69]), or whether kinetic (non-equilibrium) effects predominate (e.g. [70]).

We conclude that partitioning is a fundamental, but often neglected, feature of many geochemical problems. Our understanding of partitioning must strive to keep pace with analytical advances. A better understanding will impact on a wide range of fields from mantle dynamics to climate change.

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