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Irregularities in patterns of element partition

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SUMMARY. In clinopyroxene-melt systems the distribution of chromium and vanadium ions departs from the general pattern of element partition as a function of ionic radius. These departures may be explained by crystal-field effects. Melt structure and the nature of the coordination of cations in the melt also help to determine the pattern of distribution and the extent of the departures from regularity.

THE importance of ionic radius and charge as factors determining the distribution of elements has long been recognized (e.g. Goldschmidt, 1937). The effect of these two parameters was further emphasized by the work of Onuma *et al.* (1968) and later by Jensen (1973). Onuma *et al.* constructed plots of element partition (mineral/lava) v. ionic radius, which show, despite some anomalies, a family of fairly simple, sub-parallel, curves with each passing through those points that share a common value of charge. Jensen extended this work by plotting many more published data for mineral/matrix systems but using the better ionic radius values of Whittaker and Muntus (1970) based on those by Shannon and Prewitt (1969, 1970). Most of the anomalies disappear when the better radii values are used, and the curves clearly show that for any one mineral/matrix system the peak positions are at the same ionic radius value or values and that these maxima remain at the same radius values for different systems containing the same mineral. Therefore, it was suggested (Jensen, 1973) that each maximum is 'the optimum ionic radius for a cation in a given structural position while the width of the peak is an expression of the ability of the lattice to adapt to non-ideal cations in that position'.

If the hypothesis is accepted that the curves of the form derived by Jensen correctly depict the influence of ionic radius on element partitioning then any departure from these curves will indicate the effect of other factors. For example, diagrams for element partition between plagioclase feldspar and matrix frequently show europium plotting well above the curve for trivalent cations defined by the other rare earths. The extent of the deviation may be used to estimate the proportions of the divalent and trivalent europium ions in the magma at the time of feldspar crystallization (Jensen, 1973). Departures from the curves might also arise for particular elements from crystal-field effects (see Burns, 1970). If melt structure influences partitioning then this will modify the curves from one system to another.

It is the purpose of this paper to consider the contribution that two parameters—crystal-field effects and melt structure—could make to element distribution (Henderson, 1975) and to present new data in support of the discussion.

Crystal-field effects. Henderson and Dale (1969) and Dale and Henderson (1972) argued that crystal-field effects are dominant in determining the differences in partition of the divalent transition-element ions Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} between olivine and magma and also between pyroxene and magma. These ions were studied because they have large differences in their crystal-field octahedral site-preference energy (OSPE), ranging from zero in Mn^{2+} to 86.2 kJ/mol in Ni^{2+}, while having similar, but not identical, ionic radii and electronegativities.

Henderson and Dale (1969) used the integrated form of the van't Hoff isochore, $\ln k = -\Delta H/RT + B$, where ΔH is the difference in heats of solution of the ion in the crystal and liquid phases and B is an integration constant, to postulate that if OSPE contributes significantly to the ΔH term then there should be a linear relationship between $\ln k$ and OSPE of the ions. Such a linearity was observed for a number of cases. However, the differences in ionic radius of these ions, although quite small, are now seen from Jensen's work to be very significant and could be sufficient to account for the whole variation in $\ln k$.

Plots of the type constructed by Onuma *et al.* (1968) suggest that for many elements ionic radius is the major factor (at constant ionic charge)

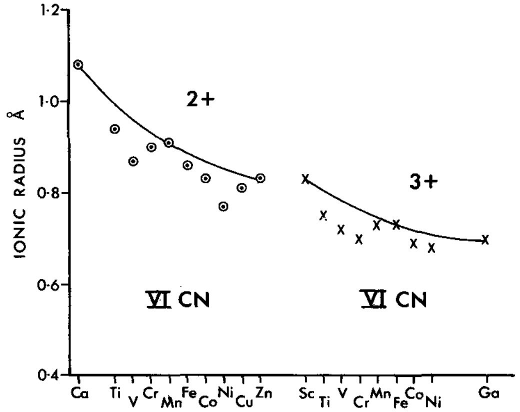

FIG. 1. Plot of ionic radius (Whittaker and Muntus, 1970, values) versus atomic number for elements of the first long period.

determining element distribution, and this is often true whether or not the ionic radius is influenced by crystal-field effects. When such an influence exists it necessarily follows that a correlation will be present between element partitioning and the crystal-field effects, but it is not profitable to regard this as an influence of the latter on partitioning since the influence of radius is more widely established and understood. Certain anomalies are, however, consistently observed in plots of this kind that lead to the suggestion that direct crystal-field effects may also have to be taken into account.

Plots of ionic radius (Whittaker and Muntus values) against atomic number for transition-element ions in high-spin state and in sixfold coordination reveal a characteristic pattern with two troughs (fig. 1) in contrast to the smooth curve shown for the lanthanides. For all the 2+ transition-element ions the extent of each deviation from the smooth curve in fig. 1 correlates well with crystal-field orbital splitting terms for octahedral coordination. This correlation could lead to a smooth variation of ionic radius with OSPE but of the seven transition-element ions for which appropriate data are available only Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} define a smooth curve (see fig. 2) (Cu^{2+}, 63.6 kJ/mol OSPE, lies slightly above the dashed curve). The existence of this smooth variation for the four ions explains, but only in part, why they can define linear ln *k* versus OSPE plots (as shown by Henderson and Dale, 1969) as well as smooth ionic radius curves (as shown by Jensen, 1973). In the case of the 3+ transition-element ions fig. 2 shows that there is a relatively small and irregular variation in ionic radius but a large variation in OSPE for the five ions Fe^{3+}, Ti^{3+}, V^{3+}, Mn^{3+}, and Cr^{3+}. For example, there is a difference of only 0.03 Å between the radii of the three ions Fe^{3+}, V^{3+}, and Cr^{3+} but a difference of 157.3 kJ/mol in OSPE. If direct crystal-field effects influence element partition then they should be discernible in the differences in partitioning behaviour of these three ions.

It is to be noted that a smooth variation between ionic radius and OSPE exists for the four trivalent ions Sc, Ti, V, and Cr but as is shown and discussed below, Sc, V, and Cr do not produce linear plots on

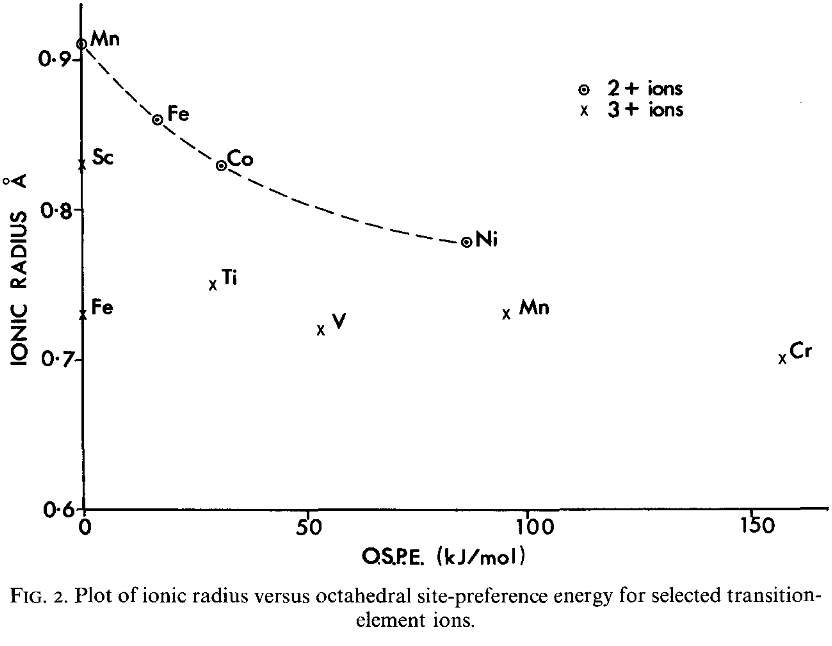

FIG. 2. Plot of ionic radius versus octahedral site-preference energy for selected transition-element ions.

ln k versus OSPE diagrams for pyroxene-matrix systems, the apparently anomalous behaviour of Sc being explicable in terms of its ionic radius value.

Melt structure. Henderson and Dale (1969) suggested that the slopes of the lines in ln k versus OSPE diagrams are dependent upon the relative availabilities of tetrahedral and octahedral cation sites in the melt as well as on temperature. Earlier, Burns and Fyfe (1964) had postulated that transition-element ions occupy tetrahedral as well as octahedral sites in a magma. This idea has been taken and extended by a number of authors (e.g. Whittaker, 1967; Dale and Henderson, 1972; Irvine and Kushiro, 1976). Furthermore, a theoretical discussion by Whittaker (1978) on the cavities in a random close-packed structure shows it may be necessary to consider the possible existence of a significant number of fivefold coordination sites in a natural silicate melt although, as yet, no direct evidence for their occurrence is available. The possible existence of all such sites in a magma and variations in the extent of their occupancy by transition-element ions is an important aspect in determining the partitioning of cations, especially those with high octahedral site-preference energies.

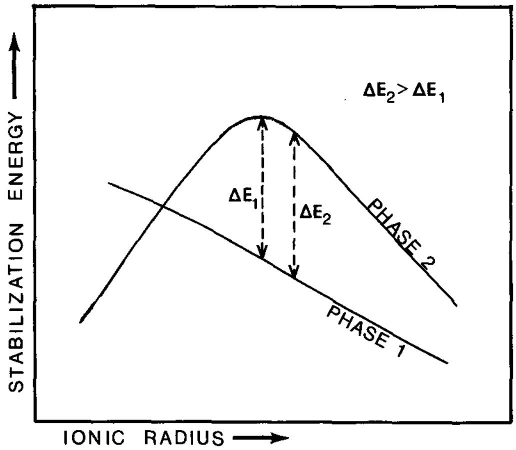

FIG. 3. Hypothetical variation in site stabilization energy of an ion with ionic radius in two phases, see text.

If in a simple hypothetical case, fig. 3, the rate of change of cation stabilization energy with change in ionic radius is sometimes greater for the site occupancy in the melt (phase 1) than in a coexisting crystal (phase 2) the ion showing the largest partition coefficient will be the one having the largest chemical potential change from melt to crystal, ΔE_2 in the diagram. Hence the equilibrium system will give rise to what might be called 'an apparent optimum radius' or an 'equilibrium optimum radius' on a partition coefficient v. ionic radius plot that is displaced relative to the 'true optimum radius' for phase 1 (position ΔE_1 on the diagram). However, the form of the cation-stabilization-energy-ionic-radius curve for a magma of any specific composition is not known and it may be that the nature of silicate melt structure produces little difference between 'apparent' and 'true' optimum radii. The still limited evidence indicates that there is little, if any, peak shift on ln k v. ionic radius plots in a given system where there are data on different magma compositions (Jensen, 1973; Matsui *et al.*, 1977) provided that the composition of the mineral phase remains constant (Philpotts, 1978). Variations in the proportions of occupied fourfold and sixfold coordination sites by a cation species in the melt will affect the partition coefficient of a cation that has a significant OSPE while other ions may not be so affected, thus giving rise to possible changes in peak heights and slopes of the curves. Studies of the effect of melt composition (e.g. Takahashi, 1978) on element partitioning will help to quantify such effects.

Results. The partition of four trivalent transition metal ions, Sc, V, Cr, and Fe, between clinopyroxene and groundmass of six basic extrusive rocks has been studied. Determinations were made by instrumental neutron activation analysis with a high resolution GeLi detector, for Sc, V, and Cr. Accuracy and precision of the analyses are estimated to be better than 2% at the 2σ level for Sc and Cr and 8% for V. Total iron concentration in the matrix of each rock was determined by atomic absorption and the ferrous iron by Wilson's method. Ferric iron content was obtained by difference. Ferrous and total iron concentrations in the separated pyroxenes (2.5 mg) were determined by a modification (Easton, 1972) of the dipyridyl-complex method of Riley and Williams (1959).

The pyroxenes were separated by the use of heavy liquids and small quantities were further purified by hand-picking. Final purity was estimated to be better than 99%.

Concentrations and the calculated partition coefficients are given in Table I. Major element compositions of the minerals and groundmass fractions, together with other trace-element concentrations, are being determined and form part of a larger study on element partition currently in progress. The partition coefficients for three samples are also plotted on ln k versus ionic radius diagrams (fig. 4), where curves of a similar form to those constructed by Jensen (1973) are given for reference. The reference curve is sketched so that its peak position is at 0.79 Å and with the line passing through the iron and scandium data points, as in fig. 8 of Jensen (1973), for an augite/matrix system.

TABLE I. *Concentrations and partition coefficients* (*k*)

	CCGG 4			CCGG 10			CCGG 15		
	pyrox.	matrix	*k*	pyrox.	matrix	*k*	pyrox.	matrix	*k*
Sc (ppm)	83	35	2.4	84	36	2.3	96	35	2.7
V (ppm)	285	340	0.84	405	330	1.2	385	370	1.0
Cr (ppm)	3120	413	7.6	2600	200	13.0	1075	54	19.9
Fe_2O_3 (%)	1.60	4.29	0.37	1.75	4.47	0.39	*	2.46	< 2.8
	CCGG 20			CCGG 23			CCGG 26		
Sc (ppm)	62	36	1.7	84	29	2.9	90	30	3.0
V (ppm)	300	210	1.4	345	n.d.	—	410	220	1.9
Cr (ppm)	3320	475	7.0	5220	680	7.7	1280	194	6.6
Fe_2O_3 (%)	0.96	2.07	0.46	1.26	2.59	0.49	1.51	2.51	0.60

n.d. = not determined.
* Total iron as Fe_2O_3 = 6.90%.
Analysts: A. J. Easton (pyroxene ferric iron determinations).
P. Henderson (INAA).
N. J. Walsh (matrix ferric iron determinations).

Discussion. If it is assumed that the ionic radius assigned to each ion is accurate then previous work (Onuma *et al.*, 1968; Jensen, 1973) and the results given here show that while a number of ions define a smooth variation of partition coefficient with radius, a few ions do not. In the case of clinopyroxene-matrix partitioning, chromium shows the strongest deviation, with vanadium showing a smaller one. Matsui *et al.* (1977) also report on the deviation from regularity of chromium partition (augite-groundmass) in an alkali-olivine basalt.

The decrease in the value of the partition coefficient in the order $Cr^{3+} > V^{3+} > Fe^{3+}$ follows the order of decreasing octahedral site-preference energy and this, together with the departures from the type of curve constructed by Jensen, suggests that crystal-field effects make a distinct contribution to element partition. It is possible, therefore, that there are also small OSPE effects as well as radius effects in determining the partition of Fe^{2+}, Co^{2+}, and Ni^{2+} so that the divalent curves drawn by Jensen and other workers are not purely radius-based. However, the prominent role that radius plays is well shown by the data given in Table I and fig. 2, where the two ions Sc^{3+} and Fe^{3+}, both with zero OSPE, have very different partition-coefficient values. It is also clear that the point for Sc^{3+} would lie well above the line defined by Fe^{3+}, V^{3+}, and Cr^{3+} on a ln*k*-OSPE plot.

Certain caveats to the statement that crystal-field effects make a distinct contribution to element

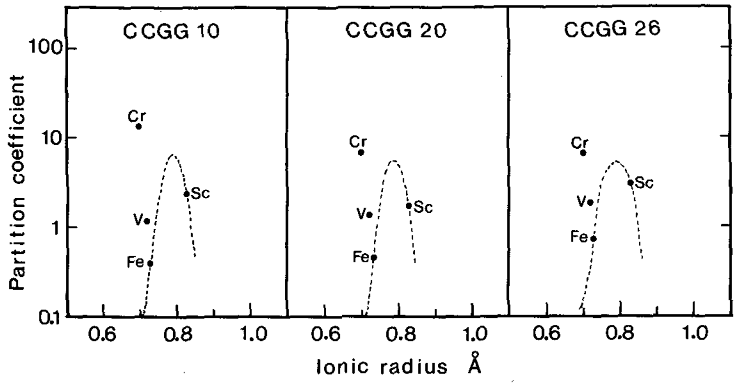

FIG. 4. Plots of partition coefficient versus ionic radius (Whittaker and Muntus, 1970, values) for the ions Sc^{3+}, V^{3+}, Cr^{3+}, Fe^{3+} in three clinopyroxene-matrix pairs. The dashed curve is drawn for reference purposes, see text.

partition are needed. First, the exact nature of the coordination of cations in the melt is not known so that the use of both simple OSPE values (as determined from spinels) and ionic radii values for particular coordination numbers may be an oversimplification. Secondly, no account has been taken of the remote possibility that oxidation states other than 3+ for the three elements Sc, V, and Cr existed at the time of crystallization of these terrestrial basalts.

There is a significant probability that the analysed phases (clinopyroxene–groundmass) were not at chemical equilibrium when the element partition, as measured, was established. Some of the pyroxenes studied here are zoned (see Appendix), and some may contain sub-microscopic or even microscopic inclusions despite the care taken over the mineral separation. Hence, the determined partition coefficients, while of use in petrological modelling, are of more limited applicability in the study of crystal-chemical controls on partition, although attempts (e.g. Leeman and Scheidegger, 1977) to identify the existence of chemical equilibrium in rock systems can be made. However, the wide differences in the behaviour of the four chosen ions is a reflection principally of crystal-chemical control, and the determined partition coefficient need not reflect the equilibrium at the time of crystallization (De Pieri and Quareni, 1978). Kinetic controls, such as crystal-growth rates can affect the partition-coefficient values (Henderson and Williams, in press), but are unlikely to alter the general pattern of partitioning. Experimental investigations of transition-element ion distribution (Seward, 1971; Duke, 1976) show the same pattern of element partition as is observed for natural systems with chromium having high partition-coefficient values into clinopyroxene.

The type of partition-coefficient plot constructed by Onuma *et al.* (1968) and Jensen (1973) allows a semi-quantitative, and in some cases quantitative, determination of element partition coefficients or oxidation states. It is also possible that any differences in the pattern of partitioning for a mineral–matrix pair from one rock system to the next reflect differences in the melt structure, which may be determinable. Furthermore, as shown by De Pieri and Quareni (1978) differences in the patterns can be informative about the existence of post-crystallization processes, such as unmixing. Thus, it is important to establish which ions produce irregularities in the partitioning patterns, and what are the causes of the deviations. Crystal-fields effects appear to be one of these causes.

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APPENDIX

Specimen details. Pyroxene compositions where given were determined by electron microprobe analysis.

CCGG 4. Olivine basalt, Reunion Island, near Rock Ecrite, Piton des Neiges. Phenocrysts: olivine abundant, clinopyroxene minor, slightly zoned $Ca_{44}Mg_{46}Fe_{10}$–$Ca_{46}Mg_{41}Fe_{13}$. Fine-grained matrix.

CCGG 10. Vesicular basalt, Zubair Island Group, Red Sea. Phenocrysts of plagioclase (slightly zoned), olivine, and pyroxene (augite, slightly zoned). Glassy to fine-grained groundmass.

CCGG 15. Basalt, Jebel at Tair, Red Sea. Phenocrysts: plagioclase, minor olivine, and rare clinopyroxene. Fine-grained matrix.

CCGG 20. Basalt, Saba Island, Zubair Group, Red Sea. Phenocrysts: large, abundant plagioclase (zoned); abundant olivine (some with included oxides); clinopyroxene, zoned, $Ca_{46}Mg_{46}Fe_{9}$–$Ca_{43}Mg_{48}Fe_{9}$. Crystalline matrix with abundant microlaths of plagioclase.

CCGG 23. Vesicular basalt, Zubair Group Islands, Red Sea. Phenocrysts: abundant olivine, slightly oxidized; minor clinopyroxene $Ca_{47}Mg_{45}Fe_{8}$. Matrix, fine-grained to glassy.

CCGG 26. Vesicular basalt, Centre Peak Island, Zubair Group, Red Sea. Phenocrysts: abundant plagioclase (zoned); olivine and minor clinopyroxene $Ca_{45}Mg_{42}Fe_{13}$–$Ca_{45}Mg_{40}Fe_{15}$. Matrix, fine-grained to glassy.

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