

Partition coefficients of alkali and alkaline-earth elements between alkali feldspar phenocrysts and their lava matrix

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SUMMARY. Plots of partition coefficients (mineral/matrix) against ionic radius of the alkali and alkaline earth elements in forty-four alkali feldspars from rhyolites and trachytes show two kinds of diagram, one for homogeneous alkali feldspars with a single peak, and the other for cryptoperthites with a wide spread of points, which cannot represent a single peak, but may probably be explicable in terms of two peaks. The difference in behaviour does not seem to be due to the chemical composition, but is apparently related to the crystallographic features of the alkali feldspar structures. In particular the presence of two peaks in the diagrams of the cryptoperthites seems to be due to the existence of lattice positions suited to receive bigger ions (K, Ba, Rb) and smaller ions (Na, Ca, Sr) in the potassic and sodic domains.

RECENT work by Onuma, Higuchi, Wakita, and Nagasawa (1968), Higuchi and Nagasawa (1969), and Jensen (1973) has shown that when the partition coefficients of major and trace elements between phenocrysts and their lava matrix are plotted against the ionic radius a family of subparallel curves is obtained, one for univalent elements, one for divalent, and so on. For a given mineral sample the curves show peaks at the same value of the ionic radius and have approximately the same general slope.

Jensen (1973) has also shown that samples of a given mineral from different localities may produce curves with different slopes and with different values of the partition coefficients, but that all produce peaks at the same values of the ionic radius. It is well known that the total chemistry of the melt, the pressure, the temperature, and the rate of crystallization may affect the partition coefficients of phenocrysts; it is therefore probable that these factors may be responsible for variations in the slopes and relative heights of the curve for a given valency for samples of the same mineral crystallizing in different environments.

Examples of these families of curves are given by

Jensen (1973) for plagioclases, clinopyroxenes and orthopyroxenes, amphiboles, olivines and micas. Peaks have been related to the mineral structures, the apex of a peak presumably indicating the optimum ionic radius for a cation in a given structural position. Thus for plagioclases Jensen observes one broad peak with its apex at 1.18 Å, defined by the curves of univalent, divalent, and trivalent cations, with an ancillary small peak at around 1.00 Å defined by the curve of trivalent cations. The broad main peak may be correlated with the fact that in this structure there are two to four crystallographically distinct sites for the large cations, the average bond lengths in these sites differing by about 0.10 Å.

The aim of the work described in the present paper is to investigate the partition coefficients of univalent and divalent cations in alkali feldspars of acidic magma, and to seek structural correlation of the observations, using diagrams similar to those of Jensen. In the high albite-sanidine series, a narrow symmetrical peak might be expected to correspond to a single structural site for the K ion or to a split close pair of sites for the Na ion.

Results

The chemical data for univalent and divalent elements of feldspar phenocrysts and their groundmasses have been taken from the work of Piccirillo, Gregnanin, and De Pieri (1975) relating to rhyolitic rocks of Amba Costantino (Wollo, Ethiopia) and from that of De Pieri, De Vecchi, Gregnanin, and Piccirillo (1977) relating to 26 rhyolitic and trachytic rocks of the Euganean Hills (Veneto, Italy). Altogether, chemical data are provided for 77 feldspars, of which 33 are plagioclases and 44 are alkali feldspars in the range of composition 18 to 58 mol. % Or.

The groundmasses were first separated from the

phenocrysts using a Frantz isodynamic separator, and were then purified manually under the microscope. The feldspar phenocryst concentrates were obtained by heavy-liquid separation and were checked under the microscope until a degree of purity 98–99% was achieved. The elements K, Ca, Mn, Sr, Rb, and Ba were determined by X-ray fluorescence using the fusion method, Na (and K again) by flame photometry, and Mg by atomic absorption. The estimated error is less than 2%. Since the MnO contents of the alkali feldspars and their groundmasses are not included in De Pieri *et al.* (1977) they are reported in Table III.

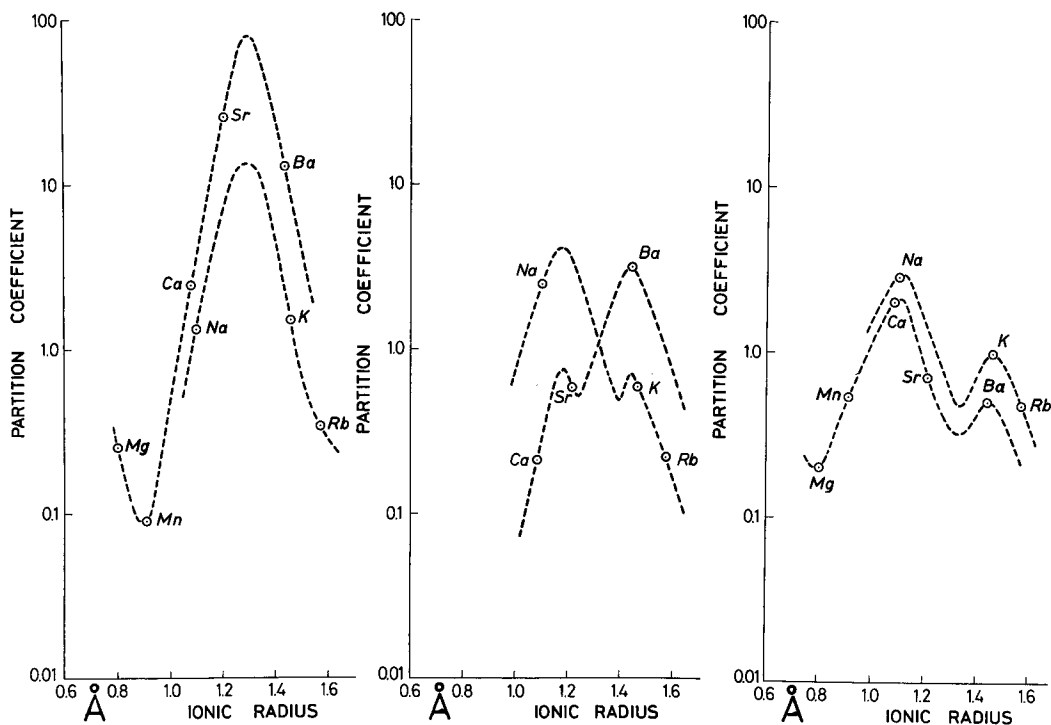
The partition coefficients of K, Na, Rb, Ca, Sr, and Ba have been calculated for all the feldspars considered; for the Euganean feldspars the coefficients of Mg and Mn have also been calculated. The partition coefficients for the alkali feldspars are listed in Tables I and II.

Semiquantitative electron-microprobe checks on feldspar phenocrysts do not show marked chemical inhomogeneity for K and Ba due to zoning.

For comparison with the curves of Jensen (1973)

the partition coefficients are plotted in figs. 1–3 against the ionic radii of Whittaker and Muntus (1970) using coordination number CN = 6. Very similar curves, of course displaced along the horizontal scale, can be obtained by using the more realistic CN = 7 for all atoms, or by using CN = 7 for the small atoms Na, Ca, and Sr and CN = 9 for the large atoms K, Rb, and Ba. In plotting the curves it is assumed (as in earlier work) that the shape of the curve remains fairly constant, and that the curve is not skewed, even though the slopes and relative heights on the vertical scale may vary. On this assumption, a reasonable estimate of the accuracy of the peak positions is $\pm 0.015 \text{ \AA}$ for plagioclases and for alkali feldspars showing a single peak; for alkali feldspars showing two-peak diagrams the estimated accuracy is somewhat lower.

Plagioclases. In agreement with the observations of Jensen (1973) the partition-coefficient diagrams show a broad asymmetrical peak in the range of ionic radius 1.16–1.19 \AA , with a maximum frequency around 1.17 \AA ; the peak is well defined by



FIGS. 1 to 3: FIG. 1 (*left*). Partition coefficient vs. ionic radius for alkali feldspar/matrix. Alkali feldspar 38D ($\text{Or}_{4.5-4}\text{Ab}_{52.3}\text{An}_{2.3}$) from a rhyolite of Euganean Hills (Italy). FIG. 2 (*middle*). Partition coefficient vs. ionic radius for alkali feldspar/matrix. Alkali feldspar 25 ($\text{Or}_{27.3}\text{Ab}_{71.5}\text{An}_{1.2}$) from a rhyolite of Amba Costantino (Ethiopia). FIG. 3 (*right*). Partition coefficient vs. ionic radius for alkali feldspar/matrix. Alkali feldspar 143 ($\text{Or}_{44.6}\text{Ab}_{54.3}\text{An}_{1.1}$) from a rhyolite of Euganean Hills (Italy).

the curves of both univalent and divalent elements. In this work no trivalent elements were involved, so that the ancillary peak around 1.00 Å observed by Jensen does not enter into consideration.

Alkali feldspars. On plotting the data for the 44 alkali feldspars listed in Tables I and II, the partition-coefficient diagrams obtained are of two quite different types. For 18 of the materials both univalent and divalent curves show a single narrow symmetrical peak, located for the different materials at various points within the rather large range of values of the ionic radius 1.21–1.32 Å (see also Discussion and fig. 4). For the remaining 26 alkali feldspars, an irregular scatter of experimental points is obtained, which cannot define one single peak; following the rules given by Jensen (1973) curves can be drawn in a number of ways, but will always define at least two peaks (figs. 2 and 3).

TABLE I. *Mineral/matrix partition coefficients of Amba Costantino rocks*

Sample	K	Na	Rb	Ca	Sr	Ba
24†	1.94	13.13	0.74	0.05	0.08	2.09
25†	0.59	2.48	0.22	0.21	0.59	3.18
44*	1.26	6.54	0.11	0.10	0.48	4.30
43†	1.41	1.86	0.48	0.47	0.86	0.46
42†	1.64	5.81	0.33	0.45	3.72	18.04
41*	0.84	2.48	0.44	0.81	3.58	2.71
39*	0.82	1.79	0.27	3.67	8.09	4.03
38†	1.12	1.60	0.27	1.61	4.27	10.89
36*	1.29	1.94	0.18	0.83	4.84	12.44
34*	0.99	5.80	0.16	0.28	0.97	4.01
32‡	1.67	2.18	1.00	0.03	0.61	0.69
31‡	1.22	1.95	0.30	0.00	1.33	2.29
29‡	1.88	2.73	0.44	0.18	1.45	2.85
27‡	1.41	1.87	0.26	0.86	1.13	4.74
30†	1.33	1.93	0.41	0.17	0.88	0.84

* Homogeneous alkali feldspars (anorthoclases).

† Fully unmixed cryptoperthites and homogeneous alkali feldspars, the former preponderant.

‡ Fully unmixed cryptoperthites.

A clue to the explanation of this striking difference in behaviour is obtained from a detailed examination of the structural state of the 44 alkali feldspars used. Under optical examination, all are homogeneous, but X-ray precession photographs of 'single' crystals are quite different for the two groups: all the 18 materials which give 'one-peak' partition-coefficient diagrams are truly homogeneous in the sense that they give a single-crystal X-ray pattern; all the 26 'two-peak' materials give X-ray patterns characteristic of cryptoperthites. Most of these 'two-peak' materials exhibit the type

of cryptoperthitic unmixing that produces the peculiar superstructure reflections described by De Pieri and Quareni (1974); only a few consist of a monoclinic potassic phase and a triclinic sodic phase with the usual characteristics of albite, pericline, or albite and pericline twins.

TABLE II. *Mineral/matrix partition coefficients of Euganean Hill rocks*

Sample	K	Na	Rb	Ca	Sr	Ba	Mg	Mn
71N‡	0.84	1.46	0.40	1.40	2.46	2.13	0.06	0.07
71O‡	1.19	1.35	0.88	0.82	1.33	1.72	0.06	0.09
71P‡	1.44	1.23	0.88	0.54	0.97	1.19	0.06	0.09
115E†	0.85	1.40	0.49	1.43	2.97	2.18	0.02	0.15
115B‡	1.29	1.24	0.84	0.73	1.27	1.60	0.02	0.10
111T*	1.74	1.19	0.79	0.83	6.45	9.85	0.00	0.03
127L*	1.65	1.08	0.61	0.72	6.70	10.00	0.00	0.22
116S*	0.64	1.57	0.26	3.81	13.00	5.70	0.11	0.37
116F*	0.79	1.53	0.35	3.04	10.17	5.52	0.17	0.22
116I‡	1.15	1.38	0.75	1.62	6.21	4.03	0.11	0.20
116Z‡	1.41	1.24	1.41	0.95	2.33	1.23	0.04	0.19
125N*	0.76	1.51	0.20	3.32	16.18	6.49	0.05	0.16
125O†	1.07	1.41	0.36	2.07	10.05	5.35	0.11	0.16
145O*	0.70	1.49	0.17	3.82	9.21	3.52	0.33	0.52
114G*	1.78	1.59	0.80	1.55	10.31	6.51	0.17	0.10
126*	1.44	1.30	0.47	0.89	6.12	5.42	0.25	0.20
54†	1.35	1.38	0.60	3.21	1.33	1.67	0.22	0.12
144‡	1.50	1.38	0.47	3.38	4.75	1.40	0.50	0.12
51D*	1.49	1.26	0.53	1.92	10.67	6.65	0.33	0.07
39D*	1.48	1.33	0.48	2.34	19.29	6.86	0.18	0.13
38D*	1.48	1.31	0.34	2.42	25.60	12.86	0.25	0.09
60D*	1.83	1.29	0.62	1.53	10.74	6.35	0.25	0.09
124B†	1.68	1.41	0.62	1.60	9.64	5.00	0.40	0.11
59B†	1.60	1.39	0.74	1.59	22.80	2.59	0.10	0.16
143‡	0.98	2.85	0.48	2.00	0.70	0.50	0.20	0.54
37D‡	1.93	1.23	0.67	0.87	1.37	0.39	0.14	0.15
142†	2.07	1.70	0.74	1.89	0.80	0.59	0.25	0.20
57G†	1.98	1.32	0.67	0.77	4.83	0.38	1.25	0.13
1D‡	1.51	1.67	0.21	1.64	2.14	0.14	0.10	0.06

* Homogeneous alkali feldspars.

† Intermediate stage cryptoperthites.

‡ Fully unmixed cryptoperthites.

There is thus strong systematic evidence that the two-peak diagrams are associated with cryptoperthitic unmixing of the feldspars. It would be quite unrealistic to regard this strikingly obvious and simple structural correlation as arising in some way from chance errors in trace-element analysis or contamination of the material for analysis by other minerals—effects that might perhaps be invoked if the irregular scatter of partition-coefficient observations were considered in isolation.

Discussion

Given the basic structural correlation of single-peak partition-coefficient curves with homogeneous alkali feldspar structure, and two-peak curves with cryptoperthitic structure, it is possible

to discuss some more detailed observations that have a bearing on the mechanisms involved.

For single-peak homogeneous alkali feldspars the position of the peak of the partition-coefficient curve (on the horizontal scale of ionic radii) is a function of the orthoclase content, the lower values (~ 1.26 Å) corresponding to the more sodic phenocrysts, higher values (~ 1.34 Å) to the more potassic (fig. 4). Assuming a disordered statistical

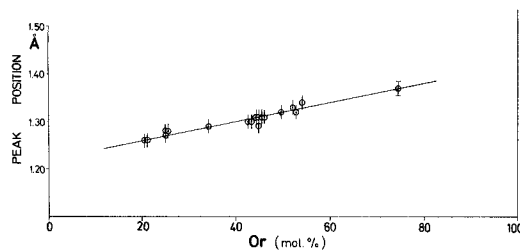


FIG. 4. Peak position vs. Or content for single peak homogeneous alkali feldspars. The vertical lines represent the estimated errors. Φ Data of Philpotts and Schnetzler (1970).

distribution of the Na and K ions in the site concerned, it is obvious that the silicate framework can adjust itself locally so as to accommodate ions of different sizes in the site, as in sanidine (Phillips and Ribbe, 1973), high albite (Ribbe, Megaw, Taylor, Ferguson and Traill, 1969), and anorthoclase (De Pieri and Quareni, 1973).

Similarly, in two-peak alkali feldspars, two sites are involved, the first corresponding to the peak at

~ 1.15 Å, the second to the peak at ~ 1.45 Å, the cavity in the silicate framework being adjusted locally so as to be suitable for smaller cations (Na, Ca, Sr) and larger cations (K, Ba, Rb) respectively. The partition coefficients of the major elements Na and K are very close to these two peaks, as would be expected.

In a few samples a stage intermediate between truly homogeneous and fully unmixed has been observed. For these materials the X-ray reflections characteristic of the homogeneous structure are accompanied by continuous streaks, which are very weak and diffuse (if the unmixing process is just beginning) or fairly sharp and strong, and almost condensed into individual reflections (if unmixing is nearing completion); there is a corresponding transition in the curve of partition coefficients from one-peak to two-peak type through an intermediate stage that might be regarded either as a broad one-peak or as an ill-defined two-peak type. It is in this intermediate stage that the two sites, both able to accept either small or large ions, are becoming differentiated as suitable for small ions or large ions respectively. It should perhaps be emphasized that chemical composition seems to have relatively little influence on the type of phenocryst observed—for example, figs. 1 and 3 show one-peak and two-peak types with very similar compositions. Again, there is no reason to think that the different types of partition-coefficient diagram are due to the crystallization process of the phenocrysts—for example, alkali feldspars of both types, of identical composition, have been found in chemically similar rocks of the same crystalline formation, coexisting with plagioclases, which always produce one-peak diagrams. And, finally, coexisting alkali feldspars of different chemical compositions have been noted in the same sample of trachytic rock, one homogeneous with a one-peak diagram, the other unmixed with a two-peak diagram.

One final point may be important in relation to any discussion of the thermal history of the rocks. Obviously all alkali feldspars were homogeneous at the time of crystallization, and would then have produced one-peak diagrams. The presence of two-peak diagrams means that unmixing after crystallization is responsible for significant changes in the partition coefficients and consequently during unmixing sensible ion-exchange took place between phenocrysts and groundmass. This may be reasonably expected since in the unmixing phenomenon there is ion movement in the solid. Therefore whenever any unmixing has taken place in the crystals, the partition coefficient between phenocrysts and groundmass may not reflect the equilibrium at the time of crystallization.

TABLE III. Matrix (*) and feldspar MnO contents of Euganean Hill rocks

Sample	MnO	Sample	MnO	Sample	MnO
71*	0.044	125N	0.005	38D	0.002
71N	0.003	125O	0.005	60*	0.021
71O	0.004	145*	0.029	60D	0.002
71P	0.004	145O	0.015	124*	0.038
115*	0.067	114*	0.029	124B	0.004
115E	0.010	114G	0.003	59*	0.064
115B	0.007	126*	0.031	59B	0.010
111*	0.038	126	0.006	143*	0.011
111T	0.001	54*	0.056	143	0.006
127*	0.023	54	0.007	37*	0.027
127L	0.005	144*	0.058	37D	0.004
116*	0.054	144	0.007	142*	0.030
116S	0.020	51*	0.058	142	0.006
116F	0.012	51D	0.004	57*	0.031
116I	0.011	39*	0.053	57G	0.004
116Z	0.010	39D	0.007	1*	0.032
125*	0.032	38*	0.023	1D	0.002

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