

## Alkali feldspars from part of the Galway granite, Ireland

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**SUMMARY.** The structural states of alkali feldspars from the eastern end of the Galway Granite show transitions from orthoclase to microcline as a result of late deformation. Analyses of twenty samples for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{S}$ ,  $\text{Cu}$ ,  $\text{Zn}$ ,  $\text{Ga}$ ,  $\text{Rb}$ ,  $\text{Sr}$ ,  $\text{Ba}$ , and  $\text{Pb}$  agree with previously determined orders of entry of elements into the 'alkali site'. A relationship between this order of entry and the melting points of feldspar end-members is discussed.

THE Galway Granite, on the north side of Galway Bay, Ireland, is of Caledonian age (384 Myr, Leggo *et al.*, 1966), and the geology of the east end of the pluton has been described by Coats and Wilson (1971). They showed that an aphyric alkali granite occurs at the margin of the pluton followed by a coarse porphyritic granite, which becomes more basic away from the margin and develops a foliation westwards (fig. 1). Alkali feldspar makes up between 20 and 35 % of the granites, occurring as megacrysts in the porphyritic granites.

*Analytical methods.* Separation of feldspars was by handpicking from the rocks so that the obliquities and chemical analyses refer to crystals greater than about 1 mm. After further crushing the samples were repeatedly passed through a magnetic separator. Twenty-five samples, located as shown in fig. 1, were studied by X-ray diffraction; twenty of these samples have been analysed for major and trace elements.

The obliquity, expressed as  $\Delta$  ( $= 12.5 (d_{131} - d_{\bar{1}\bar{3}\bar{1}})$ , Goldsmith and Laves, 1954) measured using the method of Hall (1966), was determined from X-ray powder patterns obtained using a Philips diffractometer with  $\text{Cu-K}\alpha$  radiation. The optic axial angle ( $2V_\alpha$ ) was measured by direct orthoscopic observation on a 4-axis universal stage using an average of six crystals from each rock.

The chemical determinations were by X-ray fluorescence methods as described by Leake *et al.* (1969). The precision of the method is better than 5 % for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CaO}$ ,  $\text{K}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Rb}$ ,  $\text{Sr}$ , and  $\text{Pb}$ , 10 % for  $\text{Na}_2\text{O}$ ,  $\text{Zn}$ ,  $\text{Ga}$ , and  $\text{Ba}$ , and better than 25 % for  $\text{S}$  and  $\text{Cu}$ .

*Structure.* The structural states vary from orthoclase to near maximum microcline (table 1). Most of the samples are either dominantly monoclinic ( $\Delta < 0.2$ ) or

TABLE I. *Chemical analyses (trace elements in ppm); CaO in host rock; obliquity ( $\Delta$ ); per 32 oxygen; molecular %*

	1	9	13	15	24	25	26	29	30	32
SiO <sub>2</sub>	65.8	66.4	66.0	67.2	65.5	65.3	66.2	65.4	65.4	65.6
Al <sub>2</sub> O <sub>3</sub>	19.38	18.26	18.49	18.31	19.37	19.13	18.89	18.98	18.64	19.76
TiO <sub>2</sub>	0.021	0.025	0.026	0.024	0.006	0.007	0.026	0.027	0.023	0.030
Fe <sub>2</sub> O <sub>3</sub>	0.13	0.00	0.15	0.07	0.11	0.11	0.04	0.02	0.16	0.00
CaO	0.35	0.22	0.28	0.26	0.12	0.12	0.26	0.29	0.39	0.22
Na <sub>2</sub> O	2.79	2.41	2.04	2.34	2.76	3.31	2.28	2.04	2.78	2.04
K <sub>2</sub> O	11.98	12.28	13.26	12.55	13.34	12.35	13.05	13.17	12.12	13.25
Total	100.45	99.60	100.25	100.75	101.21	100.33	100.74	99.93	99.51	100.90
S	112	30	31	82	47	32	63	35	88	114
Cu	29	17	7	7	11	11	8	11	44	62
Zn	26	20	19	16	17	17	18	16	35	46
Ga	16	16	13	17	19	23	14	16	15	14
Rb	338	535	455	500	449	617	425	417	364	400
Sr	468	168	362	248	62	23	454	496	475	521
Ba	2402	1755	2397	1840	54	74	2891	3504	2464	3624
Pb	88	89	74	90	139	140	80	79	97	88
CaO (host rock)	n.d.	0.87	1.81	1.77	§	§	1.66	2.07	1.95	2.05
$\Delta$	0.15	0.09	0.13	0.00	0.67	0.60	0.00	0.00	0.05	0.10
2V <sub><math>\alpha</math></sub>	65	62	58	55	74	75	60	58	53	56
Zoning†	1	1	1	1	0	0	0	1	1	1
Cross-hatching‡	0	0	0	0	1	1	0	0	0	0
<i>Number of ions on the basis of 32 oxygen:</i>										
Si	11.90	12.11	12.02	12.12	11.86	11.89	11.99	12.03	11.96	11.87
Al	4.13	3.92	3.97	3.89	4.14	4.10	4.03	4.11	4.02	4.21
Fe <sup>3+</sup>	0.02	0.00	0.02	0.01	0.01	0.02	0.01	0.00	0.02	0.00
Ca	0.07	0.04	0.05	0.05	0.02	0.02	0.05	0.06	0.08	0.04
Na	0.98	0.85	0.72	0.82	0.97	1.17	0.80	0.73	0.99	0.72
K	2.77	2.86	3.08	2.89	3.08	2.87	3.02	3.09	2.83	3.06
Ba	0.02	0.01	0.02	0.01	0.00	0.00	0.02	0.02	0.02	0.03
Or	72.68	76.14	79.90	76.87	75.65	70.65	77.99	79.75	72.83	80.13
Ab	25.55	22.71	18.68	21.79	23.78	28.77	20.71	18.77	25.21	18.75
An	1.77	1.15	1.42	1.34	0.57	0.58	1.30	1.48	1.95	1.12

\* variable obliquity.

§ pegmatite.

‡ 1 = observed;

dominantly triclinic ( $\Delta > 0.7$ ), variable structural states being present in samples 63 and 177.

The areal distribution of obliquity values is shown in fig. 2. Sample 9 from the biotite-poor aphyric granite at the margin of the pluton is orthoclase and occurs in a granite showing little or no signs of deformation or recrystallization. Those from the coarse porphyritic granite east of the Barna fault have obliquities of less than 0.2 in the east and greater than 0.7 in the west. To the west of the Barna fault, where the coarse porphyritic granite becomes foliated, the alkali feldspars have monoclinic or variable structures in the south, becoming maximum microcline northwards. There is a strong correlation between the ordering of the feldspars and the degree of recrystallization of the host granite as indicated by the deformation of quartz. Both increase

*optical axial angle ( $2V_\alpha$ ); presence of zoning; presence of cross-hatched twinning; atoms Or, Ab, An in alkali feldspars*

	63	64	79	108	125	151	167	177	201	209
SiO <sub>2</sub>	65.9	65.6	64.9	66.2	64.6	65.2	66.0	65.2	65.9	65.5
Al <sub>2</sub> O <sub>3</sub>	19.10	19.02	19.13	18.59	19.77	19.61	18.75	18.82	18.86	19.54
TiO <sub>2</sub>	0.021	0.018	0.022	0.025	0.023	0.028	0.024	0.025	0.020	0.021
Fe <sub>2</sub> O <sub>3</sub>	0.12	0.15	0.16	0.12	0.00	0.05	0.15	0.13	0.11	0.00
CaO	0.41	0.21	0.40	0.32	0.32	0.52	0.39	0.37	0.34	0.26
Na <sub>2</sub> O	1.97	3.50	2.62	2.49	1.83	2.06	1.92	2.29	2.54	1.92
K <sub>2</sub> O	13.34	12.12	13.12	13.07	13.45	12.87	14.17	13.64	13.48	13.41
Total	100.86	100.62	100.35	100.82	99.99	100.34	101.40	100.48	101.25	100.85
S	59	100	104	48	40	25	43	139	45	87
Cu	43	36	22	22	39	17	20	53	31	5
Zn	33	30	25	26	28	16	26	38	26	14
Ga	14	14	14	13	15	13	13	13	13	15
Rb	330	430	297	278	345	412	321	283	277	420
Sr	536	367	511	558	530	570	540	537	551	484
Ba	2637	1540	2541	3332	2917	3355	3158	2583	2202	2527
Pb	90	99	89	84	89	88	82	87	95	89
CaO (host rock)	3.62	0.94	3.08	2.44	3.59	3.55	3.45	2.90	1.70	2.92
$\Delta$	0.23*	0.11	0.94	0.83	0.93	0.78	0.88	0.54*	0.20	0.79
$2V_\alpha$	70	63	74	n.d.	81	78	76	64-84	75	78
Zoning	I	I	o	o	o	o	†	†	†	o
Cross-hatching	o	o	o	o	I	I	o	†	o	I
<i>Number of ions on the basis of 32 oxygen:</i>										
Si	11.93	11.90	11.85	11.99	11.82	11.86	11.94	11.91	11.92	11.89
Al	4.08	4.06	4.12	3.97	4.26	4.21	4.00	4.05	4.02	4.18
Fe <sup>3+</sup>	0.02	0.02	0.02	0.02	0.00	0.01	0.02	0.02	0.01	0.00
Ca	0.08	0.04	0.08	0.06	0.06	0.10	0.08	0.07	0.07	0.05
Na	0.69	1.23	0.93	0.87	0.65	0.73	0.67	0.81	0.89	0.68
K	3.08	2.80	3.06	3.02	3.14	2.99	3.27	3.18	3.11	3.11
Ba	0.02	0.01	0.02	0.03	0.02	0.02	0.03	0.02	0.02	0.02
Or	80.09	68.90	75.36	76.49	82.37	78.30	81.48	78.36	76.58	81.04
Ab	17.85	30.11	22.72	21.95	16.08	19.05	16.65	19.87	21.81	17.64
An	2.05	1.00	1.92	1.56	1.64	2.66	1.87	1.77	1.61	1.32

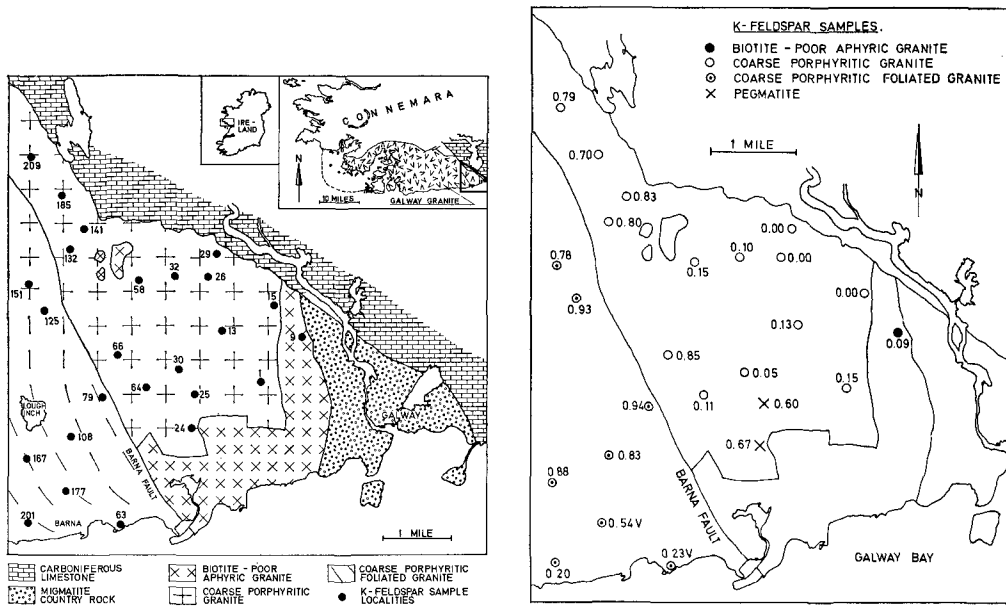
o = not observed;

† = faintly developed.

n.d. = not determined.

away from the granite margin east of the Barna fault and increase northwards west of this fault. Although ordering of alkali feldspars has often been correlated with chemical composition, obliquity is significantly correlated at the 95 % level with only SiO<sub>2</sub> and K<sub>2</sub>O and the obliquity is believed to have been produced by post-crystallization deformation (Tuttle, 1952).

Originally the alkali feldspars were orthoclase with low obliquity and low  $2V$  (fig. 3A) and this is preserved in the feldspars in the east of the area. Post-crystallization shearing in the deeper parts of the batholith caused the granite foliation and variable ordering of the alkali feldspars. The growth of triclinic domains, however, does not always keep up with the change in  $2V$ , resulting in the preservation of intermediate states with high  $2V$  and low  $\Delta$  (fig. 3B).



FIGS. 1 and 2: FIG. 1 (left). Location of area studied and geological map showing alkali feldspar sample localities. FIG. 2 (right). Areal distribution of obliquity ( $\Delta$ ) values of the alkali feldspars from the eastern end of the Galway Granite.

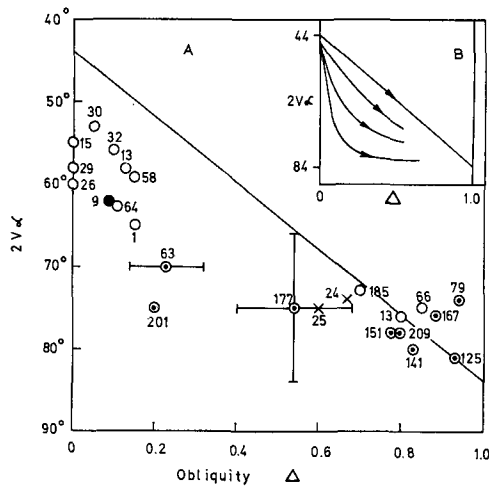


FIG. 3. A: Relationship of optic axial angle ( $2V_{\alpha}$ ) to obliquity ( $\Delta$ ) for the alkali feldspars from the eastern end of the Galway Granite. B: Diagram to illustrate the various ways in which a high-temperature alkali feldspar can become ordered (from Hall (1966), fig. 7A). (Key as in fig. 2).

Prominent zoning (table I) can be observed under the microscope in most of the samples with  $\Delta < 0.2$ . It can be faintly detected in those of variable state, but is absent when the obliquity value is greater than 0.70. This zonation may be chemical, but is more likely due to different degrees of Al-Si ordering, because the zoning is inversely related to obliquity.

The two pegmatite alkali feldspars (24 and 25) have intermediate structural states ( $\Delta = 0.60$  and  $0.67$ ) with broad asymmetric 131 peaks and show good cross-hatched twinning, being undeformed and occurring in orthoclase-bearing granite in which the quartz is unstrained. Therefore their structural state is not the result of stress and is thought to be due to the presence of water acting as a catalyst in the orthoclase-microcline inversion (Donnay *et al.*, 1960).

*Chemistry.* The chemical analyses of the twenty alkali feldspars are given in table I and the linear correlation matrix calculated from them is presented in table II. All the samples plot near the Or-Ab side-line (fig. 4) within the Or-Ab stability field in the Or-Ab-An-H<sub>2</sub>O system at 5000 bars water-vapour pressure (Yoder *et al.*, 1957).

Silica and alumina are negatively correlated, probably because of the constant sum effect, these two oxides making up most of the Z group. Silica is negatively correlated (at the 95% confidence level) with obliquity, which may indicate that during the change to microcline excess SiO<sub>2</sub> is expelled from the lattice. The excess Si could substitute for Al if some of the alkali sites are left vacant to balance the ionic charges as suggested by Hall (1967).

All the alkali feldspars are pink in colour and small orientated inclusions of a red iron oxide are sometimes present, possibly representing iron exsolved from lattice sites on cooling.

Ca in the alkali feldspars falls regularly with the composition of the host rock (table I) but not as rapidly as Ba or Sr. The early alkali feldspars contain less Ca than Ba and only in the late pegmatite stage does Ca exceed Ba.

The anorthite content does not vary significantly with the Ab/Or ratio (fig. 4) but with the calcium content of the rock, and this suggests that Ca behaves differently to Na and is not exsolved beyond the boundaries of the pieces of K-feldspar being analysed, agreeing with Hall (1967).

All the feldspars are micropertitic and X-ray study shows that most of the Na is present in albite lamellae. Na has a strong negative correlation with K, due to the constant sum effect. The Na-K composition of the analysed feldspar is probably more affected by the amount of recrystallization and segregation of albite beyond the margins of the alkali feldspars being analysed than by the composition of the magma or the water-vapour pressure at the time of crystallization.

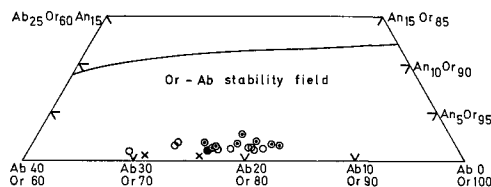


FIG. 4. Projection of part of the quaternary system  $\text{NaAlSi}_3\text{O}_8\text{-KAlSi}_3\text{O}_8\text{-CaAl}_2\text{Si}_2\text{O}_8\text{-H}_2\text{O}$  at 5000 bars pressure of  $\text{H}_2\text{O}$  (after Yoder *et al.*, 1957).



Sulphur has significant positive correlations with Cu and Zn, which are probably present as small sulphide inclusions. The sulphide content does not seem to be related to rock composition but is probably dependent on the presence of hydrothermal veins.

Ga varies over a small range in the granitic alkali feldspars, rising in the pegmatite feldspars in agreement with Heier (1962), who stated that Ga should show enrichment in feldspars of late-stage formation. This enrichment is consistent with the lower melting point of  $\text{KGaSi}_3\text{O}_8$  (1000–1020 °C) compared to  $\text{KAlSi}_3\text{O}_8$  (1170 °C) and also the larger ionic size of Ga compared to Al.

Rb is enriched in the late alkali feldspars but this enrichment is not extreme, the pegmatite feldspars only having a two-fold enrichment over the earliest-formed alkali feldspars. This is a reflection on the relatively mild nature of the fractionation in the Galway Granite compared to other plutons, where extreme differentiation can produce pegmatite alkali feldspars with more than 1000 ppm Rb (Heier and Adams, 1963). The K content of the feldspars is fairly constant so that the K/Rb ratio varies with the Rb content and falls from 400 to 170 (fig. 5D). Mean whole rock K/Rb ratios for the three major granite types range from 217 to 161 (Coats and Wilson, 1971), the higher ratios for the alkali feldspars reflecting the known preference of Rb for the 12-fold co-ordination sites in micas rather than the alkali sites in feldspars.

Sr has strong positive correlations with Ba and Ca and like these elements falls with fractionation. It has a closer association with Ba than with Ca; the Ba/Sr ratio varies from 10 to 4 in the granitic alkali feldspars and only in the pegmatite stage does it fall to 0.9 (fig. 5A). The Ca/Sr ratio rises steadily with fractionation from 4 to 37.

The Ba/Rb ratio (fig. 5B) varies from 12 to 0.1 and is thus a very good indicator of fractionation as deduced by Taylor (1965). Because of the similar Ba contents of the feldspars from the two porphyritic granites the Ba/Rb ratio does not exhibit such a regular variation as the Rb/Sr ratio (fig. 5C).

Rhodes (1969), Heier (1962), and Taylor and Heier (1960) found the distribution of Pb in alkali feldspars irregular and unpredictable. Here, however, there are positive correlations with Ga and Na and negative correlations with Ti, Ba, Sr, and Ca. The pegmatite alkali feldspars are enriched in lead in agreement with Heier (1962). The alkali feldspars are all enriched in Pb relative to the mean content for feldspars of 50 ppm found by Patterson and Tatsumoto (1964). The Pb content of alkali feldspars from lead-mining areas is known to be higher than in the other areas (Slawson and Nackowski, 1955; Cuturic *et al.*, 1968) and it is possible that this part of Ireland is a Pb-rich province. Pb probably occupies alkali sites in the alkali feldspars and is not connected with the other chalcophile elements, so there is no support for the suggestion (Rhodes, 1969) that Pb is present as galena.

*Discussion.* The elements that substitute for K in alkali-feldspars do so in the order: Ba > Sr > Ca > Pb (divalent elements) and K > Na > Rb (monovalent elements). As fractionation proceeds, elements on the left of this scale are depleted fastest. Thus as fractionation takes place Ba/Sr decreases and Ca/Sr increases. In a review of the trace elements occurring in feldspars, Heier (1962) found the same order of entry

into the 'alkali position' of K-feldspars. As a measure of this order of entry into the feldspar a depletion factor ( $D$ ) has been calculated (table III), where  $D$  is the ratio of the concentration of that element in the earliest formed feldspars (those in the coarse porphyritic foliated granite) divided by the concentration in the latest formed feldspars (those in the pegmatites).

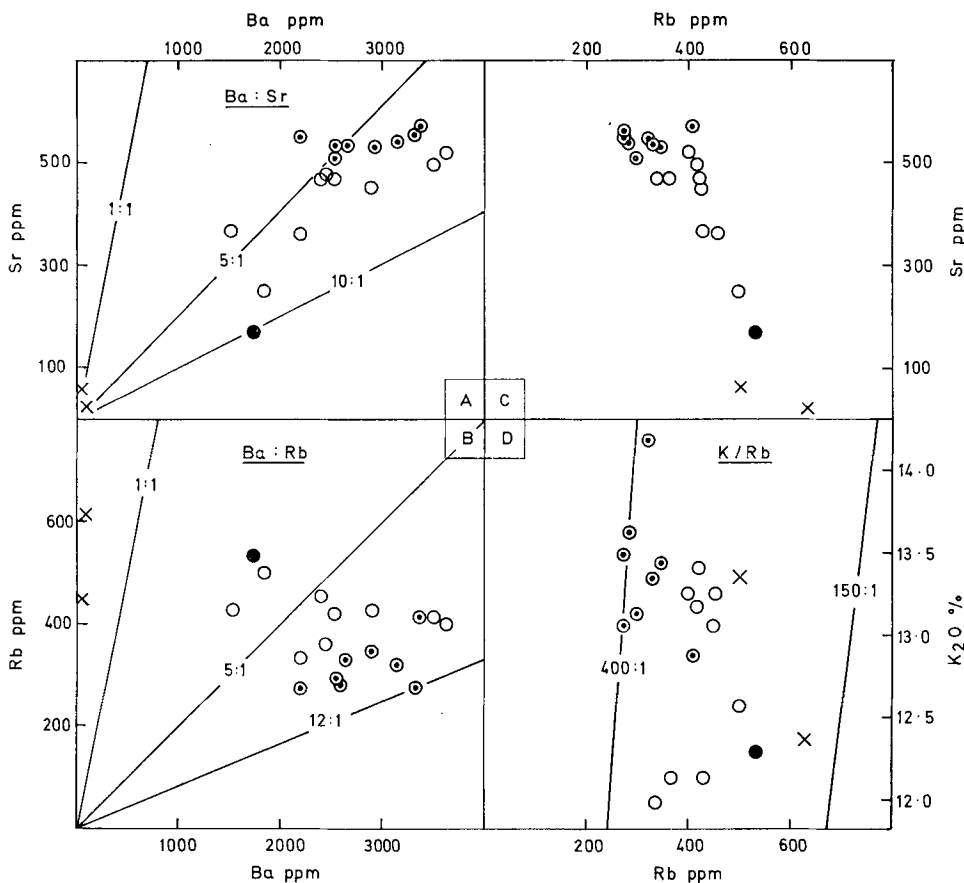


FIG. 5. Chemical variation of: A, Sr-Ba; B, Rb-Ba; C, Rb-Sr; D, Rb-K<sub>2</sub>O for the alkali feldspars from the eastern end of the Galway Granite.

Several parameters have been put forward to explain the order of uptake of ions in feldspars. Total bond energy ( $V_T$ ), which combines the effects of ionic size, charge, electronegativity, and crystal field stabilization energy, has been used by Nockolds (1966) and Damon (1968) to explain the behaviour of elements during fractionation. However there seems to be little correlation between  $V_T$  and  $D$ , except that Rb and Pb, the elements with the lowest  $V_T$  values, are enriched in the later formed feldspars. Damon (1968) suggests that the nature of the solid solution is determined primarily



by the radii of the cations and the melting points of the pure end-members are determined by the total bond energy. This does not appear to be so for the Ba, Sr, and Ca feldspars (table III), but there is a relationship between the melting points of the pure end-members and the depletion factor (fig. 6).

TABLE III. Depletion factor ( $D$ ), total bond energy ( $V_T$ ) for cation pairs, ionic radii ( $r$ ), and melting points ( $M.P.$ ) of feldspars

	$D$	$V_T$	$r$	$M.P.$		$D$	$V_T$	$r$	$M.P.$
Ba	44	545 Kcal/mole	1.46 Å	1715 °C	Na	0.73	505 Kcal/mole	1.09 Å	1118 °C
Sr	13	559	1.27	1660	Pb	0.63	478	1.35	1100
Ca	3.2	572	1.13	1553	Rb	0.58	487	1.56	—
K	1.0	493	1.43	1170					

The melting points of Ca, Na, and K-feldspars are taken from Eitel (1965), for Ba and Sr-feldspars from Dittler and Lasch (1930), and for Pb-feldspars from Sorell (1962). The  $V_T$  data are from Damon (1968) and the ionic radii from Nockolds (1966).

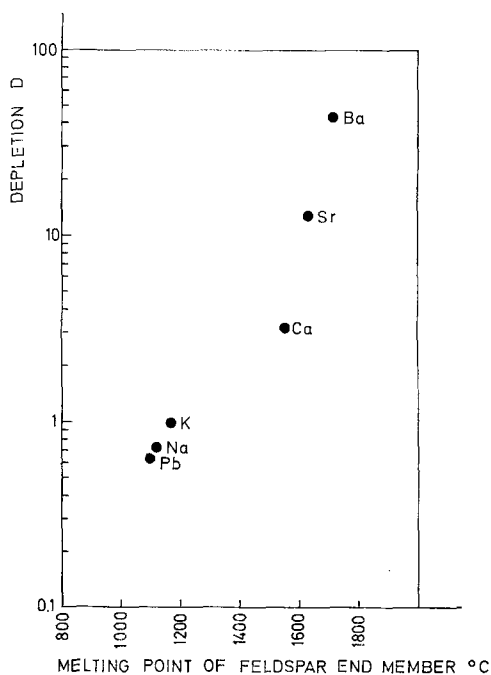


FIG. 6. Melting point of pure feldspar end-members against depletion factor ( $D$ ).

The correlation of order of entry with the melting point of the end-member feldspars does not necessitate an enrichment of the higher-melting feldspar in the early phases unless the solution is ideal. On the basis of ionic size Ba, Sr, Rb, and Pb-feldspars should form continuous solid solutions with alkali feldspars and this has

been confirmed for Ba-feldspars by Roy (1967) and for Rb-feldspars by Martin and Legache (1970). The geochemical behaviour of these elements when they enter alkali feldspars can therefore be predicted on the basis of the melting point of the feldspar end-member.

Na- and Ca-feldspars, however, do not form ideal solutions with alkali feldspar because of their ionic sizes, and have minima on the melting and freezing curves. The Na content of the alkali feldspars rises with falling temperature (Yoder *et al.*, 1957) but at lower temperatures albite is exsolved from the alkali feldspar. The final Ab content of the potash-feldspar is probably more dependent on the degree of this unmixing and segregation beyond the boundaries of the crystal than on the initial temperature of crystallization. The anorthite content of alkali feldspar decreases with the temperature of crystallization (Yoder *et al.*, 1957) but only slowly.

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