

# TRACE ELEMENTS IN FELDSPARS — A REVIEW

By

K. S. HEIER

Dept. of Geology, Rice University, Houston, Texas. [1]

## Introduction

Most of the work on feldspars during the recent years has been concerned with structural arguments and the problem of the relative stabilities of the different polymorphic forms of the feldspar minerals. The word “polymorphs” implies, of course, different structural forms with identical composition. However, the composition is often unknown, and only assumed to be the same, and the extent to which a feldspar polymorph may be stabilized by compositional difference has not been fully discussed. The question is important when the data obtained in the laboratories on pure synthetic compounds, or from heat treatment of natural compounds whose compositions are not allowed to vary with temperature, shall be applied to natural feldspars whose compositions as well as structures are dependent on the temperature. It is therefore within the scope of this seminar to discuss the geochemistry of the feldspars, and to delineate the “normal” concentrations of their most important trace elements.

Three main factors govern the extent of incorporation of minor elements in minerals:

1. ionic characteristics of the elements (size, charge, polarizing power);
2. crystal structure and composition of the mineral (nature of the chemical bonds, and coordination sites);
3. physico-chemical conditions of the environment (pressure, temperature, composition).

---

[1] Present address: Dept. of Geophysics, Australian National University, Canberra.

As petrologists we are especially interested in the third; or rather in trying to evaluate the physico-chemical conditions at the time of mineral formation. In order to use trace elements for this purpose, it is essential to understand the other governing conditions, and also what is the "normal" concentration and the range of concentration of a certain element in a mineral.

Any evaluation of geochemical data must first ascertain the location of the trace elements in the minerals. The following five locations are possible, (Moxham (1960, p. 531)): (1) in admixed foreign grains, (2) in inclusions and intergrowths in the mineral grains, (3) in voids in the lattice structure, (4) in an absorbed or adsorbed phase, developed during crystal growth, and (5) within the crystal structure occupying lattice positions. The greater the difference between a trace element and the principal structure forming elements in crystal-chemical nature (size, charge, electronegativity), the more unlikely the trace element will be to occupy a regular lattice position. The concentrations between 3 and 5 p.p.m. have been reported in K-feldspars (Adams *et al.*, 1959). This seems to be the same range as, or higher than, the average Cs concentrations in K-feldspars separated from rocks (excluding pegmatites), Heier and Adams (1962). They probably cannot substitute isomorphically for K, but Cs, or at least the bulk of it, is assumed to substitute for K in regular lattice positions. In this paper we shall only be concerned with trace elements that are likely to occupy regular lattice positions, i. e., those elements that are not too different from the major constituents in feldspars. It should be mentioned that DeVore (1955, 1957) is of the opinion that a trace element will not be accepted in regular lattice sites until its concentration is large enough to control the environment of this site.

The discussion will be restricted to the concentration and variations of trace elements in feldspars from magmatic and metamorphic rocks and will comment on their possible use in defining such processes.

The study of trace elements in feldspars for the purpose of elucidating rock forming processes has some obvious advantages:

1. The feldspars are common to a wide range of rock types. They are among the first minerals to crystallize out from a basic magma, remain characteristic minerals throughout the major crystallization sequence, and are, together with quartz, the major minerals in the residual crystallates.

In metamorphic rocks the appearance and disappearance of feldspar phases are used as facies criteria when they are viewed in conjunction with other minerals. The study of the much disputed granitization phenomena is also largely a study of variations in feldspar content and composition.

2. The feldspar structures admit cations either in 4-fold coordination replacing Al and Si, or replacing K, Na, or Ca in higher coordination. There is, in general, no uncertainty about the position in the lattice occupied by any trace element in the feldspar structures. According to the electrostatic valence rule (Pauling's rule) the alkali position in the feldspar structure will not accept any cation with a charge greater than 2. Of the mono- and divalent ions only  $\text{Li}^{1+}$  (0.78 Å) and  $\text{Be}^{2+}$  (0.34) have suitable sizes to occupy tetrahedral positions. Data on Be contents of feldspars are scarce. Goldschmidt (1954) gives 40 p.p.m. in albite, 12 p.p.m. in soda microcline, and 'not detected' in microcline micropertthite. Higazy (1953) reported between n.d. and 8 p.p.m. Be in microcline perthite. A maximum of 150 p.p.m. Be in amazonite was reported by Filippov and Tolmacev (1935). It is natural to assume that  $\text{Be}^{2+}$  replaces  $\text{Si}^{4+}$  in the  $\text{SiO}_4$  tetrahedra, and, indeed, this substitution seems to be the most important manner of occurrence of Be in mineral structures (Rankama and Sahama (1950)).

Lundegårdh (1947) suggested that  $\text{Li}^{1+}$  is able to replace  $\text{Al}^{3+}$  in the plagioclase structure. However, Heier (1960) gave data suggesting that  $\text{Li}^{1+}$  substitutes for  $\text{Na}^{1+}$  in feldspars. The amount of Li which may be admitted into the feldspar lattice is restricted, and the high concentrations that are occasionally reported (Hess (1940); Borovik-Romanova and coworkers (1957, 1958)) are exceptions. In the geochemical sense Li is not an alkali element, and its distribution in feldspars is erratic and of little petrologic significance.

*Elements occupying "alkali positions" in the feldspar structures.*

Table 1 lists calculated approximate heat of formation from the oxides of hypothetical feldspars of some univalent and divalent ions, Rankama and Sahama (1950). The pure Li-feldspar is theoretically unstable, and it is only the remaining alkali elements, the alkaline earths, Pb and Tl that form stable feldspar structures. Other elements, though present in trace amounts in most feldspars, cannot safely be

Table 1. Approximate heat of formation from component oxides ( $\Delta H$  of hypothetical feldspars of some univalent and bivalent elements (Rankama and Sahama (1950) p. 139).

Feldspar compound	Heat of formation ( $\Delta H$ , kcal/mol)
LiAlSi <sub>3</sub> O <sub>8</sub>	+ 35
NaAlSi <sub>3</sub> O <sub>8</sub>	- 59
KAlSi <sub>3</sub> O <sub>8</sub>	- 117
RbAlSi <sub>3</sub> O <sub>8</sub>	- 130
CsAlSi <sub>3</sub> O <sub>8</sub>	- 145
TlAlSi <sub>3</sub> O <sub>8</sub>	- 46
BeAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	+ 214
PbAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	- 34
CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	- 61
SrAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	- 92
BaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	- 133

assumed to occupy lattice positions in the structures, and they are therefore omitted from this discussion.

#### *Potassium feldspars*

Heier and Taylor (1959a, b) and Taylor and Heier (1958a, b) made a comprehensive study of the concentrations of Li, Na, K, Rb, Cs, Ca, Ba, Sr, Pb, Tl in K-feldspars from the Precambrian basement rocks of south Norway. Studies on the distribution of one or more of these elements in K-feldspars are also given by a number of other authors, most of whom are listed in the reference list. Heier and Adams (1962) summarized the concentration of alkali elements in feldspars, and Taylor and Heier (1960) discussed the petrological significance of trace element variation in alkali feldspar.

Histograms showing the distribution pattern of Na, K, Rb, Cs, Pb, Tl, Ca, Sr, and Ba in K-feldspars from rocks and pegmatites are given in Figure 1, and some data on the elements are tabulated in Table 2.

*Sodium* (Na<sup>+</sup> 0.98 Å).—It is interesting to note (Figure 1) that Na tends to be higher in the pegmatite feldspars than in those from other rocks. Exsolution processes in the feldspars would tend to give a proportionally higher loss of Na (albite) out of the K-feldspar crystals in the

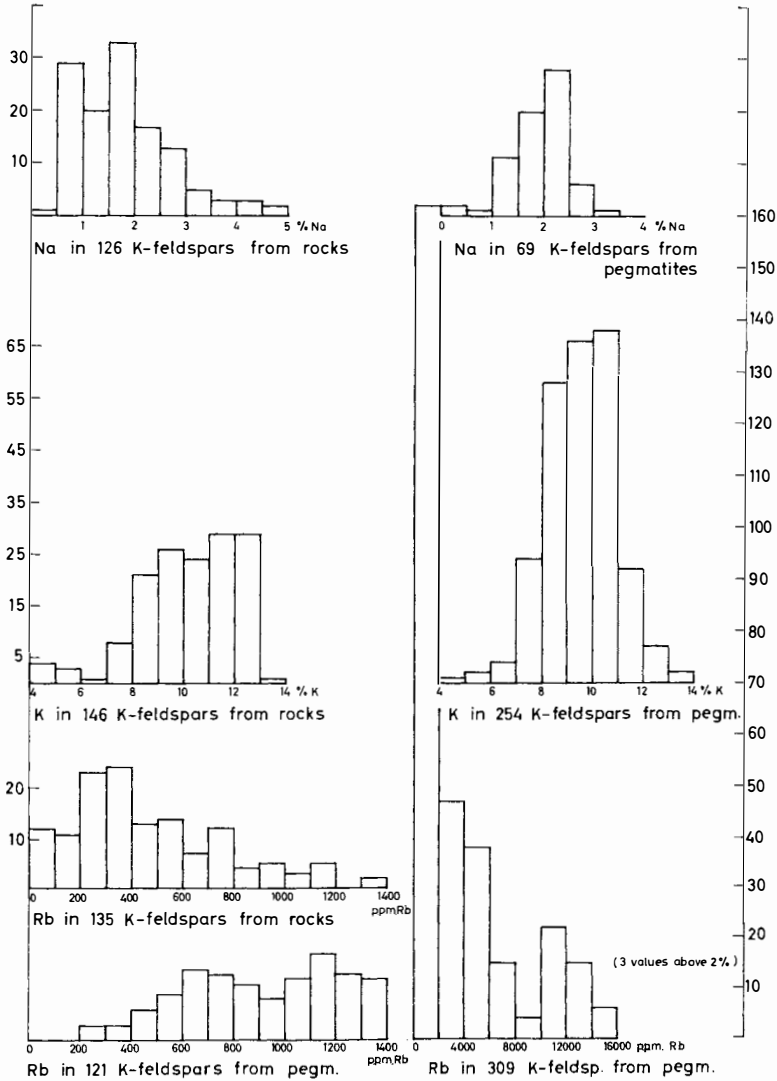


Figure 1a. Histograms showing the distribution pattern of Na, K, Rb, Cs, Tl, Pb, Ca, Sr and Ba in K-feldspars from rocks and pegmatites.

comparatively finer grained rock feldspars than the coarse pegmatite crystals. This may explain the relatively higher Na contents of the pegmatite feldspars but is probably not the complete explanation.

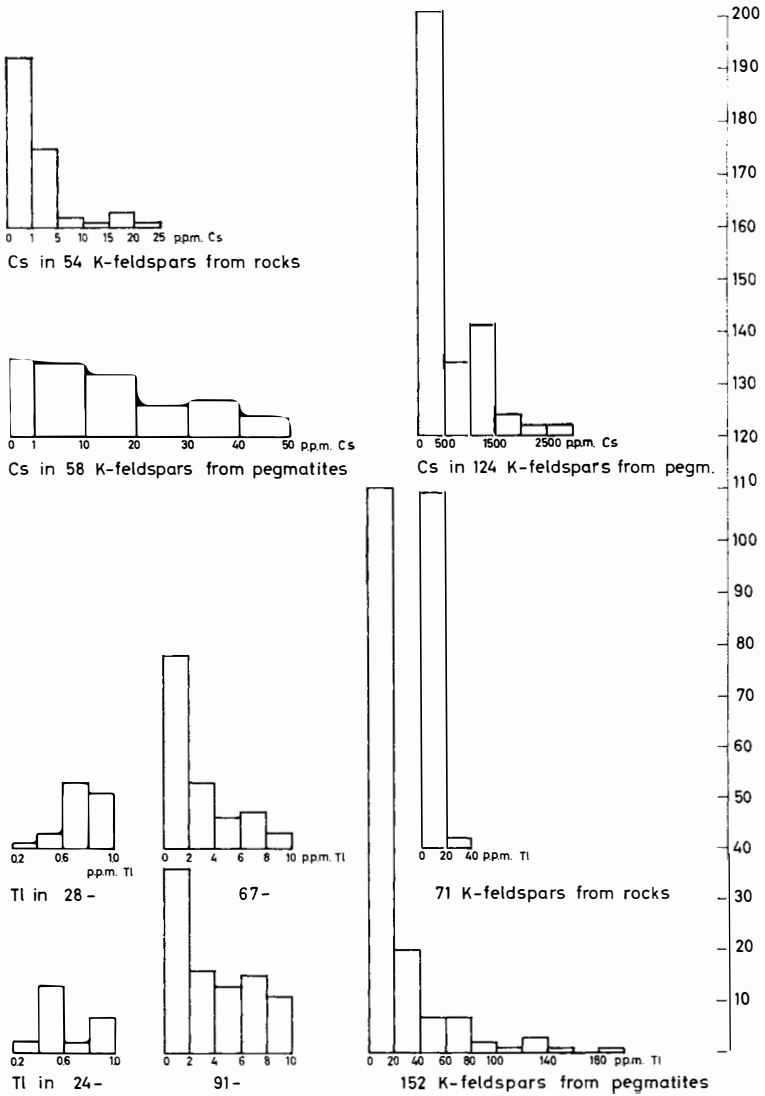


Fig. 1b

It is well known that high temperatures favor the solubility of Na in K-feldspar. The chemistry and texture of pegmatites is generally explained in terms of late stage crystallization at lower temperatures. However, most of the pegmatites studied are granite pegmatites in

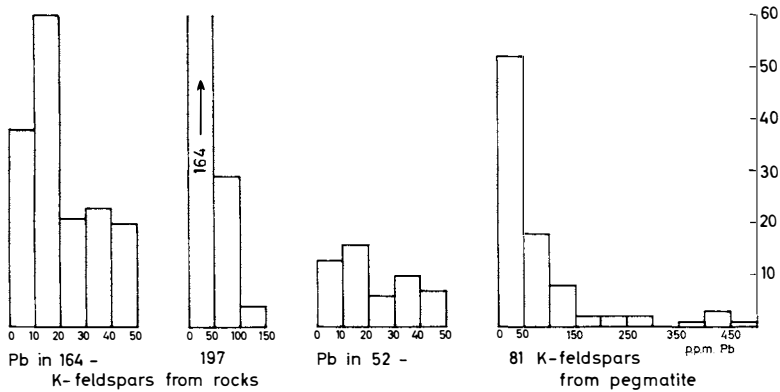


Fig. 1c

Table 2. Ionic properties of the elements occupying the "alkali position" in the feldspar lattice.

	Na	K	Rb	Cs	Tl	Pb	Ca	Sr	Ba
Electrostatic charge	1	1	1	1	1	2	2	2	2
Ionic radius (Ahrens, 1953)	0.97	1.33	1.47	1.67	1.47	1.20	0.99	1.18	1.34
Ionization potential (Ahrens, 1953)	5.14	4.34	4.2	3.9	6.1	15.05	11.9	11.03	10.0
Electronegativity	0.9	0.8	0.8	0.7	1.5	1.6	1.0	1.0	0.9

gneiss areas. There is little support for the simplified idea of the formation of such pegmatites by fractionated crystallization at decreasing temperatures. If these pegmatites formed from crystallization of locally derived anatectic melts or through diffusion processes, the temperature of their formation, at least in the beginning stages, will be close to the maximum regional temperature.

The distribution of trace elements between pegmatite and host rock feldspars, as well as variation within the pegmatites themselves, may reflect other than temperature gradients, for instance, pressure.

Na metasomatism at a late stage of pegmatite formation, and conceivably at low temperatures, is well known. It could be argued that the Na contents of the K-feldspars are related to this metasomatism and are secondary. However, it appears that this is unlikely to explain the general trend in Figure 1 even though it has certainly been effective in special cases; i.e., amazonite formation (Taylor, Heier and Sverdrup (1960)).

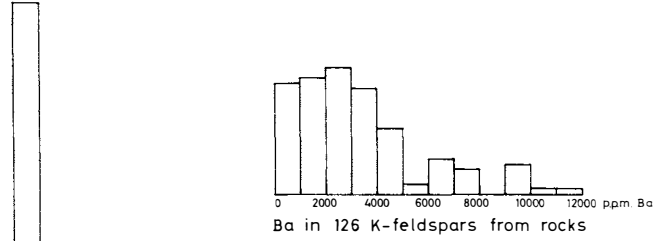
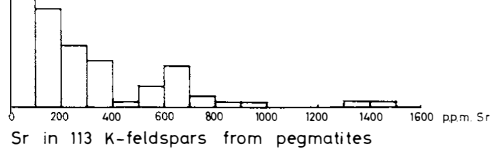
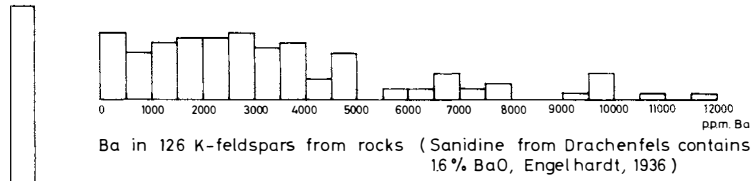
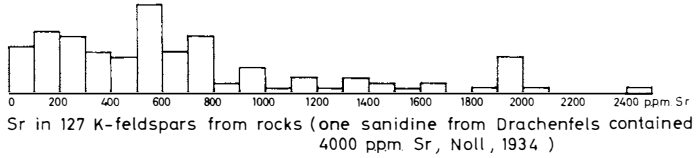
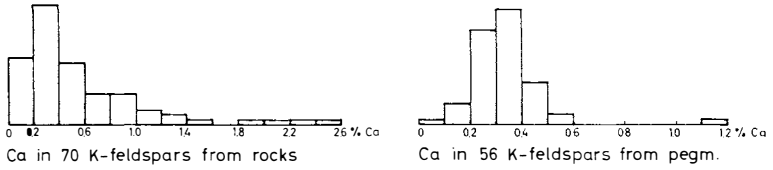


Figure 1d.



*Potassium* ( $K^+ 1.33 \text{ \AA}$ )—The concentration pattern of K in K-feldspars from rocks and pegmatites reflects that of Na. Feldspars with K-concentrations between 4 and 6 per cent are typical of syenites and the so-called mesoperthites in some granulite facies rocks. Sanidines may also be very high in Na.

*Rubidium* ( $Rb^+ 1.47 \text{ \AA}$ )—Rb is the trace element that is most ideally camouflaged in the K-feldspar structure, and it exhibits a well known coherence with K. The K/Rb ratio is altered only under extreme conditions of fractionation. The Rb content is therefore an insensitive indicator of major rock forming processes. Figure 2 shows variation of K, Rb, K/Rb, and Ba/Rb across the Fevig granite, S. Norway, Heier and Taylor (1959a); Taylor and Heier (1960).

Pegmatite feldspars are on an average higher in Rb than feldspars separated from rocks (Figure 1). However, Heier and Taylor (1959a) showed that small pegmatites (veinlets and lenses wholly within gneiss) are not enriched in Rb and show comparable K/Rb ratios with the

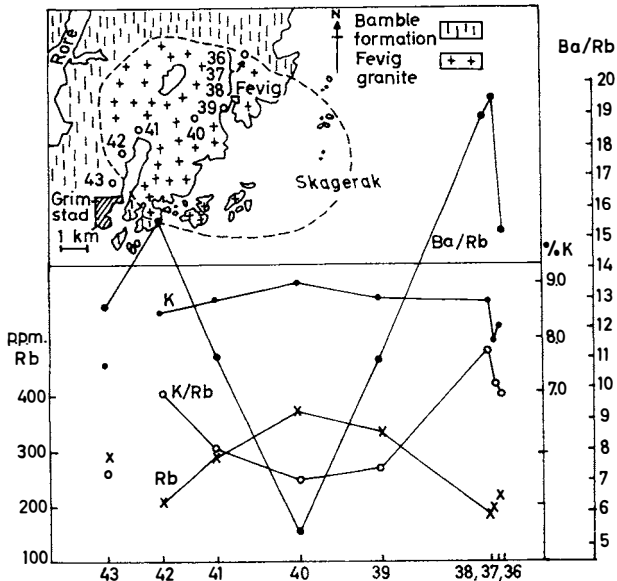


Figure 2. Variation of K, Rb, K/Rb, and Ba/Rb across the Fevig granite, S. Norway.

rocks in which they occur. Also many feldspars from large pegmatites are not significantly enriched in Rb. It appears that the late formed feldspars in these pegmatites are the ones that are especially high in Rb, and considerable variation is found within single pegmatite bodies.

Depletion of Rb (abnormally high K/Rb ratios) is much more uncommon than enrichment of this element. However, depletion seems to be characteristic for mesoperthitic feldspars from granulite facies rocks and from syenites (Taylor and Heier (1958 b); Heier and Taylor (1959 a); Upton (1960)). The feldspars depleted in Rb have a composition that place them in the field of primary crystallization of plagioclase in the three feldspar diagram (Figure 3). The depletion in Rb implies that the mesoperthites are exsolution perthites from a once homogeneous feldspar phase.

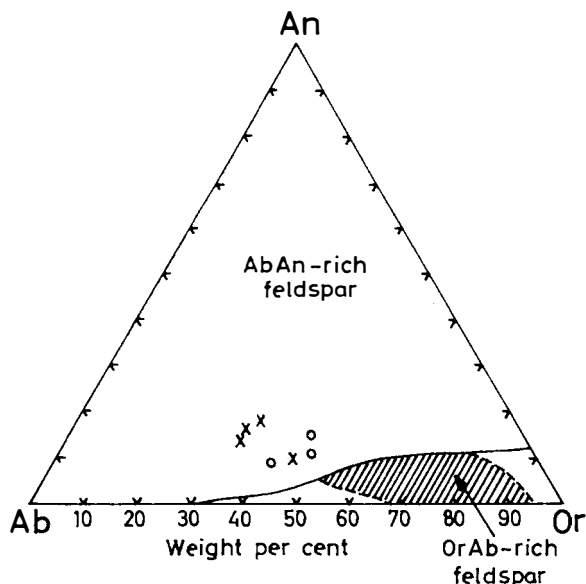


Figure 3. Compositions of natural K-feldspars plotted on the projection of the quaternary system  $\text{NaAlSi}_3\text{O}_8(\text{Ab}) - \text{KAlSi}_3\text{O}_8(\text{Or}) - \text{CaAl}_2\text{Si}_2\text{O}_8(\text{An}) - \text{H}_2\text{O}$  at 5000 bars  $\text{H}_2\text{O}$ . The shaded area indicates the compositional limits of more than eighty samples with normal or low K/Rb ratios examined by Heier and Taylor (1959 a). The solid line separates the Ab-An field (above the line) from the Or-Ab field. Alkali-feldspars that plot in the Ab-An field are depleted in Rb.

*Cesium* ( $\text{Cs}^+$  1.67 Å)—Cs is the largest of the ions entering the alkali position in K-feldspar. Although it forms more ionic bonds with  $\text{O}^{2-}$  than does any other element, has the same valency as K and forms with Si, Al, and O a very stable feldspar structure, Table 1, it is not readily accepted in the K-positions in feldspars because of the size difference. Thus Cs concentrations in K-minerals in rocks are low, and it is strongly enriched in late stage pegmatite minerals. Because of its size Cs is preferentially incorporated in the mica structures. The concentration of Cs in K-feldspars of average rocks is close to the detection limit of standard spectrographic methods, and the quality of many of the data is probably not good.

Cs is easily leached out of the feldspar structures, and its extreme solubility results in its distribution in minerals being strongly affected by hydrothermal solutions. Cs is also strongly adsorbed to mineral surfaces, especially in rocks affected by late stage hydrothermal solutions (i.e. the majority of magmatic granites), and its distribution in these rocks is likely to be erratic. Eugster (1955) determined the partition of Cs between high temperature  $\text{H}_2\text{O}$  and sanidine. He showed that the Cs content of mineral and  $\text{H}_2\text{O}$  was nearly equal at 800°C. However, the extent to which Cs occupied regular lattice positions in the feldspars could not be determined.

*Thallium* ( $\text{Tl}^+$  1.47 Å)—Tl is the same size as  $\text{Rb}^+$ , and if only size and charge were involved it might be expected to show a close coherence with Rb. However, the high electronegativity of Tl with the resulting tendency towards directed covalent bond formation, makes the Tl feldspar a much less stable compound than the Rb feldspar. Tl is therefore enriched relative to Rb in the feldspars of the most fractionated rocks (pegmatites). With increasing fractionation the Rb/Tl ratio in K-feldspar decreases from 100 to 20 (Taylor and Heier (1960)). Lack of accurate values below 5 p.p.m. makes any conclusion about the variations of the Rb/Tl ratio in feldspars from rocks other than pegmatites uncertain. In those rocks, coherence of Tl with Rb, and hence K, is probably fairly good, Ahrens (1948).

Taylor and Heier (1960) pointed out the similar distribution patterns of Cs and Tl in K-feldspars. Interestingly enough these two rather dissimilar elements enter the K-positions in a similar fashion. The larger size of Cs results in its relatively late entry into the K-feldspar

lattice. Tl, the same size as Rb, enters at a late stage because it forms a more covalent bond with O than K.

*Lead* ( $\text{Pb}^{2+}$  1.20 Å)—Pb does not show any simple relation to any of the other elements substituting for K in K-feldspars. Because  $\text{Pb}^{2+}$  is both divalent and smaller than  $\text{K}^{1+}$  it should be strongly captured according to classical distribution rules (Goldschmidt (1954) p. 399). However, the data presented by Wedepohl (1956) and Heier and Taylor (1959a) show that Pb tends to be enriched in the most fractionated (pegmatite) K-feldspars. This contradiction to Goldschmidt's rule is related to the large electronegativity value of  $\text{Pb}^{2+}$ , and the consequent increased covalent nature of the Pb–O bonds as compared to the K–O bonds. The importance of the nature of the M–O bond for the stability of trace elements in the K-feldspars is in the case of the bivalent elements especially well illustrated by the contrasted behaviour of  $\text{Sr}^{2+}$  (1.18 Å) and  $\text{Pb}^{2+}$  (1.20 Å). The Sr–O bond is largely ionic and Sr is concentrated in the early formed feldspars. Wedepohl (1956) gave the average Pb concentrations in feldspars listed in Table 3. The histograms, Figure 1, indicate that there is in general no significant difference in the concentrations of Pb in K-feldspars from rocks and pegmatites, but the maximum concentrations are always found in pegmatite feldspars. On the whole the distribution pattern of Pb in K-feldspars from different rock types is more irregular and unpredictable than for most of the other elements. The concentration of Pb in rocks increases during magmatic crystallization, Wedepohl (1956), and the somewhat confusing distribution pattern of Pb in the K-feldspars is related to that it is incorporated in other than K-feldspars in roughly equal amounts (i.e., plagioclases). The ionic properties of Pb allows it to substitute for Ca in plagioclases and for K in K-feldspars in roughly equal amounts. A rigid relation between Pb and K, or Pb

Table 3. Average Pb contents (p.p.m.) in K-feldspars of different rock types (Wedepohl (1956)).

Sanidine	21
K-feldspar from granodiorites and granites	27
K-feldspar from pegmatites	100
Adularia	62

and Ca, is therefore not to be expected. It is therefore not before the granite pegmatite stage that enrichment of Pb in the K-feldspars becomes noticeable.

*Calcium* ( $\text{Ca}^{2+}$  1.01 Å), *Strontium* ( $\text{Sr}^{2+}$  1.18 Å) and *Barium* ( $\text{Ba}^{2+}$  1.34 Å).—The distribution pattern of these elements in K-feldspars has been discussed by Heier and Taylor (1959b). The histograms (Figure 1) show that they are all captured in K-feldspars. However, Heier and Taylor (1959b) found that as the absolute amounts of Ca, Sr, and Ba decrease, the ratios between these elements alter. The relative rate of decrease in the three elements is in the order  $\text{Ba} > \text{Sr} > \text{Ca}$  so that the Ca/Sr ratio increases and the Ba/Sr ratio decreases with increasing fractionation of the K-feldspars. This relative change is evident from the histograms Figure 1, and is superficially somewhat contrary to the classical “capture” rule according to which the smaller  $\text{Ca}^{2+}$  ion should be expected to be preferentially incorporated. It is best explained by the different nature of the chemical bonds between these elements and oxygen, and it is discussed in detail by Heier and Taylor (1959b). The ionic character of these bonds increase in the series;  $\text{Ca}^{2+} \angle \text{Sr}^{2+} \angle \text{Ba}^{2+}$ . The oxides of these elements all possess the NaCl structure with each metal ion coordinated with six oxygens obey the size criterion in the classical capture principle. The melting point, heat of formation, and lattice energy decrease with increasing ionic size. However, the calculated coordination numbers for Ca, Sr, and Ba with  $\text{O}^{2-}$  are 6, 8, and 12, and the 6-coordinated structures of Sr and Ba must therefore be rather loosely packed. In K-feldspars the coordination is larger and closer to the theoretical values for Sr and Ba. Under such conditions bond type should exert a major influence on bond-strength, and the Ba–O bond with most ionic character should be the strongest. This is indicated by the calculated heats of formation of the respective feldspars, Table 1.

*Ca*, which is the third major feldspar-forming element, is rarely present in K-feldspars in amounts above 1%. Actually Ca is no more common in K-feldspars than Ba is. It is typically low in pegmatite feldspars where it rarely exceeds 0.5%. High temperatures favour the entry of Ca in K-feldspars. However, there is no continuous solid solution series between the pure Ca-feldspar (anorthite) and K-feldspar. The feldspars high in Na tend also to be enriched in Ca. It was

found, Figure 1, that Na tends on an average to be higher in the pegmatite feldspars than in K-feldspars separated from other rocks. A similar trend is not evident for Ca. However, the pegmatite phase is alkali dominant and in this case the bulk chemistry of the phase rather than the temperature is decisive for the amount of Ca to be incorporated in the feldspars.

Sr is often regarded as a close associate of Ca. However, Heier and Taylor (1959b) found that Sr in K-feldspars shows a close association with Ba, and a much weaker relation to Ca. Turekian and Kulp (1956) in a general survey of the geochemistry of Sr stated (p. 209) "in the case of the granitic rocks Sr was found to be a function of the Ca content". It is therefore interesting that such a relationship is not found in K-feldspar, which is the most common Sr-containing mineral in granite. Part of the explanation may be that Sr also substitutes for Ca in plagioclase, and that the absolute amounts of Sr in K-feldspar and coexisting plagioclase are very similar (see later). Where a trace element can substitute for two major elements and is intermediate in size between them (Sr for Ca and K), a simple relationship between the trace element and any of the major elements is not to be expected.

Ba<sup>2+</sup> is about the same size as K<sup>1+</sup>, and it forms strong ionic bond with oxygen which causes it to be markedly captured in the early formed K-feldspars. This marked tendency for capture (Figure 1) was also noted by von Engelhardt (1936), Table 4. Oftedal (1958b, 1959, 1961) studied the distribution of Ba and Sr within a pegmatite band in plagioclase gneiss, and he was able to demonstrate convincingly the preferential capture of Ba. In the 1961 paper he discussed the concentration of these elements in more than 70 microcline samples selected at random in an area of 75 square meters within the pegmatite outcrop.

Table 4. Rb and Ba contents in K-feldspars of different rock types (von Engelhardt (1936)).

K-feldspar	Rb p.p.m.	Ba p.p.m.
Sanidine from trachyte	430	14330
Orthoclase from granite	729	4390
Microclinemicroperthite from nepheline syenite pegm.	1190	80
Microcline perthite from granite pegmatite	2195	27-90
Amazonite from granite pegmatite	6220	3-9
Amazonite from granite pegmatite	23200	170

The average (arithmetic mean) concentration of these samples are 1100 p.p.m. Ba and 700 p.p.m. Sr. However, Ba is strongly concentrated (up to above 5000 p.p.m.) in the earliest formed K-feldspars in the pegmatite. (The relative age of the pegmatite feldspars was deduced from general petrographic evidence). The microclines with less than 500 p.p.m. Ba were nearly always large and light coloured crystals that had developed in the interior of the pegmatite and apparently belonged to late stages in the pegmatite development. The variation of Sr was much less, and it is not concentrated to the same extent in the early feldspars. Thus microclines with Ba concentrations lower than about 500 p.p.m. Ba were nearly always considerably higher in Sr than in Ba, while for Ba concentrations higher than about 1000 p.p.m. the opposite holds true.

### Summary

Of the available data for the elements that occupy the "alkali position" in K-feldspars it can be deduced that they enter the lattice in the following order:

(univalent)	Na > Rb > Tl > Cs
(bivalent)	Ba > Sr > Ca > (Pb)

This is the sequence with increasing fractionation of the rocks. In magmatic processes this corresponds to falling temperatures. The sequence could be deduced from considerations of ionic size, valency and electronegativity. It is of interest to consider briefly the host rock and pegmatite feldspar relations. Much of the pegmatite data reviewed here are from granite pegmatites in gneiss areas. In such areas a simple fractionated crystallization relationship between host rock and pegmatite is not reasonable. The pegmatites, whether crystallized from injected magmas (melts), anatectic magmas, or formed by some sort of diffusion process, will begin to crystallize at temperatures equal to, or even slightly above the temperatures of the surrounding rocks. In such areas the trace element content in feldspars of pegmatites and host rocks is not a function of the temperature only but must be brought about by another genetic relationship leading to the same result. It has been found (Heier and Taylor, (1959a, b)) that feldspars from small pegmatites are very similar in chemical composition to feldspars of the surrounding country rocks. Even the Ba/Rb ratios,

which Taylor and Heier (1960) found to be the most sensitive indicator of fractionation processes in feldspars, are similar in feldspars from such systems. This is probably evidence for the very local, or in situ, derivation of such pegmatites.

However, the feldspars of large pegmatites are often enriched in the elements that are last to be concentrated in feldspars, and the Ba/Rb ratios are typically significantly lower than those of the host rock feldspars. However, perhaps the most interesting aspect of the large pegmatites is the considerable range in element concentrations, and of Ba/Rb and K/Rb ratios within the same veins. Other studies indicate that only mild fractionation takes place in granite bodies of much larger size than pegmatites. One would therefore assume that large volumes of material must be required to produce significant changes in these element concentrations and ratios. It would appear that an area much larger than the present dimensions of even the largest pegmatites must be involved, although this of course cannot be considered as established. If the pegmatites have formed from magmas it is necessary to postulate repeated injection of magma from a much larger reservoir which must itself undergo some sort of fractionation in order to explain the increasingly fractionated nature of the pegmatite magma with time.

If the large pegmatites formed by some sort of diffusion process, or even by crystallization of anatectic magma involving repeated melting of the country rock, sufficient parent volumes can certainly be assumed. This mode of formation could be expected to be demonstrable by a comparative geochemical study, involving trace elements, of pegmatites and host rocks on a regional scale. Such studies are conspicuously lacking, although a few petrographic studies involving pegmatites and the immediate host rock(s) are described in the literature (i. e., Reitan (1956, 1958, 1959)). Certainly relevant to this discussion are Andersen's (1931) observations that the pegmatites of southern Norway are isolated bodies, and that 60% of them occur in gabbro and amphibolite country rocks which cover about 5% of the total area.

Whether a diffusion model can account for the observed trace element variations and concentrations in K-feldspars is, because of lack of data, difficult quantitatively to evaluate, and it is also outside the scope of this paper. It suffices to mention that the much mentioned



general enrichment of trace elements in pegmatites agrees with the fact that (at least at constant temperatures) diffusion is driven by free energy gradients, and that diffusion of an element always goes from high to low partial free energy (activity) of that constituent (Ramberg (1961)). In diffusion processes the rate determining step is the liberation of the reacting particles from their initial lattice rather than their rate of diffusion. The trace elements which do not determine the mineral structures, will in general be more unstable in the minerals and more easily activated, than the major elements for which they substitute. Thus the heat of formation of the hypothetical feldspars

Table 5. Range and arithmetic means of concentrations of K, Rb, Cs, Pb, Tl, Ba, and Sr in plagioclase feldspars.

\* no. of samples, \*\* arithmetic mean.

Plagioclase	K %	Rb p.p.m.	Cs p.p.m.	Pb p.p.m.	Tl p.p.m.	Ba p.p.m.	Sr p.p.m.
Anorthite	0.08-0.31					10-81	253-1000
An 90-100	11*, 0.08**				0.017	10*, 50**	10*, 345**
Bytownite	0.08-0.24	2-3		30		30-320	253-1800
An 70-90	15*, 0.12**	2*		1*		21*, 85**	19*, 791**
Labradorite	0.025-0.56	3-8 [1]		6-15		45-1500	255-3000
An 50-70	14*, 0.30**	7*, 6**		4*, 10**		24*, 315**	26*, 1129**
Andesin	0.04-1.62	4-80 [2]		6-52		30-1500	169-3000
An 30-50	52*, 0.48**	12*, 26**		19*, 22**		76*, 383**	76*, 898**
Oligoclase	0.04-1.19	3-10 [3]		5-10		44-1791	140-4250
An 10-30	27*, 38**	4*, 6**		5*, 9**		34*, 390**	34*, 1140**
Albite	0.09-0.44	5-40		2-13	0.3-1.1	1-45	3-169
An 0-10	9*, 21**	7*, 14**		8*, 7**	6*, 0.6**	6*, 16**	5*, 55**
Cleavelandite	0.31	2-92	7	7-43	1.2-1.4	5-49	15-100
	2*	3*, 54**	2*	6*, 21**	2*	3*, 26**	3*, 59**

[1] one value of 200 p.p.m. excluded; [2] one value of 350 p.p.m. excluded; [3] values of 200 p.p.m. excluded.

Data from (see Fig. 5-11): Bray, 1942 (13-24); Emmons, 1943; von Engelhardt, 1936; Heier, 1960 (29-36) (41-44); Higazy, 1953; Howie, 1955; (10-12); Nockolds and Mitchell, 1948 (1-4); Oitodal, 1959 (37-40); Ottoman, 1941; Sen et al, 1959 (5-9); Sen, 1959, 1960; Shaw, 1952; Taylor et al, 1960 (26-28); Tilton, 1955 (25); Turekian, and Kulp, 1956; Wedepohl, 1956.

listed in Table 1 does not give a correct picture of the relative free energy (activities) of the elements when they occur as trace elements and substitute for K in K-feldspars.

*Trace elements substituting for Ca and Na in plagioclase*

Less data are available on the trace elements in plagioclases. The available data are summarized in Table 5, and histograms showing the distribution of K, Sr and Ba in plagioclases ranging in composition from albite to anorthite are shown on Figure 4. The large alkali elements Rb and Cs, and Tl are present in very low concentrations in the plagioclases. Their highest concentrations are in cleavelandites, and Cs has so far only been reported in that mineral. Taylor, Heier and

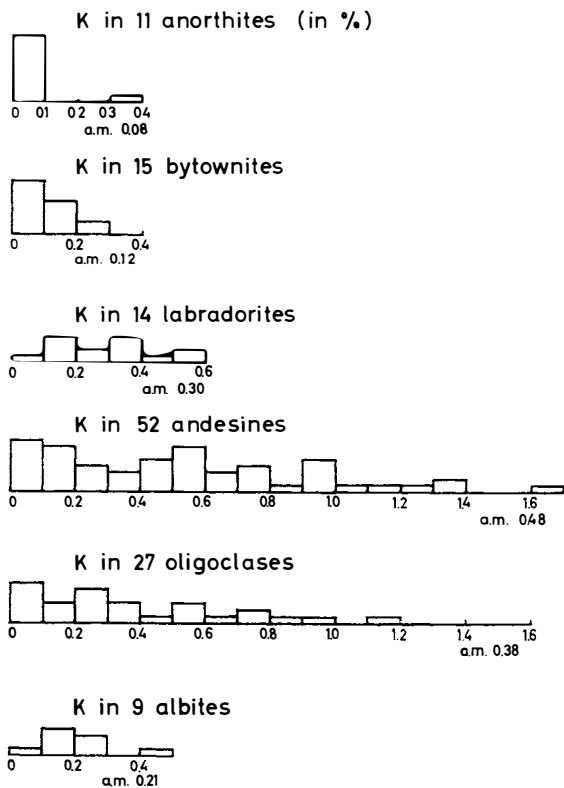


Fig. 4a

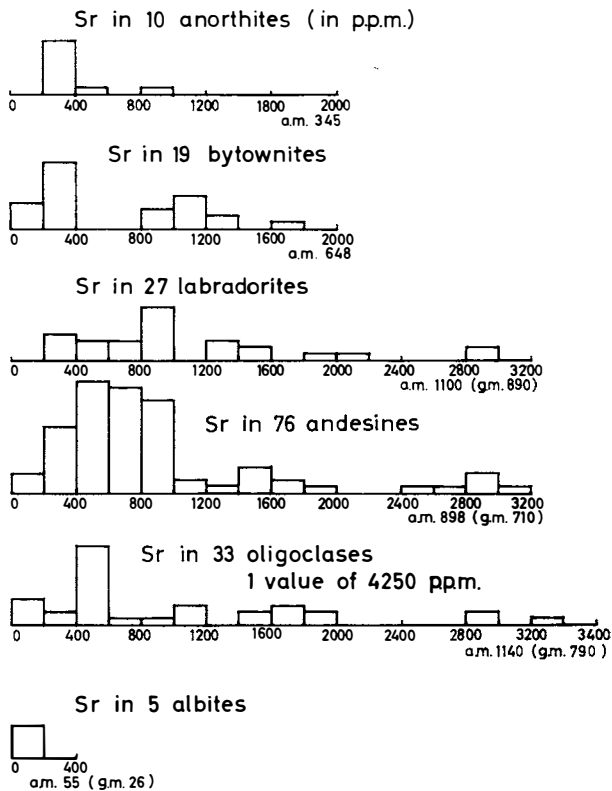


Fig. 4b

Sverdrup (1960) made the interesting observation that the K/Rb and K/Cs ratios in some cleavelandites were lower than in coexisting amazonites (enrichment of Rb and Cs relative to K in the cleavelandites). This is in accord with the suggestion that amazonite results from the diffusion of Na into an earlier microcline. The concentration levels of both Rb and Cs in cleavelandites are low, and this may enable the crystals to reflect the composition of the liquid from which it is crystallizing without apparent rejection of the larger ions.

The K-content of natural plagioclases has been made the subject of a special study by Sen (1959). He analyzed plagioclases from amphibolite facies, granulite facies, and volcanic rocks, and found a definite tendency for K-contents to increase with increasing temperature of formation. The temperature dependence of K in plagioclase was

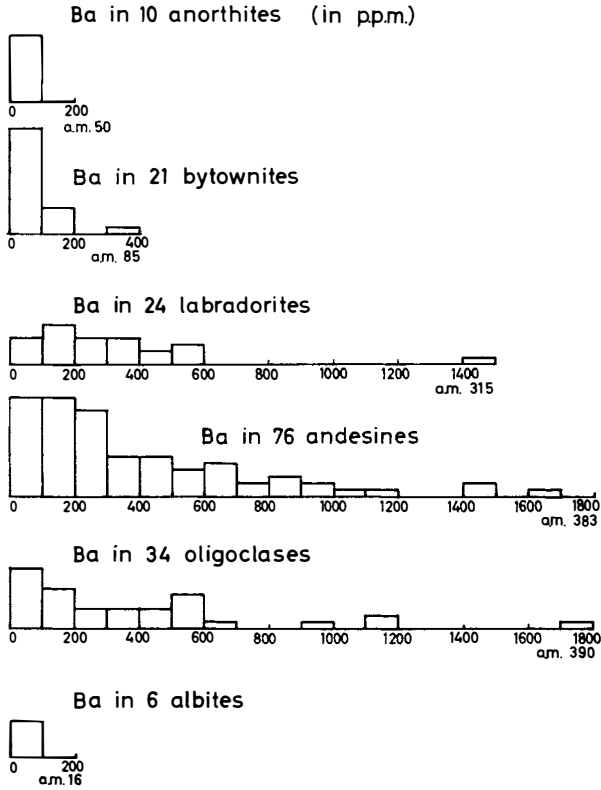


Figure 4c. Histograms showing the distribution pattern of K, Sr, and Ba in plagioclase.

explained by: (a) increasing "openness" of plagioclase structure, (b) strengthening of Si-O bonds by accepting K, and (c) facilitated coordination of K by oxygen with increasing disorder in plagioclase.

Anorthite and bytownite have low K contents, and labradorites, andesines, oligoclases, and albites have slightly higher, similar K-contents. The slight maximum K-content observed in andesines is probably related to the fact that andesine is the most typical plagioclase in granulite facies rocks. In this connection it is interesting to note that Rb and Pb also have slight maxima in andesines. This is probably a reflection of the close geochemical association between these elements and K. On the whole Pb shows only little variation in concentration in plagioclases of different compositions but shows a maximum in

some cleavelandites reflecting the slight enrichment of Pb in the late stage pegmatite phase.

*Ba* is low in the most calcic plagioclases, and in albites and cleavelandites. Its low concentration in the latter is obviously related to the overall low *Ba* content in the pegmatite phase. However, the unfavorable structure and bulk chemistry of the albites would also tend to reject *Ba*, even if more were present in the system. The large difference in ionic size between Ca and Ba (~30%) suffices to explain the low *Ba* content in An rich plagioclases, even though in these the bulk chemistry, especially the Al/Si ratio, would be favorable for *Ba*. The maximum *Ba* concentrations are found in the oligoclase to labrador range, and may reflect the general higher K content in the plagioclases in this range. The extent to which *Ba* is able to replace either Ca or Na in the plagioclase structure is not well known. Sen (1960) showed that plagioclases from rocks formed at higher temperatures had the greatest *Ba* (and Sr) contents. The tendency for ions to assume lower coordination at higher temperatures is, of course, well known (Buerger (1948, 1961)), and it is conceivable that under conditions of maximum dilation of the alkali position *Ba* may replace Ca in the feldspar structure. The writer is, however, more inclined towards the assumption that *Ba* has a dependence relation to K in the plagioclases, even though this dependence is somewhat obscured by the frequent bad quality of the *Ba* determinations.

The histograms show a wide range of *Ba* in the plagioclases within each An interval, and the geometric means are less than the arithmetic means. Whether this large variation is real or related to: (a) analytical error, or (b) impurities of K-feldspar, is not certain. *Ba* is especially susceptible to analytical errors.

*Sr* shows a distribution pattern in plagioclases that is very similar to that of *Ba* even though *Sr* should be able to substitute for Ca (and Na) in the structure. It is interesting that the data show no direct relation between *Sr* and Ca in plagioclase. The low *Sr* contents in albites might readily be explained as lack of availability in systems where albite forms. The relatively low *Sr* contents in the most basic members may also be related to lack of availability. In the series labradorite to albite the geometrical means of the *Sr* contents are 890, 710, 790, and 26. Most of the andesines listed are in the range An 30–35, most of the oligoclases An 25–30. Turekian and Kulp (1956) found

that in the case of granitic rocks Sr was a function of the Ca content. Feldspars are the most important carriers of Sr in magmatic and metamorphic rocks, and some relation between Ca and Sr in albites and intermediate plagioclases is therefore to be expected. It was mentioned that Sr in K-feldspars shows a close association with Ba, and a much weaker relation to Ca. Turekian and Kulp (1956) also found that the Sr content in basaltic rocks is essentially independent of the Ca-content. This agrees with the assumption that the low Sr contents in the most basic plagioclases is explained by lack of availability. However, Butler and Skiba (1962) studied Sr in plagioclase feldspars from four layered basic masses in Somalia. Sr contents of feldspars from 3 of the masses are similar for comparable An content; Sr varies between 1000 and 1850 p.p.m. and tend to increase as An decrease from An 68 to An 48. In feldspars from the other mass Sr also increases with decreasing An content (An 74 to An 56) but is at much higher general tenure (1650 to 2350 p.p.m.).

### **Distribution of trace elements between coexisting feldspars**

One of the most interesting aspects of the study of trace elements in feldspars is the distribution of elements between coexisting feldspars. The use of the distribution of Na (or albite) between coexisting plagioclase and K-feldspar as a geothermometer has been advocated especially by Barth (1934, 1951, 1956, 1961), and its use and shortcomings repeatedly discussed, Dietrich (1960, 1961); Heier (1960, 1961); Winkler (1961). Heier (1960, 1961) suggested that the distribution of elements present in only trace amounts, and having crystal chemical properties which make substitution in the two types of feldspar lattices roughly equally feasible, would make a better geothermometer. In a restricted survey within a limited area he found the distribution of Sr, Ba, and Pb between coexisting feldspars to be temperature dependent. This was further elaborated by Barth (1961). Unfortunately less than a score of papers give data on trace element distribution in coexisting feldspars, and the data are of uneven quality.

It is evident that Rb prefers K-feldspars, Figure 5 (similar plots of Cs and Tl would show an even stronger preference for the K-feldspar for these elements). Barth (1961) found no relation to temperature of the ratio of distribution of Rb between K-feldspar and plagioclase (nor

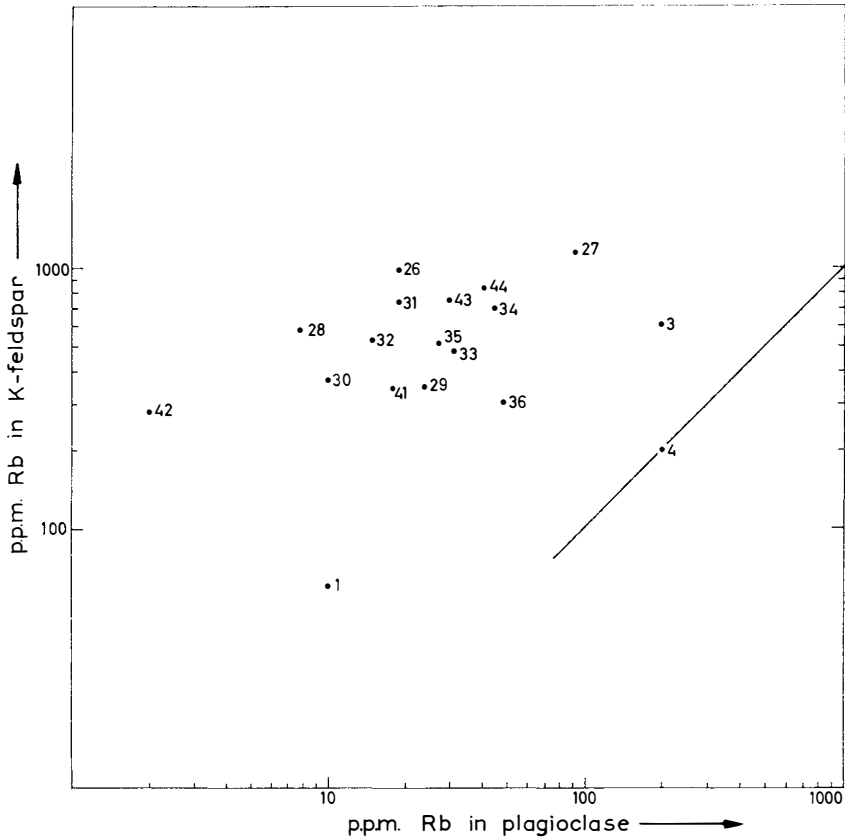


Figure 5. Plots of Rb in K-feldspars vs. Rb in coexisting plagioclase (nos. from Table 5). Solid line shows ratio = 1.

for Li, Cu, and Pb), and he invoked as an explanation DeVore's (1955) postulate that a trace element is not accepted in regular lattice positions until its concentration is large enough to control the environment of this site. Below this concentration level the elements are fixed in positions outside the regular lattice sites. They do not replace a main element of similar size but are present as imperfections in the crystal structure. The importance of ascertaining the position of trace elements was emphasized in the beginning of this paper, and a number of elements typically present in trace amounts in feldspars were excluded from discussion because of uncertainties about their position.

It is safe to assume that Rb is located in normal lattice positions (substituting for K) in the K-feldspars. The constancy of the K/Rb ratio in common rock types, as well as the change in this ratio under conditions of extreme fractionation in a direction predictable from electrostatic energy considerations suggests this. It cannot be so readily assumed that Rb can occupy the Na and/or Ca positions in plagioclase. The size difference between the ions may be prohibitive, and in any case only very limited substitution is indicated by the low, and rather uniform Rb contents observed in plagioclases of different An contents. Because of this low, uniform Rb content in plagioclase only slight contamination by K-feldspar (in other words—analytical error based on mineral separation) will seriously affect the distribution ratio. For this reason the distribution between two phases of an element that is markedly concentrated in one of the phases is not suitable for stringent discussions of this sort.

Thermodynamic considerations predict that the distribution ratio of any two elements between any two phases is dependent on temperature, pressure, and variations in the concentration of a third species in either phase. The latter effect was studied theoretically by Kretz (1961) and it was concluded that “in general the distribution coefficient with reference to any species is a function not only of the concentration of this species but also of the concentrations of other species in either phase.” However, in simple cases of coexisting phases of general formulae  $(A, B)$  and  $(A, C)$  the distribution of albite ( $A$ ) between plagioclase ( $B = \text{anorthite}$ ) and K-feldspar ( $C = \text{orthoclase}$ ), and  $(A, B)M$  and  $(A, B)N$  (distribution of Fe and Mg between ortho- and clinopyroxene) the distribution coefficient does not vary with composition if the mixtures are ideal, or in case of non-ideality if the concentration of one species is present in dilute concentrations in both phases. In more complex cases of coexisting phases  $(A, B, C)M$  and  $(A, B, C)N$ ;  $(A, B)(C, D)_qM$  and  $(A, B)(C, D)_rN$ ;  $(A^a, B^b)(C^c, D^d)_qM$  and  $(A^a, B^b)(C^c, D^d)N$  the distribution coefficients are a function also of the concentration of other species in either phase.

Rb in plagioclases seems to have some relation to the K content. Thus in discussing the distribution of Rb between coexisting phases the K content in plagioclases should not be neglected. A plot of Rb vs. K in plagioclase (Figure 6) shows an apparently simple relationship. This relationship cannot be entirely explained by contamination of the



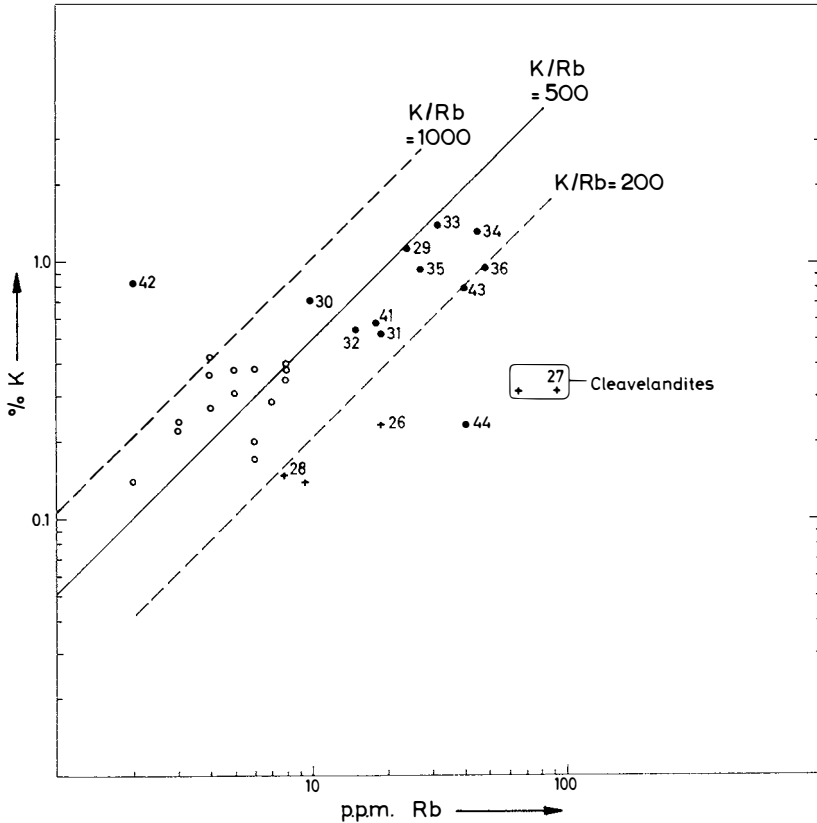


Figure 6. Plots of Rb vs. K in plagioclase. ● Heier (1960), + Taylor, Heier and Sverdrup (1960); ° Emmons (1953).

plagioclase with K-feldspar as the K/Rb ratio is higher in the plagioclases (except for those high in K) than is characteristic for K-feldspars ( $\sim 200$ ).

The distribution ratio of Pb between coexisting plagioclase and K-feldspar is on an average close to unity (Figure 7), and a small contamination of one phase in the other will not seriously disturb the ratio. Pb is also intermediate in size between Ca, Na and K, and its activity in the two phases should not be different in the extreme. The double charge of  $\text{Pb}^{2+}$  may favor its entry in plagioclase but a relation between Pb content and An content of the plagioclase has not been detected.  $\text{Pb}^{2+}$ , of course, has a larger electronegativity, and a pro-

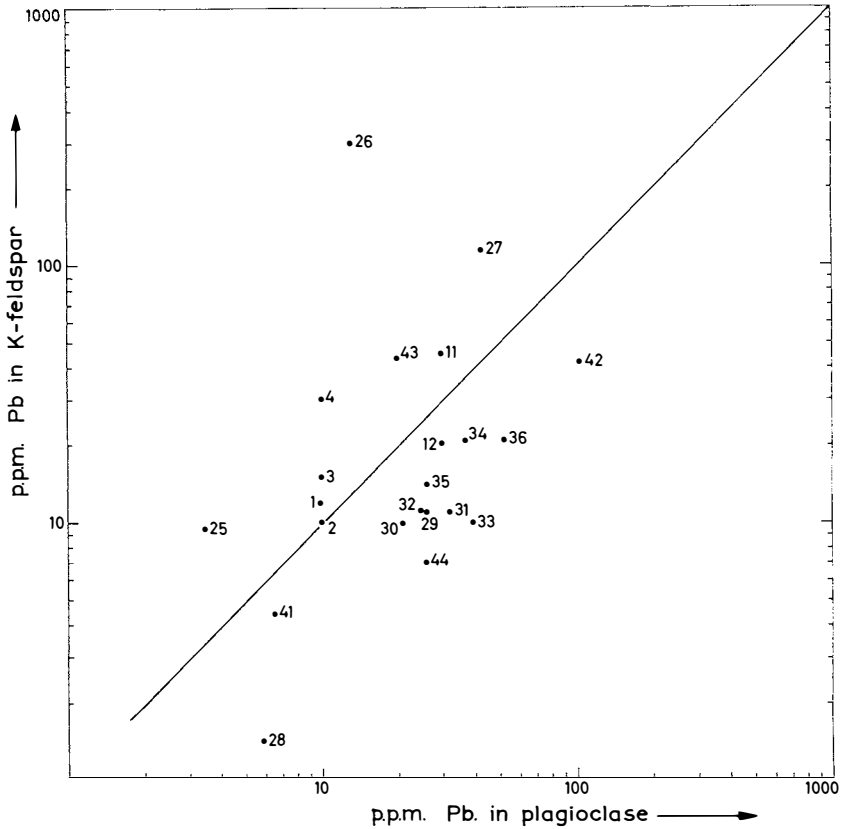


Figure 7. Plots of Pb in K-feldspars vs. Pb in coexisting plagioclase (nos. from Table 5). Solid line shows ratio = 1.

nounced tendency towards covalent bond formation. This may explain why Barth (1961) found no relationship between the distribution ratio of Pb and temperature. The electronegativity value explains why Pb tends to be concentrated in the very late stage pegmatite feldspars. The concentration factor is larger in the late stage K-feldspars than in coexisting albites. However, in the early pegmatite feldspars Pb is preferentially incorporated in the plagioclases as shown by Heier and Taylor (published in Heier (1960) p. 173), Table 6. According to their data Pb preferentially enters albite in the exsolved lamellae of perthites.

Table 6. Some elements in coexisting K-feldspar and plagioclase from pegmatites in Southern Norway.

	Li p.p.m.	Na %	K %	Rb p.p.m.	Cs p.p.m.	Pb p.p.m.	Tl p.p.m.
1a K-feldspar perthite, Snarum	0.76	2.71	9.55	344	8.9	4.4	2.4
1b purified K-feldspar lamella from 1a	0.66	1.07	11.83	450	12.0	4.5	3.4
1c purified albite lamella from 1a	1.66	6.53	2.99	110	n.d.	10.0	n.d.
1d coexisting oligoclase (An 11)	1.60	7.57	0.58	18	n.d.	6.5	1.0
2a K-feldspar, As, Evje	1.00	1.97	10.13	280	n.d.	42.0	1.91
2b plagioclase ,, ,,	5.80	6.38	0.83	1-2	n.d.	105.0	n.d.
3a K-feldspar, Iveland	n.d.	1.14	11.54	760	18.0	43.0	2.57
3b Plagioclase, Iveland	4.7	7.57	0.79	40	n.d.	20.0	n.d.
4a K-feldspar, Kristiansand	0.8	1.82	10.58	825	46	7.0	12
4b plagioclase, ,,	6.1	7.76	0.23	41	n.d.	26.0	n.d.

On the whole the available data on Pb is confusing. Some data indicate that the ratio

$$\frac{\text{Pb in plag.}}{\text{Pb in K-feldsp.}} \geq 1$$

in most rocks but that this ratio may be reversed in the very late stage of pegmatite formation.

Heier (1960, 1961) discussed the potential use of Ba and Sr geothermometers, and Barth (1961) showed, on the basis of data mainly from Heier (1960), a straight line relationship between plots of the natural logs to the ratio of distribution of Ca, Sr, and Ba between coexisting feldspars versus logarithmic plots of the inverse of the absolute temperature of formation as derived from the albite geothermometer (Figure 8). Barth (1961) deduced that below ca. 250°C plagioclase is preferred as the host mineral for Ba. This writer, however, knows of no reported case where the ratio of Ba in plag. to Ba in K-feldspars is more than one, Figure 9. In a few cases, however, it is close to unity. The feldspars are from rocks ranging from intermediate types to pegmatites, and it is not possible to distinguish trends in the Ba distribution according to rock types. The temperature of formation may vary considerably within the petrographically similar types.

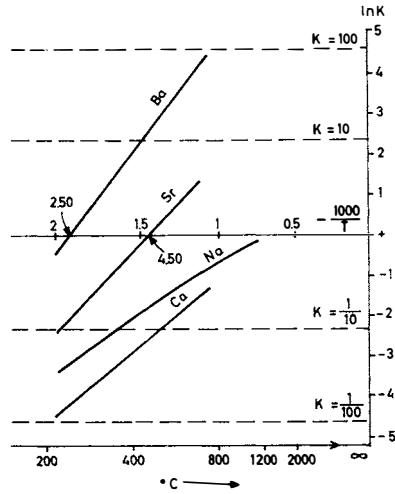


Figure 8. Relation between temperature and the ratio of distribution of Na, Ca, Sr, and Ba between alkali feldspar and plagioclase. Abscissa: the inverse of the absolute temperature. Ordinate: natural logarithms to the ratio of distribution. (Barth, 1961).

However, studies within restricted areas indicate a change of the ratio towards unity with decreasing temperature. Heier (1960) found typically lower ratios for feldspars from amphibolite facies rocks than from granulite facies rocks. Some data derived from a study of feldspars within one pegmatite by Taylor, Heier, and Sverdrup (1960) are also of interest here. Feldspars nos. 26–28, Figure 9 are all from one pegmatite. No. 26 with a ratio (Ba in Or/Ba in plag.) of 12 represent the feldspar pair of the first stage of pegmatite crystallization; no. 27, ratio about 1, is a cleavelandite-amazonite pair of probable late formation. The K-feldspar no. 28 is the latest feldspar to have crystallized but is believed not to be genetically related to the major pegmatite crystallization, and the genetic relation between this feldspar and the albite occurring with it is uncertain.

In conclusion, the strong preference that Ba, largely because of its size, has for K-feldspars in major rock types makes its distribution between coexisting feldspars somewhat unsuitable for a rigid treatment, as was discussed for Rb. Furthermore, Ba determinations with emission spectrographic methods (the method used for all the determinations in Figure 9) tend to be very inaccurate if extreme care is

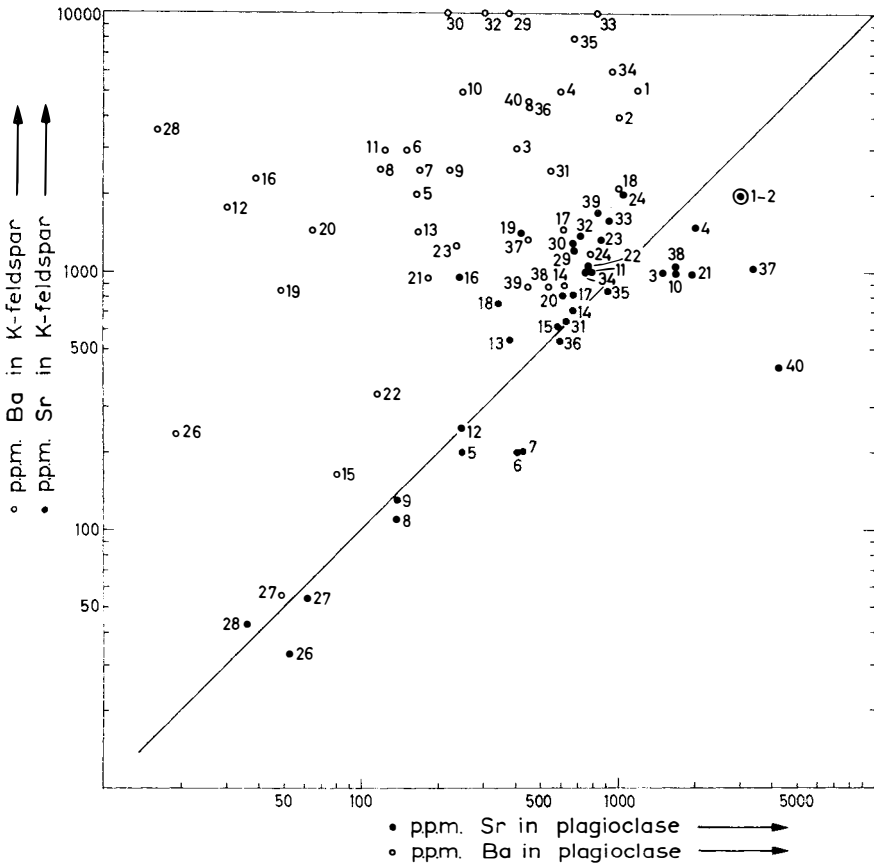


Figure 9. Plots of Ba (o) and Sr (●) in K-feldspars and coexisting plagioclase (nos. from Table 5). Solid line shows ratio = 1.

not taken. The quality of the data presented here may vary within an order of magnitude and no serious discussion can be undertaken before this is improved.

The ratio of the Sr distribution is much closer to unity, and show a remarkable small spread in values. Excepting a couple of extremes (nos. 16, 19, 37, 40) the ratio Sr in K-feldspar/Sr in Plag. ranges between 0.5 and 2. It should be mentioned that this is not in agreement with information given by Oftedal ((1958b) p. 228, (1961) p. 272). who found for Archean granites from Norway that the Sr content was 5 to 10 times higher in the plagioclases than in the coexisting K-feld-

spars "if the Ba-concentration is  $X$  in the plagioclase, it is about  $10X$  in the microcline; then the Sr-concentration is not far from  $10X$  in the plagioclase, and  $X$  in the microcline." Oftedal's (1958b) data on coexisting feldspars in pegmatites show a ratio which is typically closer to unity (variation from 1.5 to 7, average 3 to 4, with one exception with a ratio of  $> 30$ ). These determinations by Oftedal are not incorporated in Table 5, and Figure 9 as it is serious doubt about their accuracy (Oftedal (1958a) p. 225).

Theoretically Sr could be expected to be well suited as indicator of temperature of formation of feldspars; it is intermediate in size between Na, Ca, and K, it forms ionic bonds with oxygen, its concentration is large enough to allow it to be determined by standard methods, and the environment of its site in the feldspar lattice should be the same in all cases and it still is low enough to be considered as a dilute solute in the feldspars. The available data do not seem to indicate that Sr in K-feldspars is related to the Ca-content (Heier and Taylor (1959b)). It is, however, possible that the distribution ratio of Sr is to insensitive towards variations in temperature, and towards fractionation processes in general, to be of much use in petrology. This is partly indicated in Figure 9. It is not possible to separate between different rock types on the basis of the ratio, and the ratio itself shows little variation. However, the data are compiled from different authors and variations may be hidden by analytical errors. Oftedal (1958a) concluded on the basis of his own observations that (p. 229) "the coefficient of distribution of Sr and Ba between the feldspar phases are approximately constant within the temperature interval in which granites may crystallize."

### Elements substituting for Si and Al (Ge and Ga)

A number of elements may substitute for Si and Al in the tetrahedral positions in feldspars:  $B^{3+}$ ,  $Be^{2+}$ ,  $Fe^{3+}$ ,  $Ga^{3+}$ ,  $Ge^{4+}$ ,  $P^{5+}$ ,  $Ti^{4+}$ . Of interest is the recent discovery of Reedmergnerite,  $NaBSi_3O_8$ , the boron analogue of albite (Milton *et al.*, 1960) in the Green River formation, Utah. This mineral is isostructural with albite, which is surprising because of the small size of  $B^{3+}$  (0.20 Å), but the possible existence of a complete solid solution series between reedmergnerite and albite is unknown as is the extent of B substitution in tetrahedral

positions in feldspars. The existence of real borosilicates, datolite and danburite, where  $B^{3+}$  replaces  $Si^{4+}$  has long been known, and the camouflage of B in common silicate structures is of geochemical interest. Goldschmidt (1954) could not detect B in amazonite feldspars.

Faust (1936) showed that a ferric compound corresponding to K-feldspar will form in the ternary system  $K_2O-Fe_2O_3-SiO_2$ . However, in general the Fe content of feldspars is low (except a ferriferous orthoclase from Madagascar containing 2.88%  $Fe_2O_3$ ). The hematite flakes which are often present in certain feldspars (aventurines) may be exsolution products of the ferric feldspars. However, Divljan (1960) found that aventurinization of plagioclase is a consequence of a direct introduction of Fe ions into the crystal lattice of these minerals during metamorphic-metasomatic processes, and thus was not related to the temperature of formation of the feldspars. Some information indicate that iron is in the ferrous state in orthoclase from granulite facies rocks but is ferric in lower grade of metamorphism. This seems to offer some information on the problem of changes in the red-ox potentials under metamorphism, which is a much discussed problem.

The similarity of the radii of  $Si^{4+}$  and  $P^{5+}$  makes a diadochic replacement of Si by P plausible. Extensive replacements of  $(SiO_4)$  groups by  $(PO_4)$  groups has been noted in some zircons. Mason and Berggren (1941) suggested that small amounts of P may be common and of significant geochemical importance in silicate minerals. The writer knows of no determination of P in feldspars. It may be that the tectosilicate framework does not favor P. In phosphate minerals the  $(PO_4)$  groups are not linked together but are always present as separate groups.

The trace elements that are always present in the  $SiO_4$  groups in feldspars are Ge and Ga, and they are the only ones that will be discussed in any detail. Because of their size and charge relationships Ga is clearly associated with Al and Ge with Si. Table 7 lists some pertinent data on the four elements.

The melting points of the pure synthetic feldspars were determined by Goldsmith (1950). The pure Ga and Ge anorthites could not be crystallized directly from a melt. However, melting points of partially substituted anorthites show the same trend as the albites and K-feldspars. The depression of the melting point with introduction of Ga and Ge is as much as would be expected from considerations of size

Table 7. Some data on Al, Ga, Si, Ge, and the Ga and Ge feldspars

Element	Charge	Ionic radius	Ionization potential	Electro-neg.	Ionic potential	radius ratio $M/O^{2-}$	calc. coord. no.	M.P. of oxide	M.P. of feldspars
Al	3	[1] 0.51	[1] 28.44	[2] 1.5	[3] 5.88	0.36	4	[4] 2015	[5] NaAlSi <sub>3</sub> O <sub>8</sub> 1118; KAlSi <sub>3</sub> O <sub>8</sub> 1170 (incongr.)
Ga	3	0.62	30.7	1.6	4.83	0.44	6	1900	NaGaSi <sub>3</sub> O <sub>8</sub> 1015; KGaSi <sub>3</sub> O <sub>8</sub> 1000-1020 (incongr.)
Si	4	0.42	45.1	1.8	9.52	0.30	4	1710	NaAlSi <sub>3</sub> O <sub>8</sub> 1118; KAlSi <sub>3</sub> O <sub>8</sub> 1170 (incongr.)
Ge	4	0.53	45.7	1.7	7.56	0.38	4	1115	NaAlGe <sub>3</sub> O <sub>8</sub> 1067; KAlGe <sub>3</sub> O <sub>8</sub> 1120 NaGaGe <sub>3</sub> O <sub>8</sub> 952; KGaGe <sub>3</sub> O <sub>8</sub> ~ 1000

[1] Ahrens (1953); [2] Pauling (1948); [3] Ringwood (1955); [4] Handbook of Chemistry and Physics; [5] Goldsmith (1950).

and electronegativities of the ions. Goldsmith (1950) made the observation that Ga has a greater influence on the melting temperatures than Ge, and this is also evident from Table 7. The reason is probably the large size of Ga which would favor a 6-coordination with oxygen, and the tetrahedral structure around Ga is rather loosely packed. In addition the higher ionization potential and electronegativity of Ga would indicate a more covalent nature of the Ga-O bond than of the Al-O bond. Ge, on the other hand, has a theoretically stable tetrahedral structure with oxygen; its ionization potential is practically identical with Si; and the electronegativities reported are less than those of Si.

Ga would be expected to show some definite enrichment in feldspars of late stages of formation. Shaw (1957) reviewed the geochemistry of Ga. The relevant data for the feldspars are reproduced here in Table 8, Figure 10, and they substantiate the above. The lowest concentrations (2-15 p.p.m.) are given by Howie (1955) for feldspars from the high temperature Madras charnockites, 10-60 p.p.m. Ga seems to be the range for plutonic magmatic, and metamorphic quartz-feldspathic rocks in mineral facies lower than granulite facies. The



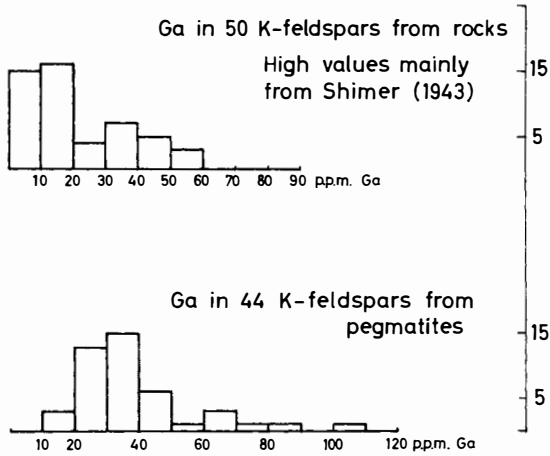


Figure 10. Histograms showing the distribution pattern of Ga in K-feldspars from rocks and pegmatites.

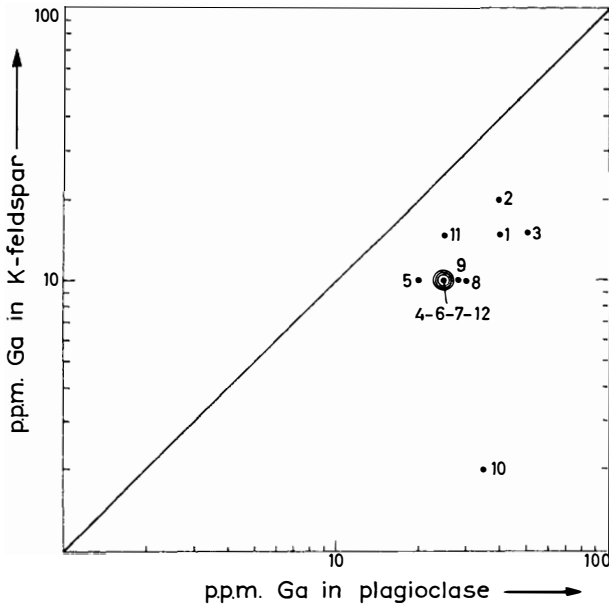


Figure 11. Plots of Ga in K-feldspars vs. Ga in coexisting plagioclase (nos. from Table 5). Solid line shows ratio=1.

Table 8. Ga in feldspars (from Shaw (1957)).

	No. of samples	Ga		10.000 Ga/Al range
		range	mean	
K-Feldspar (pegmatite) [1]		4-74		
K-feldspar (hydrothermal) [1]			4	
K-feldspar (igneous) [2]	14	10-30		1.0-3.0
K-feldspar (igneous) [3]	9	2-15		0.2-1.3
Perthite (pegmatite) [4]	17	30-50	33	
Perthite [5]	1		10	
Alkali feldspar (pegmatite) [1]			44	
Alkali feldspar (igneous) [6]		12-62		
Feldspar (pegmatite) [7]	22	20-100		
Granite feldspar (granite) [7]	22	10-60		
Bytownite (anorthosite) [1]	1		4	
Labradorite (anorthosite) [1]	1		7	
Labradorite (igneous) [8]	1		40	
Plagioclase (igneous) [2]	9	20-50		1.0-4.0
Plagioclase (igneous) [9]	6	35-200		
Plagioclase (igneous) [3]	6	20-45		1.5-3.0
Albite [5]	2	10-100		
Albite (hydrothermal) [1]			4	
Cleavelandite [1]		74		
Cleavelandite [4]		70		

[1] Goldschmidt and Peters (1931); [2] Nockolds and Mitchell (1948); [3] Howie (1955); [4] Higazy (1953); [5] Borovik and Sosedko (1937); [6] Webber (1952); [7] Shimer (1943); [8] Walker et al (1952); [9] Wager and Mitchell (1951).

highest concentrations are found in pegmatite feldspars but the range is considerable (4-110 p.p.m. Ga). However, Shimer (1943) found very similar Ga contents in K-feldspars from pegmatites and granite host rocks. Goldschmidt (1954) found the maximum Ga concentrations in the feldspars of the cryolite deposits of Ivigtut, S. Greenland, and in amazonite from Pikes Peak, Colorado, U.S.A. Shaw (1957) gave an average of 37 p.p.m. Ga in amazonite, as compared to rock-forming feldspars with 14 p.p.m. Ga.

Even though the concentration of Ga in plagioclase is not considerably above that of K-feldspars it can be shown that when the two feldspars coexist the K-feldspar is the less receptive host for Ga, Figure 11. It may be that the distribution of Ga between coexisting

feldspars could elucidate petrogenetic processes. The extent to which Ga will vary with the An content of plagioclase is unknown and should first be investigated. In addition, problems of nucleation may be an obstacle for an equilibrium distribution of Ga.

Ge is nearly perfectly camouflaged by Si but it shows a selective preference for the least linked silicate frameworks. Very little data exist on Ge in feldspars but it is likely to be low, and show little variation with fractionation as well as in its distribution between coexisting feldspars. The crustal abundance of Ge is only 1.1 p.p.m. (igneous rocks, Wardani (1957)). Wardani (1957) determined 0.9 p.p.m. Ge in a composite of five feldspars including K-feldspars and plagioclase, (and 0.0 p.p.m. in quartzes). According to him the average Ge concentrations in different rock types are: granites, 1.3 p.p.m.; intermediate rocks, 1.5 p.p.m.; basalt and disbases, 1.3 p.p.m.; gabbros, 1.2 p.p.m.; ultramafic rocks, 1.0 p.p.m.

### Conclusion

This paper has reviewed the existing data on trace elements in feldspars. The concentration ranges of a number of elements in feldspars from pegmatites and other rocks are now sufficiently well known to allow a prediction of what concentrations can be expected in feldspars from different environments. The manner in which trace elements are incorporated in the mineral lattices and the factors that control their concentration are not well understood. The writer is of the opinion that the effect of temperature, though admittedly the most important single factor in most geologic processes, may well be overemphasized. Although trace element distributions are habitually discussed in terms of high and low temperatures, such factors as rate of growth, pressure gradients, pressure release, bulk chemistry, may be equally decisive. In the case of products of metamorphic differentiation processes the temperature concept is often difficult to invoke, and even fractional crystallization may take place under pressure release rather than a temperature decrease.

### REFERENCES

- ADAMS, J. A. S., OSMOND, J. K., and ROGERS, J. J. W. (1959): The geochemistry of thorium and uranium. *Phys. and Chem. of the Earth*, vol. 3 (1959) pp. 298.

- AHRENS, L. H. (1945): The geochemical relationship between thallium and rubidium in minerals of igneous origin. *Trans. Geol. Soc. South Africa*, vol. 48 (1945) pp. 207.
- (1948): The unique association of Tl and Rb in minerals. *Jour. Geol.*, vol. 56 (1948) pp. 578.
- (1953): The use of ionization potentials—I. Ionic radii of the elements. *Geochim. Cosmochim. Acta*, vol. 2 (1953) pp. 155.
- ALDRICH, L. T. et al. (1956): Radioactive ages of minerals from the Brown Derby Mine and Quartz Creek granite near Gunnison, Colorado. *Jour. Geophys. Res.*, vol. 61 (1956) pp. 215.
- ANDERSEN, O. (1931): Discussion of certain phases of the genesis of pegmatites. *Norsk Geol. Tidsskr.*, vol. 12 (1931) pp. 1.
- BARTH, T. F. W. (1934): Temperaturen i lava og magma masser, samt et nytt geologisk termometer. *Naturen* (1934) pp. 187.
- (1951): The feldspar geologic thermometers. *Neues Jahrb. Mineral. Abh.*, vol. 82 (1951) pp. 143.
- (1956): Studies in gneiss and granite, I and II. *Norske Vidensk. akad. Oslo, Skr. I, Mat. Nat. vidensk. kl.* (1956) no. 1. pp. 1.
- (1961): The feldspar lattices as solvents of foreign ions. *Instituto Lucas Mallada (Madrid) Cursos y Conferencias*, fasc. 8, pp. 3.
- BOROVIK, S. A. and SOSEDKO, A. F. (1937): Ga in mineral samples collected by the expedition from the Lomonosof Institute of the Academy of Sciences of U.S.S.R. *Compt. rend. acad. sci. U.S.S.R.*, vol. 14 (1937) pp. 31 (C.A. 31, 3621).
- BOROVIK-ROMANOVA, T. F. and KALITA, E. D. (1958): Cesium-rubidium microcline-perthite and its rare alkali metal content. *Geokhimiya*, 1958, pp. 141.
- and SOSEDKO, A. F. (1960): Relation between the thallium and rubidium contents, and spectral analytical data of minerals from pegmatite veins of the Kola peninsula. *Geokhimiya*, 1960, pp. 31.
- SOSEDKO, A. F., and SAVINOVA, E. N. (1958): The potassium-rubidium ratio in minerals from pegmatites of the Kola peninsula, as shown by spectrographic analysis. *Geokhimiya*, 1958, pp. 420.
- BRAY, J. M. (1942): Spectroscopic distribution of minor elements in igneous rocks from Jamestown, Colorado. *Bull. Geol. Soc. Amer.*, vol. 53 (1942) pp. 765.
- BUERGER, M. J. (1948): The role of temperature in mineralogy. *Amer. Mineral.*, vol. 33 (1948) pp. 101.
- (1961): Polymorphism and phase transformations. *Fortschr. Mineral.*, vol. 39 (1961) pp. 9.
- BUTLER, J. R. and SKIBA, W. (1962): Strontium in plagioclase feldspars from four layered basic masses in Somalia. *Abstract; Notice No. 117, Mineralogical Society (London)*.
- CATANZARO, E. J. and GAST, P. W. (1960): Isotopic composition of lead in pegmatitic feldspars. *Geochim. et Cosmochim. Acta*, vol. 19 (1960) pp. 113.
- DEMIN, A. M. and KHITAROV, D. N. (1958): Geochemistry of potassium, rubidium, and thallium in application to problems in petrology. *Geokhimiya* (1958) pp. 721.
- DEVORE, G. V. (1955): Crystal growth and the distribution of elements. *Jour. Geol.*, vol. 63 (1955) pp. 471.

- DEVORE, G. V. (1957): The association of strongly polarizing cations with weakly polarizing cations as a major influence in element distribution, mineral composition, and crystal growth. *Jour. Geol.*, vol 65 (1957) pp. 178.
- DIETRICH, R. V. (1960): Banded gneisses of the Randesund area, southeastern Norway. *Norsk Geol. Tidsskr.*, vol. 40 (1960) pp. 13.
- (1961): Comments on the "Two—feldspar geothermometer" and K-feldspar obliquity. Instituto Lucas Mallada (Madrid), *Cursillos y Conferencias*, fasc. 8, pp. 9.
- DIVLJAN, S. (1960): The results of field and laboratory studies of aventurine plagioclases from some Norwegian pegmatites. Report 21st. Int. Geol. Congr. Norden (1960) Pt. 17, pp. 94.
- EMMONS, R. C. (editor) (1953): Selected petrogenic relationships of plagioclase. *Geol. Soc. Amer.*, Memoir 52.
- ENGELHARDT, W. VON (1936): Die Geochemie des Bariums. *Chem. der Erde*, vol. 10 (1936) pp. 187.
- EUGSTER, H (1955): The cesium-potassium equilibrium in the system sanidine-water: Annual Report, Director Carnegie Inst. Wash. pp. 95.
- FAUST, G. T. (1936): The fusion relations of iron-orthoclase, with a discussion of the evidence for the existence of an iron-orthoclase molecule in feldspars. *Amer. Mineral.*, vol. 21 (1936) pp. 735.
- GOLDSCHMIDT, V. M. (1933): Grundlagen der quantitativen Geochemie. *Fortschr. Mineral. Kristal. Petrogr.*, vol. 17 (1933) pp. 112.
- (1954): *Geochemistry*. Oxford Univ. Press (A. Muir, editor).
- and PETERS, CL. (1931): Zur Geochemie des Ga. *Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl. 1*, pp. 165.
- GOLDSMITH, J. R. (1950): Gallium and germanium substitutions in synthetic feldspars. *Jour. Geol.*, vol. 58 (1950) pp. 518.
- and LAVES, F. (1955): Cation order in anorthite as revealed by Ga and Ge substitutions. *Zeitschr. Krist.*, vol. 106 (1955) pp. 213.
- HEIER, K. S. (1960): Petrology and geochemistry of high grade metamorphic and igneous rocks on Langoy, Northern Norway. *Norges Geol. Unders.* no. 207.
- (1961): The amphibolite-granulite facies transition reflected in the mineralogy of potassium feldspars. Instituto Lucas Mallada (Madrid), *Cursillos y Conferencias*, fasc. 8, pp. 131.
- and ADAMS, J. A. S. (1962): The geochemistry of the alkalis. *Phys. and Chem. of the Earth*, 5 (in press).
- and TAYLOR, S. R. (1959a): Distribution of Li, Na, K, Rb, Cs, Pb, and Tl in southern Norwegian pre-Cambrian alkali feldspars. *Geochim. Cosmochim. Acta*, vol. 15 (1959) pp. 284.
- and TAYLOR, S. R. (1959b): Distribution of Ca, Sr, and Ba in southern Norwegian pre-Cambrian alkali feldspars. *Geochim. Cosmochim. Acta*, vol. 17 (1959) pp. 286.
- HIGAZY, R. A. (1953): Observations on the distribution of trace elements in the perthite pegmatites of the Black Hills, South Dakota. *Amer. Mineral.*, vol. 38 (1953) pp. 172.

- HITCHON, B (1960): The geochemistry, mineralogy, and origin of pegmatites from three Scottish Pre-Cambrian metamorphic complexes. Rept. 21st. Int. Geol. Congr., Norden, Pt. 17, pp. 36.
- HOWIE, R. A. (1955): The geochemistry of the charnockite series of Madras, India. Trans. Roy. Soc. Edinb., 62, pp. 725.
- KAPUSTIN, N. P. (1939): Dependence of color of amazonite on rubidium content of the mineral. Izv. Akad. Nauk. S.S.S.R. B. Ser. Geolog. 3, pp. 11.
- KOGARKO, L. N. (1959): Distribution of alkali elements and thallium in granitic rocks of the Turgoyak massif (Central Ural). Geokhimiya, 1959, pp. 455.
- KOUVO, O. (1958): Radioactive age of some Finnish Precambrian minerals. Bull. Comm. Geol. Finlande, no. 182.
- KOWALSKI, W. and WALENCZAK, Z. (1957): Rubidium in feldspars of pegmatites of the Sudeten Mts. Archiv der Mineral., vol. 21 (1957) pp. 427.
- KRETZ, R. (1961): Some applications of thermodynamics to coexisting minerals of variable composition. Jour. Geol., vol. 69 (1961) pp. 361.
- LEBEDEV, N. A. (1959): Regularities of isomorphism. I. Distribution of Mg, Fe, Mn, Ca, Sr, Ba, Li, K, Rb, and other elements in minerals associated with processes of crystallization of magmas. Geokhimiya, 1959, pp. 483.
- LUNDEGÅRDH, P. H. (1947) Rock composition and development in Central Roslagen, Sweden. Arkiv för Kemi, Mineral, Geol., vol. 23 A (1947) pp. 1.
- MILTON, C. et al (1960): Reedmergnerite,  $\text{NaBSi}_3\text{O}_{11}$ , the boron analog of albite, from the Green River formation, Utah. Amer. Mineral., vol. 45 (1960) pp. 188.
- MOXHAM, R. L. (1960): Minor element distribution in some metamorphic pyroxenes. Canadian Mineral., vol. 6 (1960) pp. 522.
- NOCKOLDS, S. R. and MITCHELL, R. L. (1948): The geochemistry of some Caledonian plutonic rocks. Trans. Roy. Soc. Edinb., vol. 61 (1948) pp. 533.
- NOLL, W. (1934): Geochemie des Strontiums mit Bemerkungen zur Geochemie des Bariums. Chem. der Erde, vol. 8 (1934) pp. 507.
- OFTEDAL, I. (1958 a): On the distribution of strontium and barium in the eruptive rocks of the Oslo region. Norsk Geol. Tidsskr., vol. 38 (1958) pp. 221.
- (1958 b): On the development of granite pegmatite in gneiss areas. Norsk Geol. Tidsskr., vol. 38 (1958) pp. 231.
- (1959): Distribution of Ba and Sr in microcline in sections across a granite pegmatite band in gneiss. Norsk Geol. Tidsskr., vol. 39 (1959) pp. 343.
- (1961): Remarks on the variable contents of Ba and Sr in microcline from a single pegmatite body. Norsk Geol. Tidsskr., vol. 41 (1961) pp. 271.
- OTTEMANN, J. (1941): Untersuchungen zur Verteilung von Spurenelementen, insbesondere Zinn, in Tiefengesteinen und einigen gesteinsbildenden Mineralien des Hayes. Zeitschr. für angew. Mineral., vol. 3 (1941) pp. 143.
- PAULING, L. (1948): Nature of the chemical bond. Cornell University Press. 1948.
- RAMBERG, H. (1961): A study of veins in Caledonian rocks around Trondheimsfjord, Norway, Norsk Geol. Tidsskr., vol. 41 (1961) pp. 1.
- RANKAMA, K. and SAHAMA, Th. G. (1950): Geochemistry. University of Chicago Press. 1950.
- REITAN, P. (1956): Pegmatitic veins and the surrounding rocks: I. Petrography and structure. Norsk Geol. Tidsskr., vol. 36 (1956) pp. 213.

- REITAN, P. (1958): Pegmatitic veins and the surrounding rocks, II. Change in the olivine gabbro surrounding three pegmatite veins, Risør, Norway. *Norsk Geol. Tidsskr.*, vol. 38 (1958) pp. 279.
- (1959): Pegmatite veins and the surrounding rocks: III. Structural control of small pegmatites in amphibolites, Rytterholmen, Kragerøfjord, Norway. *Norsk Geol. Tidsskr.*, vol. 39 (1959) pp. 175.
- (1959): Pegmatite veins and the surrounding rocks: IV. Genesis of a discordant pegmatite vein, St. Hansholmen, Risør, Norway. *Norsk Geol. Tidsskr.*, vol. 39 (1959) pp. 197.
- RINGWOOD, A. E. (1955): The principles governing trace element distribution during magmatic crystallization. I. The influence of electronegativity. *Geochim. Cosmochim. Acta*, 7, pp. 189.
- (1955): The principles governing trace element distribution during magmatic crystallization. II. The role of complex formation. *Geochim. Cosmochim. Acta*, 7, pp. 242.
- ROGERS, J. J. W. (1958): Textural and spectrochemical studies of the White Tank quartz monzonite, California. *Bull. Geol. Soc. Amer.*, vol. 69 (1958) pp. 449.
- SEN, N., NOCKOLDS, S. R., and ALLEN, R. (1959): Trace elements in minerals from rocks of the S. Californian batholith. *Geochim. Cosmochim. Acta*, vol. 16 (1959) pp. 58.
- SEN, SISIR, K. (1959): Potassium content of natural plagioclases and the origin of antiperthites. *Jour. Geol.*, vol. 67 (1959) pp. 479.
- (1960): Some aspects of the distribution of barium, strontium, iron, and titanium in plagioclase feldspars. *Jour. Geol.*, vol. 68 (1960) pp. 638.
- SHAW, D. M. (1952): The geochemistry of Tl. *Geochim. Cosmochim. Acta*, vol. 2 (1952) pp. 118.
- (1957): The geochemistry of gallium, indium, thallium—a review. *Phys. and Chem. of the Earth*, vol. 2 (1957) pp. 164.
- SHIMER, J. A. (1943): Spectrographic analysis of New England granites and pegmatites. *Bull. Geol. Soc. Amer.*, vol. 69 (1943) pp. 449.
- SLAWSON, W. F. and NACKOWSKI, M. P. (1959): Trace lead in potash feldspars associated with ore deposits. *Econ. Geol.*, vol. 54 (1959) pp. 1543.
- SOLODOV, N. A. (1958): Distribution of rare elements in minerals of rare-metallic granite pegmatites. *Geokhimiya*, 1958, pp. 749.
- (1959a): Some regularities in the distribution of rare elements in distinctly zonal granite pegmatites. *Geokhimiya*, 1959, pp. 316.
- (1959b): Geochemistry of the rare metal granitic pegmatites. *Geokhimiya*, 1959, pp. 628.
- TAUSON, L. V. and BUZAEV, N. N. (1957): Geochemistry of thallium in granitoids of the Susamyr batholith, Central Tian-Shan. *Geokhimiya*, 1957, pp. 703.
- TAYLOR, S. R. and HEIER, K. S. (1958a): Alkali elements in potash feldspar from the pre-Cambrian of southern Norway. *Geochim. Cosmochim. Acta*, vol. 13 (1958) pp. 293.
- and HEIER, K. S. (1958b): Rubidium depletion in feldspars. *Nature (London)*, vol. 182 (1958) pp. 202.
- and HEIER, K. S. (1960): The petrological significance of trace element variations in alkali feldspars. *Report 21st. Intern. Geol. Congr.*, Norden, pt. 14, pp. 47.

- TAYLOR, S. R. HEIER, K. S., and SVERDRUP, T. L. (1960): Contributions to the mineralogy of Norway. No. 5. Trace element variations in three generations of feldspars from the Landsverk 1 pegmatite. *Norsk Geol.Tidsskr.*, vol. 40 (1960) pp. 133.
- TILTON, G. R. et al. (1955): Isotopic composition and distribution of lead, uranium, and thorium in a Precambrian granite. *Bull.Geol.Soc.Amer.*, vol. 66 (1955) pp. 1131.
- TUREKIAN, K. K. and KULP, J. L. (1956): The geochemistry of strontium. *Geochim. Cosmochim.Acta*, vol. 10 (1956) pp. 245.
- UPTON, B. G. J. (1960): The alkaline igneous complex of Kungnat Fjeld, South Greenland. *Medd.Grønland*, 123, No. 4.
- WAGER, L. R. and MITCHELL, R. L. (1951): Distribution of trace elements during strong fractionation of basic magma—a further study of the Skaergaard intrusion, East Greenland. *Geochim.Cosmochim.Acta*, vol. 1 (1951) pp. 129.
- WALKER, F., VINCENT, H. C. G., and MITCHELL, R. L. (1952): The chemistry and mineralogy of the Kirchell tholeiite, Stirlingshire. *Mineral.Mag.*, vol. 29 (1950-52) pp. 895.
- WARDANI, SAYED, A. EL, (1957): On the geochemistry of germanium. *Geochim.Cosmochim.Acta*, vol. 13 (1957) pp. 5.
- WEBBER, G. R. (1952): Spectrochemical analysis of the White Montain magma series and some Finnish granites. M.Sc. thesis, McMaster University (unpublished).
- WEDEPOHL, K. H. (1956): Untersuchungen zur Geochemie des Bleis. *Geochim.Cosmochim.Acta*, vol. 10 (1956) pp. 69.
- WINKLER, H. G. F. (1961): On coexisting feldspars and their temperature of crystallization. *Instituto Lucas Mallada (Madrid) Cursos y Conferencias*, fasc. 8, pp. 9.
- ZLOBIN, B. I. (1958): Geochemistry of Tl in alkalic rocks. *Geokhimiya*, 1958, pp. 560.