Minor element chemistry of leucite and pseudoleucite

By C. M. B. Henderson, B.Sc., Ph.D., D.I.C.

Geology Department, Imperial College, London, S.W. 7.[1]

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Summary. Leucite and pseudoleucite invariably have lower K/Rb ratios and higher K/Sr and K/Ba ratios than the groundmasses of the rocks in which they occur. The distribution of Rb, Sr, and Ba between K-rich minerals (e.g. alkali feldspars) and the liquids from which they crystallize is generally such that Rb is impoverished and Sr and Ba enriched, relative to K, in the crystallizing phase. Leucite shows the opposite relationship and this is attributed to the leucite structure being sensitive to the size and valency of the ions replacing K.

PSEUDOLEUCITE normally consists of a fine-grained intergrowth of nepheline and alkali feldspar and is believed to be formed by reaction of primary leucite with Na-rich magma (Bowen and Ellestad, 1937), subsolidus breakdown of primary Na-rich leucite (Fudali, 1963), or breakdown of K-analcime (Larsen and Buie, 1938).

During a recent geochemical and mineralogical investigation of the Marangudzi igneous complex, Southern Rhodesia (Rees, 1960; Gifford, 1961) I found that pseudoleucites usually have larger concentrations of Rb and smaller concentrations of Sr and Ba than the rocks in which they are contained. This means that the groundmasses of these rocks have lower Rb and higher Sr and Ba concentrations. Pseudoleucites from other areas show a similar distribution of these elements relative to their bulk rock or groundmass composition.

Leucite phenocrysts from fine-grained or glassy lavas also show high concentrations of Rb and low concentrations of Sr and Ba relative to their bulk rocks or groundmasses.

The above relationships do not conform with those expected considering the normal laws of trace element distribution (Goldschmidt, 1937; Ringwood, 1955) and the possible reasons for this are discussed in this paper.

The Marangudzi complex. The Marangudzi igneous complex, Southern Rhodesia, consists of a large gabbro mass intruded by ring dykes of quartz-syenite, cone sheets of nepheline-syenite (pulaskites, foyaites,

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[1] Present address: Geology Department, The University, St. Andrews, Scotland.

and juvites) and a suite of tinguaite dykes (Rees, 1960; Gifford, 1961). I shall be publishing the geochemistry and mineralogy of the complex elsewhere and it is sufficient, at this stage, to state that the rocks are characterized by high concentrations of K_2O. Pseudoleucites are found in the nepheline syenites, especially in the juvite, and in the tinguaites.

Chemistry of leucite and pseudoleucite. The concentrations of Na_2O, K_2O, Rb, Sr, and Ba in pseudoleucites, leucites, and their respective bulk rocks or groundmasses are given in table I together with the (wt) ratios for K/Rb, K/Sr, and K/Ba.

The Marangudzi pseudoleucites contain considerable amounts of Rb. The juvite pseudoleucites have similar K/Rb ratios to those of the bulk rocks but the tinguaite pseudoleucites have lower K/Rb ratios than the rocks by a factor of two (averages of 190 and 380 respectively). Pseudoleucite from Serra da Tingua, Brazil (P.L. 180) and the leucite phenocrysts from various localities also have lower K/Rb ratios relative to their fine-grained groundmasses or bulk rocks. This enrichment of Rb in pseudoleucite and leucite relative to the groundmass shows that during crystallization of leucite from a magma the leucite is enriched in Rb relative to K.

The Marangudzi pseudoleucites contain lower concentrations of Sr and Ba than the rocks in which they are contained; Sr and Ba must, therefore, be concentrated in the groundmass. For all samples K/Sr and K/Ba ratios (table I) are appreciably higher in the pseudoleucites than in the bulk rocks. The Serra da Tingua pseudoleucite (P.L. 180) shows a similar relationship. Zies and Chayes (1960) found the same relationship for K/Ba in a pseudoleucite-bearing tinguaite from the Bearpaw Mountains, Montana (table I).

The Marangudzi and Serra da Tingua pseudoleucites are rather altered and sometimes contain secondary analcime and zeolites. The presence of analcime in the tinguaite pseudoleucites (P.L. 10, 22, 24, and 180) is reflected by their high Na_2O contents (table I). It is possible that this alteration might have been accompanied by a preferential leaching away of Sr and Ba. However, the pseudoleucite analysed by Zies and Chayes (1960) is unaltered and there can, therefore, have been no loss of Sr and Ba from this sample.

Fresh leucite phenocrysts also have lower concentrations of Sr and Ba than their fine-grained groundmasses (table I). Washington (1906, p. 191) found that phenocrystic leucite from a leucite-tephrite had only 800 ppm Ba while a similar leucite-tephrite had 3000 ppm Ba. K/Sr and K/Ba ratios for the leucites in table I are much larger than those in

Table I. Analyses of leucites or pseudoleucites and their bulk rocks or groundmasses. Na_2O and K_2O were determined by flame photometry, Rb by X-ray fluorescence, Ba by optical spectrography, and Sr by X-ray fluorescence and by optical spectrography. Analyst (except Z & C) C. M. B. Henderson

		Na_2O	K_2O	Rb	Sr	Ba	K/Rb	K/Sr	K/Ba
		wt %	wt %	ppm	ppm	ppm	(wt)	(wt)	(wt)
28	P.L.	3·71	13·29	560	2050	4000	200	54	28
	R.	5·99	11·16	550	2000	6050	170	46	15
30	P.L.	1·30	13·85	590	350	1450	190	330	79
	R.	6·21	8·76	390	1950	6300	180	37	12
276	P.L.	4·46	12·98	660	310	540	160	350	200
	R.	5·43	10·45	690	800	1450	130	100	60
10	P.L.	7·56	9·84	430	840	2300	190	97	35
	R.	8·36	7·49	210	2100	4400	380	30	14
22	P.L.	8·25	9·45	410	900	2650	190	87	30
	R.	7·64	7·79	170	1800	3600	380	36	18
24	P.L.	8·84	8·65	—	770	—	—	93	—
	R.	8·09	8·20	170	1750	3550	390	39	19
180	P.L.	7·46	9·41	390	260	50	200	300	1550
	G.	8·09	7·91	200	250	50	330	260	1300
Z&C	P.L.	4·78	13·40	—	—	2500	—	—	44
	G.	6·85	9·53	—	—	6000	—	—	13
3120	L.	1·49	18·66	1530	300	710	100	520	220
	G.	3·42	7·96	360	2150	1950	180	31	34
3141	L.	0·54	19·90	1290	180	850	130	910	195
	G.	2·01	8·88	420	1800	2050	170	41	36
4354	L.	0·81	19·85	770	110	800	210	1500	210
	G.	5·21	5·82	110	1900	2150	440	25	22
1488	L.*	1·70	15·84	—	420	2250	—	310	58
	R.	2·95	7·14	—	1350	2800	—	44	21
7044	L.*	3·64	14·13	—	1400	1300	—	83	90
	R.	6·48	7·41	—	2400	2050	—	26	30

* Leucite concentrate only; P.L. Pseudoleucite; G. Groundmass; L. Leucite; R. Bulk rock

28, 30, and 276: Juvite, Marangudzi, Southern Rhodesia.
10, 22, and 24: Tinguaite, Marangudzi, Southern Rhodesia.
180: Tinguaite, Serra da Tingua, Brazil.
Z & C: Tinguaite, Bearpaw Mountains, Montana, U.S.A. (Zies and Chayes, 1960).
3120: Leucitophyre, Monte Cimini, Italy.
3141: Leucitite, Capo di Bavo, Rome, Italy.
4354: Mikenite, Bufumbira, Congo.
1488: Leucite basanite, Vesuvius, Italy.
7044: Nosean leucitophyre, Eifel, Germany.

the groundmasses and this reflects the great enrichment of Sr and Ba in the groundmasses. This means that the magma from which leucite crystallized was continuously enriched in Sr and Ba relative to K.

The data discussed above show that Rb, Sr, and Ba have the same distribution in pseudoleucite and leucite relative to their groundmasses. It is reasonable to assume that pseudoleucite has formed from soda-rich leucite by subsolidus reaction (Fudali, 1963). It is, therefore, interesting to consider why leucite should show enrichment of Rb, and impoverishment of Sr and Ba, relative to K.

Geochemistry of Rb, Sr, and Ba. The most distinctive feature in the geochemistry of Rb is its coherence with K during the major part of the magmatic process and Rb is 'camouflaged' in K-minerals. Rb and K have similar valencies, ionization potentials, and electronegativities. Owing to the smaller size of K^+ relative to Rb^+ (1·33 Å and 1·47 Å respectively), the latter should be enriched in the liquid with differentiation and progressively formed late-stage rocks should show decreasing K/Rb ratios (Taylor *et al.*, 1956; Butler *et al.*, 1962). Under these circumstances the K/Rb ratio of the crystallizing phase would be expected to be greater than that for the liquid. The opposite is true for leucite.

Heier and Adams (1965, p. 276) suggested that for coexisting K-minerals in equilibrium, the one with the highest co-ordination number for the alkali-element ions in the lattice should concentrate the large Rb^+ relative to K^+. They concluded that Rb should be enriched in biotite ($K^{[12]}$) relative to coexisting K-feldspar ($K^{[9]}$); the former thus having a lower K/Rb ratio than the latter.

Sr^{2+} (1·12 Å) and Ba^{2+} (1·34 Å) both replace K^+ in K-minerals. Because of their divalent state they should be enriched, relative to K, in early-crystallizing phases. Larsen *et al.* (1941) analysed the sanidine phenocrysts in a mafic analcime-phonolite from the Highwood Mountains, Montana. They found that the feldspar phenocrysts were much enriched in Ba relative to the bulk rock and groundmass. K/Ba ratios for feldspar, bulk rock, and groundmass are 1·2, 8·4, and 37 respectively. R. Berlin (personal communication) analysed the alkali-feldspar phenocrysts of trachytes and kenytes and found that Sr and Ba were much enriched in the feldspars relative to their groundmasses (liquids). K/Sr and K/Ba ratios for K-minerals should therefore be less than those for the liquid from which they are crystallizing. The opposite is true for leucite.

Rankama and Sahama (1950) have suggested that Ba^{2+} is enriched in micas, relative to K^+, because of its divalent state; Sr^{2+} is too small an ion to be stable in the 12-co-ordinated sites of micas.

Bearing these facts in mind one may conclude that K-rich minerals generally contain large amounts of Rb, Sr, and Ba. Leucites contain up to 20 % K_2O and their comparative lack of Sr and Ba is difficult to reconcile with their high potash content. The problem therefore seems to be a structural one.

The structure of analcime and its analogues. Deer, Howie, and Zussman (1963) have summarized the structures of analcime, leucite, and pollucite. Leucite ($KAlSi_2O_6$) is tetragonal below 625° C and cubic above this temperature. Its structure is based on a (Si,Al)–O framework similar to that of analcime ($NaAlSi_2O_6.H_2O$) and pollucite ($CsAlSi_2O_6$). The unit cell has cavities of two different sizes. The 16 larger sites (*W* sites) have 12-fold co-ordination. These sites are in line with the centres of large channels that run along four non-intersecting triad directions. Thus the structure is permeated by a channel system that facilitates ion-exchange reactions (Taylor, 1930). The *W* sites contain H_2O in analcime and K-analcime ($KAlSi_2O_6.H_2O$), Cs in pollucite, and K in cubic leucite. The 24 smaller sites (*S* sites), of which only 16 are occupied, have 6-fold co-ordination. The *S* sites are occupied by Na in analcime, K in K-analcime, and are vacant in cubic leucite and pollucite. The cell edges of cubic leucite, analcime, K-analcime, and pollucite are respectively 13·4, 13·7, 13·8, and 13·6 Å. The Ca analogue of analcime is wairakite ($CaAl_2Si_4O_{12}.2H_2O$) which is monoclinic (pseudo-cubic) and has a similar (Si,Al)–O framework to analcime (Coombs, 1955). The maximum and minimum cell-dimensions of wairakite are 13·68 and 13·56 Å. Barrer and Denny (1961) prepared a synthetic cubic wairakite with cell edge 13·62 Å. Beattie (1954) suggested that the 24 (*S*) sites in the analcime structure are made up of 16 (NaAlSi4[O]) groups and 8 (2Si4[O]) groups. He also suggested that these 24 sites might be arranged 8 (Na2Al4[O]), 8 (Na2Si4[O]) and 8 (2Si4[O]). Coombs (1955) considered that the Ca atoms in wairakite would most likely be associated with the first of these three groups. The structure would therefore consist of 8 (Ca2Al4[O]) and 16 (2Si4[O]) groups. Thus wairakite would have a different and more specialized distribution of Si and Al than analcime.

Coombs (1955) suggested that this difference in structure might explain the lack of solid solution between natural wairakite and analcime (Steiner, 1955). The analysed wairakite had 11·7 % CaO and 1·06 % Na_2O while analcime commonly has more than 13 % Na_2O and less than 1 % CaO.

Limited solid solution is also found in leucite and natural leucites generally contain less than 2 % Na_2O and less than 1 % CaO. The position of Ca in the leucite lattice is uncertain. The limited solid solution between analcime and wairakite might be expected considering their low-temperature environments (cf. exsolution of alkali feldspars at low temperatures). However, the leucite of volcanic rocks must have crystallized at temperatures in excess of 1000° C and more solid solution would be expected.

Experimental syntheses of analcime and its analogues. Barrer (1950) prepared leucite from analcime and vice-versa by ion-exchange at low temperatures (200° C). Clarke and Steiger (1900) synthesized ammonium analcime from natural analcime or leucite by ion-exchange at low temperatures. Barrer also found that in synthetic analcimes there is free interchange between Na^+ and K^+, NH_4^+, Ag^+, Tl^+, and Rb^+ but only limited or negligible exchange between Na^+ and Li^+, Cs^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}. Cs^+ is locked in the pollucite structure and the mineral cannot be prepared by ion-exchange with analcime, it can only be prepared by direct synthesis. In contrast to analcime, chabazite ($CaNa_2Al_2Si_4O_{12}.6H_2O$) freely exchanged the cations Li^+, Na^+, K^+, NH_4^+, Rb^+, Cs^+, Ag^+, Tl^+, Ca^{2+}, Sr^{2+}, and Ba^{2+}.

Barrer (1950) used the concept of ion-sieve effect (which allows Rb to diffuse in the analcime structure but not Cs) to explain why Ca- and Ba-rich analcimes are difficult to obtain. In the analcime structure the interstitial channels have periodic constrictions that are sufficiently narrow to prevent diffusion of Cs ions (Barrer, 1950, p. 2350, fig. 1). Divalent cations cannot occupy positions at these narrow constrictions and their presence in only half of the sites normally occupied by univalent cations would lead to local disturbance of cationic and anionic charge with the introduction of vacancies into the structure (*ibid.*, fig. 2). Neither of these configurations would be stable and therefore exchange of univalent and divalent cations would be limited in extent. Barrer suggested that in chabazite the constrictions are less marked and there would be room for divalent cations to occupy sites at the channel constrictions (*ibid.*, fig. 4).

These relationships are in good agreement with those found in natural minerals. Analcime contains little Ca whereas chabazite contains large concentrations of Ca as well as Na and K. Reichert and Erdléyi (1935) reported the presence of Sr and Ba in chabazites; one sample contained 7·46 % CaO, 1·50 % Na_2O, 0·67 % K_2O, 0·54 % SrO, and 0·24 % BaO.

Coombs (1955) suggested that if analcime and wairakite have different Si–Al arrangements then the latter would not be expected to be synthesized from analcime by ion-exchange reactions. The same argument could be used to explain the lack of ion-exchange between Na and Ba (and presumably Sr) in synthetic analcime. However, Barrer and Denny (1961) directly synthesized wairakite at 260° C, while K-analcime was formed at 420° C, Rb-analcime at 190° C, and pollucite at 120° C. Wairakite is therefore rather easily prepared by direct synthesis. In contrast to this Sr-analcime was only prepared metastably (at 350° C) while Ba-analcime was not obtained at all. The analcime structure therefore seems to be sensitive to the size of the substituting divalent ions; the Ca^{2+} ion is easily admitted and the larger Sr^{2+} and Ba^{2+} are almost excluded.

Conclusions. Owing to the similar structures of analcime and cubic leucite a similar hypothesis to that stated above could be used to account for the enrichment of Rb and the impoverishment of Sr and Ba in leucites. Although the ion-exchange experiments with analcime and the direct syntheses of the analogues of analcime were carried out at temperatures considerably below the crystallization temperature of leucite, it seems likely that the ease of entry of elements into the leucite lattice can be compared to that into the analcime lattice. However, the absolute amounts of the various elements entering the leucite lattice at high temperature would differ from those entering the analcime lattice at low temperature. Thus Rb would be expected to enter the leucite lattice more easily, and in higher concentration relative to the liquid, than either Sr or Ba. This relationship is, in fact, found naturally.

Another factor influencing the concentration of Rb in leucite relative to liquid is the co-ordination state of the cation sites in leucite. In cubic leucite the K atoms occur in 12-co-ordinated sites. By analogy with the micas, Rb^{+} (1·47 Å) should enter these sites rather than the smaller K^{+} (1·33 Å) thus causing the liquid to be depleted in Rb relative to K. The large divalent Ba^{2+} (1·34 Å) should also enter these 12-co-ordinated sites rather than K^{+} but Sr^{2+} (1·12 Å) is too small an ion to be stable in these large sites. A partial separation of Sr from Ba would therefore be expected during the crystallization of leucite. It is therefore interesting to note that even though both Sr and Ba are concentrated in the groundmass, rather than in leucite, Sr is concentrated to a greater extent than Ba. K/Sr and K/Ba ratios for the leucites and groundmasses given in table I show this relationship very clearly.

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