The beryls of the Rosses district, Donegal

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SUMMARY. Chemical analyses and physical properties are given for six samples of beryl from greisenized granites, pegmatites, and beryl–quartz veins in the Rosses granite complex. The beryls studied were all very similar in composition and contain significant amounts of alkali elements and water in addition to the constituents represented by the formula $Be_3Al_2Si_6O_{18}$. Calculation of the empirical unit cell contents indicates that most of the H_2O+ is present in the mineral as water molecules. The effects of these extra constituents on the physical properties are discussed, and it is suggested that the variation in refractive indices displayed by beryl is to a large extent attributable to the variable water content.

BERYL has been known to occur in the Rosses district of Donegal for over 100 years, and fine specimens of the mineral from this area are to be found in many mineral collections. The mineral is present in three different types of occurrence: disseminated in greisenized granite; in beryl-bearing pegmatite; and in beryl–quartz veins. This paper describes the composition and properties of beryls in each of the three parageneses.

Beryl has been found at a number of localities in Sheskinarone, Meenbannad, and Meenmore townlands (fig. 1), within the outcrops of the G3 and G4 units of the Rosses granite complex (Pitcher, 1953). Most of the G3 granite, and a small part of the G4 granite, are medium-grained biotite-granites that do not contain beryl, but in parts of both granites the normal biotite-granite has been altered metasomatically into a quartz-rich muscovite-granite ('greisenized-granite'), which contains beryl in the areas of most intense alteration. Although the greatest amount of beryl is found in the metasomatized granite, the mineral also occurs in numerous pegmatites and quartz veins in the same area. Details of the postmagmatic alteration, and of the beryllium mineralization, are given by Harvey (1969) and by Burke, Cunningham, Gallagher, and Hawkes (1964) respectively. The beryl itself has previously been studied by Haughton (1862), and Haughton's paper contains one analysis of beryl from Sheskinarone, although several important minor constituents were not determined.

Chemical composition. Beryl crystals were separated by hand from two samples of each paragenetic type, and freed from any contaminating material by a combination of magnetic and heavy liquid methods after crushing and sieving to a grain size of 60 to 150 mesh. The minerals were analysed by a combination of gravimetric and instrumental methods.

The SiO_2 content was determined by the conventional gravimetric method, i.e. fusion with sodium carbonate and double dehydration with hydrochloric acid. The R_2O_3 group (Al_2O_3, BeO, Fe_2O_3, etc.) was then precipitated by ammonia in the usual manner. After fusion of the resulting ignited precipitate with potassium pyrosulphate, the BeO content was determined by atomic absorption spectrophotometry. This method was found to be more satisfactory than attempting to separate beryllium

and aluminium chemically. Al_2O_3 was determined by difference but was also checked by atomic absorption. The remaining elements were determined on a separate portion of the mineral. This was dissolved, after grinding, in a mixture of hydrofluoric and perchloric acids. Beryl is relatively insoluble in HF and repeated attack was necessary to ensure complete solution. For this reason, no attempt was made to determine the FeO content because of the risk of oxidation during the prolonged attack; all the iron is quoted as Fe_2O_3. Total iron and titanium were determined colorimetrically, but no titanium was detected in any of the samples. Magnesium, calcium, and manganese were determined by atomic absorption, lanthanum chloride being used to suppress the aluminium interference with calcium and magnesium. Emission flame photometry was used to measure sodium, potassium and lithium. Rubidium and caesium were determined in a separate portion of sample by X-ray fluorescence.

The chemical analyses are given in table I. All the analyses are very similar to one another, the only indication of a difference in composition between the beryls of different environments being a slightly lower silica content in the beryls from the pegmatites, and slightly lower alkali contents in the samples from beryl–quartz veins. The analyses are quite similar to other published analyses of beryl from granitic rocks, and the only rare element detected was caesium, which is well known to occur as a minor constituent of beryl.

The presence of between 3 and 4% of alkalis and water (H_2O+) presents difficulties in the recalculation of the analyses to structural formulae, because the accepted formula for beryl, $Be_3Al_2Si_6O_{18}$, contains no provision for these constituents. Some authors believe that some of the alkali ions, i.e. lithium and perhaps sodium, may substitute isomorphously for beryllium, but it is generally accepted that the larger alkali ions can not substitute for beryllium, aluminium, or silicon, and must be accommodated in non-stoichiometric fashion in the open hexagonal channels of the beryl structure. It is also believed that some or all of the water in beryl is present not as hydroxyl ions substituting for oxygen, but as actual water molecules, also occupying the open channels. The presence of molecular water is indicated by measurements of the rate of loss of water on heating (Ginzburg, 1955), by infra-red absorption spectra (Wood and Nassau, 1968), by X-ray diffraction intensities (Vorma, Sahama, and Haapala, 1965), and by nuclear magnetic resonance spectra, although some NMR spectra have been interpreted as indicating the presence only of molecular water (Paré and Ducros, 1964), while others have been taken to indicate the presence of both molecular water and hydroxyl ions (Sugitani, Nagashima, and Fujiwara, 1966).
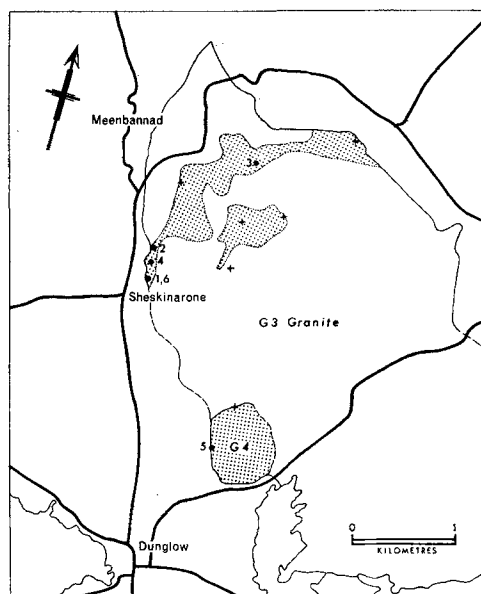

FIG. 1. Map of the Rosses district, showing areas of muscovite-granite and greisen (shaded). Numbered dots represent the localities of analysed samples. Crosses represent other known beryl localities (after Burke *et al.* 1964.)

The empirical unit cell contents have been calculated from the analyses (not including H_2O-) and the measured values of the density and cell dimensions, as suggested by Hey (1939), using a revised value of 0.6024×10^{24} for Avogadro's constant. The cell

TABLE I. *Chemical analyses and physical properties of beryls from the Rosses district of Donegal*

	Beryls from granites		Beryls from pegmatites		Beryls from veins	
	1	2	3	4	5	6
SiO_2	64·43	64·54	63·01	63·25	64·11	64·23
Al_2O_3	16·72	17·36	17·97	18·29	17·54	17·98
Fe_2O_3	0·82	0·75	0·67	0·79	0·68	0·67
BeO	13·14	12·69	12·95	12·85	12·88	12·81
MnO	0·01	0·02	0·02	0·02	0·02	0·02
MgO	0·68	0·63	0·57	0·60	0·51	0·43
CaO	0·49	0·09	0·17	0·30	0·42	0·41
Na_2O	1·11	1·04	1·06	1·05	1·00	0·90
K_2O	0·32	0·22	0·20	0·26	0·23	0·20
Li_2O	0·10	0·11	0·14	0·07	0·10	0·08
Rb_2O	0·01	0·01	0·01	0·01	0·01	0·01
Cs_2O	0·15	0·15	0·14	0·10	0·10	0·12
H_2O+	1·92	1·94	1·95	1·78	1·82	1·89
H_2O-	0·15	0·20	0·44	0·00	0·44	0·18
Total	100·05	99·75	99·30	99·37	99·86	99·93

Empirical unit cell contents, divided by 2, with a suggested allocation to structural positions

	1		2		3		4		5		6	
Be	2·911	2·91	2·819	2·86	2·919	3·00	2·875	2·94	2·866	2·88	2·831	2·83
Al	—		0·039		0·077		0·063		0·009		—	
Al	1·812		1·821		1·821		1·835		1·845		1·866	
Fe	0·057		0·051		0·046		0·055		0·047		0·045	
Mg	0·093	2·00	0·087	2·00	0·080	2·00	0·083	2·00	0·070	2·00	0·059	2·00
Mn	0·001		0·001		0·001		0·001		0·001		0·001	
Li	0·037		0·040		0·052		0·026		0·037		0·029	
Si	5·943	5·95	5·968	6·00	5·911	6·00	5·890	6·00	5·939	6·00	5·908	5·99
Al	0·006		0·032		0·089		0·110		0·061		0·083	
O	17·778	18·00	17·789	18·00	18·00	18·00	17·972	18·00	17·845	18·00	17·692	18·00
OH	0·222		0·211		—		0·028		0·155		0·308	
Ca	0·048		0·009		0·017		0·030		0·041		0·040	
Na	0·198		0·186		0·193		0·189		0·179		0·160	
K	0·037		0·026		0·024		0·030		0·027		0·023	
Cs	0·006	0·77	0·006	0·72	0·005	0·87	0·003	0·79	0·003	0·74	0·004	0·65
H_2O	0·479		0·493		0·610		0·539		0·485		0·426	
excess O	—		—		0·025		—		—		—	

Physical properties

	1	2	3	4	5	6
ϵ	1·580	1·582	1·580	1·580	1·581	1·580
ω	1·583	1·585	1·584	1·584	1·583	1·583
S.G.	2·710	2·706	2·726	2·721	2·710	2·702
a	9·224 Å	9·230	9·236	9·222	9·226	9·225
c	9·206 Å	9·200	9·189	9·212	9·199	9·193
c/a	0·998	0·997	0·995	0·999	0·997	0·997
V	678·3 Å³	678·8	678·8	678·5	678·1	677·5

contents are divided by 2 in table I to facilitate comparison with the standard formula $Be_3Al_2Si_6O_{18}$. On this basis, Be, Al, and Si total just less than 3, 2, and 6 atoms per formula unit respectively.

The possible isomorphous substitutions may be considered in the light of the ionic radii of the elements present: Be^{2+} 0·33, Si^{4+} 0·40, Al^{3+} 0·49 (tetrahedral) or 0·51 (octahedral), Fe^{3+} 0·64, Mg^{2+} 0·66, Li^+ 0·68, Fe^{2+} 0·74, Mn^{2+} 0·80, Na^+ 0·97, Ca^{2+} 1·03, K^+ 1·42, Cs^+ 1·82 Å. Although the substitution of alkali elements for beryllium has been assumed by several previous workers, it can be seen from the ionic radii that

substitution of these elements for beryllium is virtually impossible; the volumes of the sodium and calcium ions are more than twenty-five times the volume of the beryllium ion, and even lithium is much larger. The only atoms that could conceivably substitute for beryllium in its tetrahedral sites are silicon and aluminium, the latter being more likely since it does not differ so much in charge and occupies similar positions in the structurally related mineral, cordierite. Aluminium is also the only element likely to substitute for silicon in its tetrahedral positions. Most of the aluminium in beryl is octahedrally coordinated, and the small amounts of iron, magnesium, and manganese present may also be expected to occupy octahedral sites. The position of lithium is more doubtful, and it has been considered: to substitute for beryllium (Bakakin, Rylov, and Belov, 1967); to substitute for aluminium (Schaller, Stevens, and Jahns, 1962); or to occupy the open channels, along with the large alkali elements. The first possibility is difficult to reconcile with the difference in ionic size between Be^{2+} and Li^+. The second possibility is the most probable because lithium is known to substitute for octahedral aluminium in other minerals, for example in the lithium micas. In the allocation of atoms to structural positions in table I, the octahedral positions have been filled by Fe, Mg, Mn, Li, and Al, and the excess Al allocated to Si and then to Be positions. The remaining cations, Ca, Na, K, Rb, and Cs, total between 0·2 and 0·3 atoms per formula unit. None of these ions is small enough to substitute for aluminium, and as the aluminium positions are in any case fully or almost fully occupied by Al, Fe, Mg, and Li, it is reasonable to suppose that the calcium and the larger alkali ions are present in the large channels and not in any of the regular structural positions.

The numbers of oxygen atoms are in every case larger than the eighteen required by the standard formula, and the excess corresponds to the amount needed to convert most of the hydrogen to molecular water. Only a small proportion of the hydrogen could be present as hydroxyl ions. In one analysis (no. 3) there is a slight excess of oxygen atoms, possibly due to the assumption that all the iron is in the ferric condition. The largest proportion of hydroxyl ions is shown by analysis 6, in which 0·308 H atoms per formula unit can be allocated to hydroxyl ions compared with 0·852 allocated to water molecules.

Physical properties. The refractive indices, unit cell dimensions, and specific gravities of the analysed beryls are given in table I. The refractive indices were measured by the dispersion method, and the values quoted are for the wavelength of sodium light. The unit cell dimensions of beryl are difficult to measure because the X-ray powder pattern contains many overlapping reflections; the values given in Table I were obtained from careful diffractometer measurements of the unequivocally indexed $21\bar{3}2$ and $11\bar{2}2$ reflections, using silicon as an internal standard. The cell dimensions are believed to be accurate to within 0·005 Å. The specific gravities were measured on between 0·6 and 2·0 g of material, dried at 110 °C, using a 10 ml/S.G. bottle; measurements were corrected for temperature.

The refractive indices are all close to ω 1·584, ϵ 1·580. These values are higher than those of synthetic beryl but lower than those of alkali-rich beryls. The variation in

refractive indices of beryl is rather large in relation to the small amount of compositional variation shown by this mineral, and the relationship between composition and optical properties does not appear to be very well understood. Graphs have been published by Winchell (1951) and by Deer, Howie, and Zussman (1962), showing the relationship between refractive indices and composition expressed in terms of a series from $Be_3Al_2Si_6O_{18}$ to $R_3Al_2Si_6O_{18}$. This, however, is an unrealistic representation of the variation in composition, as very little direct substitution of other elements for beryllium actually occurs; moreover, the values for the refractive indices of the $Be_3Al_2Si_6O_{18}$ end-member extrapolated from these graphs (ω 1·578, ϵ 1·571, Deer et al., 1962; ω 1·567, ϵ 1·562, Winchell, 1951) are much higher than those of synthetic anhydrous end-member beryl, ω 1·560, ϵ 1·557 (Schaller, Stevens, and Jahns, 1962).

The very small amount of isomorphous substitution that occurs in beryl is unlikely to have much effect on the refractive indices, and the variation in optical properties is dominated by the non-stoichiometric occupancy of the open channels in the structure by alkali ions and water. It might not be expected that the presence of a small amount of alkalis would have the effect of raising the refractive indices appreciably, and the presence of water usually has exactly the opposite effect; for example opal (hydrated cristobalite) has a lower refractive index than ordinary cristobalite, and hydrated montmorillonite has a lower refractive index than dehydrated montmorillonite. However, in beryl the alkali ions are not substituting isomorphously for other ions of similar ionic refractivity, nor can the water in beryl be considered to be physically admixed with anhydrous beryl. The alkalis and water are both occupying what would otherwise be empty spaces in the beryl structure, and consequently they both have the effect of substantially increasing the refractive indices. In fact, because of the high specific refractive energy of water, the presence of water has a greater effect on the refractive indices than a similar amount of alkalis.

Whereas the influence of caesium and other alkali elements on the refractive indices is widely appreciated, the effect of water has not been generally recognized, although Flanigen et al. (1967) have observed that hydrothermally grown synthetic emeralds have higher refractive indices than flux-grown emeralds, and it is known that the refractive indices of natural beryls decrease when they are heated to a high temperature (Gavrusevich and Sarapulov, 1941). A similar effect has been noted in the structurally similar mineral, cordierite, the refractive indices of which can be lowered by heating to drive off the water (Iiyama, 1958). The influence of water content on the optical properties of cordierite has been discussed at length by Schreyer and Yoder (1964), who showed that the mean refractive index of synthetic Mg-cordierite increases linearly with H_2O+ content by approximately 0·009 for every one per cent of water.

Schreyer and Yoder (1964) also showed from the refractive indices that the water content of synthetic Mg-cordierite is directly related to the temperature and water pressure during crystallization, being greatest at low temperatures and high water pressures. By analogy, the rather similar water contents of the Rosses beryls in each of the three parageneses may reflect similar physical conditions during their formation; alternatively, those which crystallized at the highest temperature also crystallized at the highest water pressure.

It may be observed in passing that the dispersion of the refractive indices of the Rosses beryls was found to be approximately 0·004, measured as $\omega_F - \omega_C$, in all the samples. This is appreciably less than the values of 0·009–0·013 listed for beryl by Winchell (1929). This property was found to be useful in checking the purity of the beryls separated for analysis, since it is considerably less than the dispersion of quartz ($\omega_F - \omega_C = 0 \cdot 008$), which was also present in the rocks and which looks very similar to beryl under the microscope. The dispersion of beryl, unlike that of quartz, is sufficiently different from those of the liquids used as immersion oils for the beryl grains to be conspicuous by their coloured Becke line fringes.

The unit cell dimensions of the Rosses beryls are all similar to one another, lying in the range a 9·222–9·230 Å, c 9·189–9·212 Å. Sosedko (1957) has suggested that the presence of alkali ions causes an increase in the c dimension, but Bakakin, Rylov, and Belov (1967) consider it unlikely that the alkalis could have much effect on the cell dimensions, in view of their structural position, and attribute variations in a to substitutions in octahedral lattice positions and variations in c to substitutions in tetrahedral positions. The cell dimensions of the Rosses beryls are close to those of synthetic anhydrous beryl, a 9·21, c 9·20 Å (Schaller et al., 1962), suggesting that neither water molecules nor alkali ions have much effect on the cell dimensions.

The specific gravities lie in the range 2·70–2·73, and are similar to those of other beryls from similar occurrences. The specific gravity of beryl appears to be affected by the presence of molecular water in the same way as the refractive indices. Determinative curves for beryl given by Winchell (1951) and by Deer, Howie, and Zussman (1962) show extrapolated end-member values of 2·65 and 2·68 respectively, which are higher than the specific gravity (2·635) of synthetic anhydrous (flux-grown) beryl (Schaller et al., 1962), but close to that (2·66) of hydrothermally grown synthetic beryl (Flanigen et al., 1967).

REFERENCES

[Bakakin (V. V.), Rylov (G. M.), and Belov (N. V.)] Бакакин (В. В.), Рылов (Г. М.), и Белов (Н. В.) 1967. *Dokl. Acad. Sci. U.S.S.R., Earth Sci. Sect.* (English translation), **173**, 129–32.

Burke (K. C.), Cunningham (M. A.), Gallagher (M. J.), and Hawkes (J. R.), 1964. *Econ. Geol.* **59**, 1539–50.

Deer (W. A.), Howie (R. A.), and Zussman (J.), 1962. *Rock-forming minerals*, **1**, *Ortho- and Ring Silicates.* London (Longmans).

Flanigen (E. M.), Breck (D. W.), Mumbach (N. R.), and Taylor (A. M.), 1967. *Amer. Min.* **52**, 744–72.

[Gavrusevich (B. A.) and Sarapulov (F. Ya.)] Гаврусевич (Б. А.) и Сарапулов (Ф. Я.) 1941. [*Compt. Rend. (Doklady) Acad. Sci. U.R.S.S.* **31**, 775], abstr. M.A. 9–135.

[Ginzburg (A. I.)] Гинзбург (А. И.), 1955. [Труды мин. муз. акад. наук СССР (*Trans. Min. Mus. Acad. Sci. U.S.S.R.*), 7, 56], abstr. M.A. 13–183.

Harvey (J. J. T.), 1969. *Postmagmatic alteration in the Rosses granite complex, Donegal.* Ph.D. thesis, University of London.

Haughton (S.), 1862. *Quart. Journ. Geol. Soc.* **18**, 403–20.

Hey (M. H.), 1939. *Min. Mag.* **25**, 402–12.

Iiyama (T.), 1958. *Compt. Rend. Acad. Sci. Paris*, **246**, 795–8.

Paré (X.) and Ducros (P.), 1964. *Bull. Soc. franç. Min. Crist.* **87**, 429–33.

PITCHER (W. S.), 1953. *Proc. Geol. Assoc., Lond.* **64**, 153–82.
SCHALLER (W. T.), STEVENS (R. E.), and JAHNS (R. H.), 1962. *Amer. Min.* **47**, 672–99.
SCHREYER (W.) and YODER (H. S.), 1964. *Neues Jahrb. Min., Abh.* **101**, 271–342.
[SOSEDKO (T. A.)] Соседко (T. A.), 1957. Зап. всесоюз. мин. общ. (Mem. All-Union Min. Soc.),
    86, 495–99.
SUGITANI (Y.), NAGASHIMA (K.), and FUJIWARA (S.), 1966. *Bull. Chem. Soc. Japan*, **39**, 672.
VORMA (A.), SAHAMA (Th. G), and HAAPALA (I.), 1965. *Bull. Comm. Géol. Finlande*, **218**, 119–29.
WINCHELL (A. N.), 1929. *Amer. Min.* **14**, 125–49.
—— 1951. *Elements of optical mineralogy. Part II. Descriptions of minerals.* 4th edn., New York
    (John Wiley and Sons).
WOOD (D. L.) and NASSAU (K.), 1968. *Amer. Min.* **53**, 777–800.