

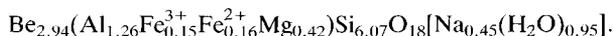
# A blue sodic beryl from southeast Ireland

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## Abstract

Deep azure-blue beryl is reported from veins in Upper Devonian conglomerate from southeast Ireland. Microprobe analysis, Mössbauer spectroscopy and loss on ignition suggest an unusual chemistry with an exceptionally high degree of substitution of Fe and Mg for Al, and extreme amounts of Na and water held within channel sites in the structure. The calculated structural formula is:



Refractive indices (1.603 and 1.595) and the cell edge,  $a$ , (9.292 Å) are also unusually high. Colourless beryl from the same locality, some of which forms cores to blue beryl prisms, has less octahedral substitution and a lower Fe/Mg ratio. The origin of the beryl is tentatively linked to contemporaneous volcanic activity.

KEYWORDS: beryl, Mössbauer spectroscopy, sodium, Ireland.

## Introduction

BLUE beryl as a vein-filling mineral in sedimentary rocks is not widely known. It is not specifically mentioned in the review by Deer *et al.* (1986), though in recent years at least two examples have been reported (Fontan and Fransolet, 1982; Aurisicchio *et al.*, 1988, sample 1). Both examples have a high degree of substitution of Fe and Mg for Al on the octahedral site and for this reason they are referred to by Aurisicchio *et al.* (1988) as 'octahedral' beryls. In this paper we report an occurrence of blue beryl from veins cutting a Devonian conglomerate in southeast Ireland. We show it to be an 'octahedral' beryl with extreme substitution, coupled with the highest reported water content.

## Field occurrence

The beryl occurs within a single northeast-southwest trending outcrop of conglomerate measuring some 50 m by 10 m on the southern slopes of Croughaun Hill (Irish grid ref. S 372100) about 10 km south of the town of Carrick on Suir. Exposure in the general vicinity is good (about 25% bare rock), yet careful searching has revealed only one other beryl occurrence, a tiny showing about 300 m north of the main outcrop.

The conglomerate contains well rounded pebbles, up to 10 cm, of vein quartz and quartzite in a gritty, quartz-rich, pale greyish-green sandy matrix. It is locally clast supported; elsewhere it

contains rare, strongly cleaved, siltstone lenses. It dips fairly steeply northeast, and its geological contacts appear to be faults. Penney (1980) mapped the conglomerate and named it the Croughaun Formation. He suggested that it belongs to the local Old Red Sandstone facies, of Upper Devonian age, which rests with an angular unconformity on Lower Palaeozoic rocks.

The beryl is most prominently developed near the eastern side of the main outcrop area. Here it forms a conspicuous blue central zone, up to 2 cm wide, in a few broad, milky-white quartz veins. It also fills narrower (mm scale) veins, in the vicinity of which it replaces the conglomerate. It is nowhere of gem quality, and larger prisms (up to 5 cm long) are commonly cracked and bent. It is bright blue in colour when fresh, but its weathered appearance is a dull bluish green. One particular vein was chlorite-rich, and brecciated, and here the beryl formed colourless prisms.

## Petrography

In thin section the beryl is distinctly pleochroic from pale blue ( $n_e$ ) to colourless ( $n_o$ ). Its vein-filling habit includes discrete prisms and larger (2–3 cm) anhedral grains. The latter commonly contain several sub-grains in near-parallel growth. They have been slightly deformed and are cut by quartz-filled micro-fractures. Some prisms have a euhedral, colourless core whose birefringence is slightly lower than that of the blue overgrowth.

The milky quartz lining the beryl veins is seen under crossed polars to consist of fine, radiating crystallites growing out from single-crystal cores. Beryl has clearly replaced both quartz crystals and country rock in places. The quartz is ragged and corroded, while the outlines of relic sand grains of the country rock may be visible as dusty inclusions in the beryl. Minor secondary chlorite is common, but this mineral is a major constituent in the brecciated vein with prisms of colourless beryl.

### Chemical and physical data

Energy-dispersive electron microprobe analyses were obtained from 7 neighbouring points on a single blue beryl prism in a narrow vein, and from 4 points on its colourless core. Analyses were also obtained from 4 separate colourless prisms in the chlorite-rich, brecciated rock mentioned above. Average analyses for these three beryls are given in Table 1. The instrument used is housed in the Department of Earth Sciences, University of Cambridge. Operating conditions were 20 kV accelerating voltage, 45 nA beam current and 80 s counting time. Iterative peak stripping (Statham, 1976) and ZAF correction methods (Sweatman and Long, 1969) were employed. Precision (relative deviation) is about 2% for elements above 5% concentration. Oxide totals varied by up to 3% during the period of analysis owing to instrumental drift, but apart from uncertainty in the oxide total itself the drift is not regarded as a problem since atomic proportions were apparently unaffected. Satisfactory operation of the system was confirmed by obtaining perfect stoichiometric analyses of an olivine and a diopside standard.

Additional compositional data for the blue beryl alone were obtained by Mössbauer, atomic emission and energy dispersive X-ray fluorescence analysis (EDXRF). A hand-picked and powdered separate of the blue beryl gave the Mössbauer spectrum at room temperature shown in Fig. 1. From this spectrum the ratio  $\text{Fe}^{2+}$  to total iron is estimated as 47%. An almost identical Mössbauer spectrum was obtained from the same sample at 77 °K (cf. Goldman *et al.*, 1978). Atomic emission spectroscopy confirmed that Li was not detectable (<10 ppm) and EDXRF showed that K and Rb were effectively absent (<200 ppm K, <20 ppm Rb) and Cs was present only in trace amounts (<100 ppm). Be, although a major element, was not determined owing to lack of in-house facilities. As Be is the only important element that could be missing from the analysis, its value was calculated assum-

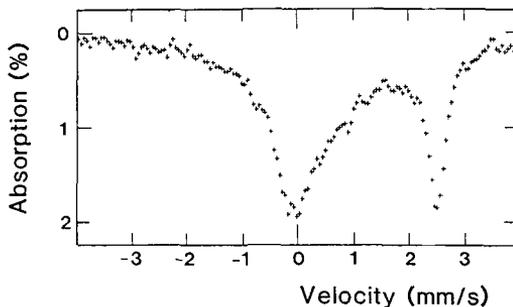


Fig. 1. Mössbauer spectrum of the blue beryl at room temperature.

ing full site occupancy, using a procedure described in the discussion below.

Weight loss on ignition after overnight drying at 110 °C of a crushed, sieved, magnetically separated and hand-picked sample of blue beryl was 2.74%, and the ignited sample was pale orange. Thermogravimetric analysis showed continuous, rather than episodic, weight loss. With a temperature rise of 20 °C per minute in a nitrogen atmosphere, the rate of loss increased slowly to 600 °C, more rapidly to 800 °C, then declined until final dehydration at 900 °C.

A least-squares refinement of cell dimensions based on 36 reflections on a powder diffraction trace using quartz as an internal standard gave  $a = 9.292(1)$  Å and  $c = 9.193(1)$  Å. Beryl peaks were also obtained from the pale orange ignited sample, but the  $a$  cell dimension was slightly larger, and  $c$  slightly smaller than for the un-ignited sample.

Refractive indices of the blue beryl were determined on sieved grains, and found to be uniform, with  $n_e$  (blue absorption colour) =  $1.595(\pm 1)$ ,  $n_o$  (colourless) =  $1.603(\pm 1)$ .

### Discussion

*Calculation of structural formula.* The calculation of a beryl structural formula from a microprobe analysis in the absence of a beryllium determination can be made in a number of ways. Simple approaches are to normalise atomic proportions to Si = 6, or alternatively, to  $(\text{Al} + \text{Fe} + \text{Mg}) = 2$ . However, examination of published beryl analyses suggests that these two methods will only be approximate. The procedure adopted here is believed to be more reliable. It assumes (1) that Na alone enters channel sites, and (2) that all other sites are fully occupied by atoms other than Na. It follows that the sum  $(\text{Si} + \text{Be} + \text{Al} + \text{Fe} + \text{Mg})$  must equal 11. Also, the sum  $(4\text{Si} + 2\text{Be} + 3\text{Al} + \text{Fe}^{3+} + 2\text{Fe}^{2+} + 2\text{Mg} + \text{Na})$  must equal 36,

Table 1. Average beryl microprobe analyses and calculated structural formulae

| wt%                            | blue beryl     | colourless    | colourless      |
|--------------------------------|----------------|---------------|-----------------|
|                                | prism<br>n = 7 | core<br>n = 4 | prisms<br>n = 4 |
| SiO <sub>2</sub>               | 64.49          | 64.97         | 64.69           |
| Al <sub>2</sub> O <sub>3</sub> | 11.38          | 14.65         | 14.66           |
| FeO                            | 3.89           | 0.71          | 1.88            |
| MgO                            | 2.97           | 2.44          | 1.70            |
| Na <sub>2</sub> O              | 2.44           | 2.00          | 1.51            |
| total                          | 85.17          | 84.77         | 84.44           |
| structural formulae            |                |               |                 |
| Si                             | 6.072 (7)      | 6.009         | 6.024           |
| Al                             | 1.263 (8)      | 1.597         | 1.609           |
| Fe <sup>3+</sup>               | .144 (6)       | .026          | .069            |
| Fe <sup>2+</sup>               | .162 (6)       | .029          | .078            |
| Mg                             | .416 (13)      | .335          | .237            |
| Be                             | 2.943 (10)     | 3.004         | 2.983           |
| Na                             | .446 (14)      | .360          | .273            |
| O                              | 18.000         | 18.000        | 18.000          |
| H <sub>2</sub> O               | .946           | nd            | nd              |
| Al+Fe+Mg                       | 1.985          | 1.987         | 1.993           |
| cations                        | 11.446         | 11.360        | 11.273          |

Standard deviations (in brackets) relate to last digit.  
nd = not determined

being the total positive charge to balance the 18 oxygens in the formula unit. Eliminating Be (which is not known) from these two simultaneous equations, it follows that the sum (2Si + Al + Fe<sup>3+</sup> + Na) must equal 14. The beryl analyses have therefore been normalized so that this sum is exactly 14 to obtain a charge-balanced structural formula and a calculated value for Be (Table 1). Fe<sup>3+</sup> has been assumed in all three cases to be 47% of the total iron, although it was only determined for the blue beryl. The method makes no preconditions regarding the number of Si atoms (ideally 6), the number of Be atoms (ideally 3), or the total number of Al, Fe and Mg atoms (ideally 2).

In the structural formulae the sum (Al + Mg + Fe) in all cases is very close to 1.99 and in the two colourless beryls Be is close to 3 and Si close to 6. These unconstrained values, being nearly integral, suggest that the analyses are good but not quite perfect. The blue beryl shows a slight, but significant, excess of Si and a corresponding deficiency in Be.

*Classification.* Aurisicchio *et al.* (1988) demonstrated the existence of two important kinds of substitution in beryl, giving rise to two distinct solid-solution series. These are 'tetrahedral' beryl in which the dominant substitution is of Li<sup>+</sup> for Be<sup>2+</sup> on the distorted tetrahedral site, and

'octahedral' beryl in which the dominant substitution is of Fe<sup>2+</sup> and Mg<sup>2+</sup> for Al<sup>3+</sup> on the octahedral site. In both cases charge balance is maintained by alkali ions entering channel sites. The two series may be distinguished by their *c/a* ratio which is 0.991–0.996 for 'octahedral', and 0.999–1.003 for 'tetrahedral' beryls.

The blue beryl described here, having no Li, substantial substitution of Fe and Mg for Al, and *c/a* equal to 0.989 is clearly an 'octahedral' type. Moreover, the amount of octahedral substitution it exhibits exceeds the range reported by Aurisicchio *et al.* (1988). To our knowledge only a single recorded beryl (Schaller *et al.*, 1962) has a greater degree of octahedral substitution (Table 2). The extreme composition and cell edge, *a*, of the blue beryl are apparent from Fig. 2, which shows the negative correlation of *a* and Al content in octahedral beryl. Consistent with its unusual composition and cell dimensions, its refractive indices are also amongst the highest recorded.

*Water content.* Assuming loss on ignition to be due to water, and allowing for oxidation of ferrous iron (0.162 atoms per formula unit), the H<sub>2</sub>O content of the beryl is 2.97 weight per cent. This amount of water corresponds to 0.946 H<sub>2</sub>O molecules per formula unit, and is the highest value recorded for beryl. Fontan and Fransolet's (1982) blue beryl is similar to ours (Table 2) with 0.914 H<sub>2</sub>O molecules in its structural formula. Perhaps significantly, this beryl also occurs in veins in a sediment (which incidentally is Devonian in age).

Assuming water can only occupy the [12] coordinated (0,0,1/4) channel site (Brown and Mills, 1986), the maximum water content of beryl is 1 molecule per formula unit. The number of water molecules in the blue beryl is close to this theoretical maximum and slightly exceeds twice the number of Na atoms (0.45). A similar ratio of H<sub>2</sub>O to Na has been noted in other beryls by Hawthorne and Černý (1977). It suggests that most, if not all the Na is bonded to two water molecules (Type II water), and that the Na is located on the (000) site at the centre of the 6-membered silicon–oxygen ring (Brown and Mills, 1986). Aurisicchio *et al.* (1988), in contrast, propose that water is located on the (000) site, and that all alkalis are confined to the larger (0,0,1/4) site. However, the marked discrimination by beryl in favour of Na and Cs, and against K and Rb, suggests to us that two sites are involved, one (000) with a preference for the small Na ion, and the other (0,0,1/4) with a preference for the very large Cs ion (and also water molecules).

Retention of much of the channel water to

Table 2. Chemical and physical data for selected octahedral beryls

| wt%                            | 1       | 2       | 3     | 4      | 5     | 6       |
|--------------------------------|---------|---------|-------|--------|-------|---------|
| SiO <sub>2</sub>               | 62.86   | 59.52   | 62.3  | 64.42  | nd    | 63.61   |
| TiO <sub>2</sub>               | 0       | 0.05    | -     | -      | -     | -       |
| Al <sub>2</sub> O <sub>3</sub> | 13.72   | 10.63   | 12.5  | 11.72  | nd    | 11.22   |
| Sc <sub>2</sub> O <sub>3</sub> | -       | 0.10    | -     | -      | -     | -       |
| Cr <sub>2</sub> O <sub>3</sub> | -       | 0.09    | .03   | -      | -     | -       |
| Fe <sub>2</sub> O <sub>3</sub> | 3.23    | 2.08    | -     | -      | -     | 2.00    |
| FeO                            | 0.22    | 2.24    | .91   | 4.62   | 3.4   | 2.03    |
| MnO                            | 0.07    | .29     | -     | -      | -     | -       |
| MgO                            | 1.96    | 2.16    | 3.21  | 2.31   | 1.5   | 2.92    |
| CaO                            | -       | .11     | .04   | -      | .1    | -       |
| Na <sub>2</sub> O              | 1.88    | 1.16    | 2.26  | 2.21   | 2.05  | 2.41    |
| K <sub>2</sub> O               | 0.07    | .16     | .01   | -      | .08   | -       |
| Li <sub>2</sub> O              | -       | .23     | -     | .07    | -     | -       |
| Cs <sub>2</sub> O              | -       | 6.68    | -     | .31    | -     | -       |
| BeO                            | 13.10   | 12.49   | nd    | 12.55  | nd    | 12.83   |
| H <sub>2</sub> O               | 2.90    | 1.62    | nd    | 1.7    | nd    | 2.97    |
| sum                            | 100.01  | 99.82   | 81.26 |        |       | 100.00* |
| structural formulae            |         |         |       |        |       |         |
| Si                             | 5.941   | 5.986   |       | 6.111  |       | 6.072   |
| Al                             | 1.528   | 1.260   | 1.43* | 1.310  |       | 1.263   |
| Fe <sup>3+</sup>               | .230    | .157    |       | .074   |       | .144    |
| Fe <sup>2+</sup>               | .017    | .188    | .07   | .292   |       | .162    |
| Mg                             | .276    | .324    | .46   | .327   |       | .416    |
| Be                             | 2.974   | 3.017   |       | 2.859  |       | 2.943   |
| Na                             | .344    | .226    | .42   | .406   |       | .446    |
| O                              | 18.000* | 18.000* |       | 18.000 |       | 18.000  |
| H <sub>2</sub> O               | .914    |         |       |        |       | .946    |
| a                              | 9.254   | 9.30    |       | 9.274  |       | 9.292   |
| c                              | 9.195   | 9.20    |       | 9.191  |       | 9.193   |
| n <sub>O</sub>                 | 1.601   | 1.608   |       | 1.603  | 1.604 | 1.603   |
| n <sub>e</sub>                 | 1.591   | 1.599   |       | 1.595  | 1.596 | 1.595   |

1. Blue in fissures, associated with ferroan dolomite, Ariege, France. (Fontan and Fransolet, 1982) \*includes Mn .006, K .008, P .013.

2. Blue in pegmatite. (Schaller et al. 1962) \*includes Ti .004, Cr .007, Sc .009, Ca .012, K .021, Li .093, Cs .286.

3. Bright green emerald in talc schist, Habachtal (Franz et al., 1982) \*normalized to Al + Fe + Mg = 2.00.

4. Dark blue, in feldspathic vein in Monte Leone Gneiss (quoted in Aurisicchio et al., 1988).

5. Blue, zoned, in quartz vein cutting granite (Watters, 1963)

6. This paper. \* The oxide weight percent analysis has been 'back calculated' from the structural formula in Table 1.

nd = not determined, - = not determined, presumed negligible.

temperatures of about 800°C is presumed to reflect the one-dimensional nature of the channels, and the presence of dumb-bell shaped [Na + 2H<sub>2</sub>O] 'plugs' in their necks. The strong increase in rate of weight loss approaching 800°C is attributed to the mechanism proposed by Aines and Rossman (1984). At this temperature the degree of dissociation of type II water from Na reaches the point where large numbers of neigh-

boring channel necks become unplugged simultaneously, letting the water escape.

*Atomic substitution.* Assuming that each Na ion on its (000) site is co-ordinated to two water molecules, one above and one below, it follows that Na will not exceed 0.5 a.f.u. Significantly, beryls in which Na exceeds 0.5 a.f.u. are so far unknown. In this case the theoretical limit to octahedral substitution of the type Al + □ =

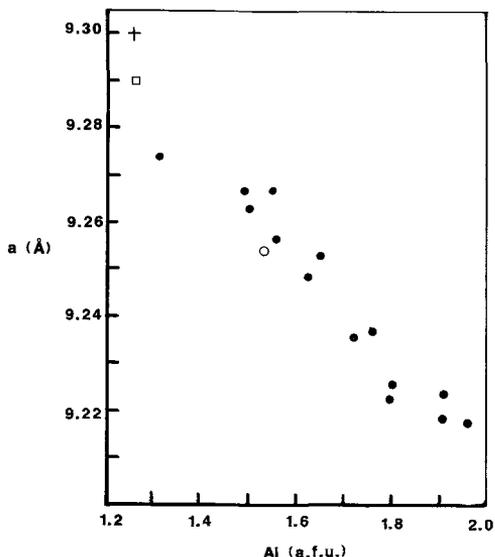


FIG. 2. Plot of cell edge,  $a$  against Al (a.f.u.) for the blue beryl (square symbol) compared with published data for 'octahedral' beryls. Dots from Aurisicchio *et al.* (1988), circle—Fontan and Fransolet (1982), cross—Schaller *et al.* (1962).

( $\text{Fe}^{2+}$ , Mg) + Na will be the end member  $\text{Be}_3\text{Al}_{1.5}(\text{Mg}, \text{Fe}^{2+})_{0.5}\text{Si}_6\text{O}_{18}[\text{Na}_{0.5}\text{H}_2\text{O}]$ . Where, as in the present case, Al falls below 1.5 a.f.u., additional types of substitution are required. One of these is simply  $\text{Al} \rightleftharpoons \text{Fe}^{3+}$ . Another relates to the significant excess of Si (Table 1) which, according to Aurisicchio *et al.* (1988) is not uncommon (e.g. Table 2, analysis 4), particularly in 'octahedral' beryl. The excess Si substitutes for Be on the distorted tetrahedral site, permitting the coupled substitution  $\text{Be} + 2\text{Al} = \text{Si} + 2(\text{Fe}, \text{Mg})$ .

The marked hiatus between colourless core and blue overgrowth suggests the possibility of a compositional gap in 'octahedral' beryls. However, no gap is seen among the 'octahedral' beryls reported by Aurisicchio *et al.* (1988). Since the compositional jump relates to Fe and Mg which readily substitute for each other, the hiatus probably reflects a sudden change in the environment of crystal growth. Watters (1963) also records blue beryl overgrowing a colourless core, though only limited compositional data for it are available (Table 2).

*Geological setting.* The incompatible geochemical behaviour of the element beryllium leads to the formation of beryl as a late-stage fractionation product of granite, and accounts for the familiar occurrence of beryl in pegmatites. Igneous fractionation does not account so easily

for the development of blue 'octahedral' beryl in veins and schists far removed from any granite outcrop. In these cases the scavenging and concentration of beryllium from the surrounding rocks by hydrous fluids has been suggested (e.g. Fontan and Fransolet, 1982; Franz *et al.*, 1986). It is also possible that the beryl developed from fluids emanating from unexposed granite at depth. Blue octahedral beryls are, after all, known from granitic pegmatites (e.g. Schaller *et al.*, 1962) and granites (e.g. Watters, 1963; Abrecht and Hänni, 1980), as well as from schists and veins in sediments.

With regard to the blue beryl described here, we note that Penney (1978, 1980) refers to volcanic activity contemporaneous with deposition of the Old Red Sandstone succession in the area. Lavas are reported from both the nearby Coumshingaun Formation and the Nier Formation which are believed to be, respectively, older and younger than the conglomerate which hosts the beryl (the Croughaun Formation). Penney also mentions a green crystal tuff within the Croughaun Formation itself, though he found no evidence for the slaty tufts, agglomerates and thin felsite intrusions reported from the same formation by Capewell (1957).

In view of this evidence for early magmatism, before regional deformation, we postulate that the beryl was precipitated from hydrothermal fluids released from granitic magma crystallizing at depth. We further postulate that the unusual composition of the beryl reflects considerable chemical exchange between the upwardly migrating Be-laden fluids and the country rock. Some support for this view comes from the Harding Pegmatite (Jahns and Ewing, 1977) where blue beryl is found in small cavities in the country rocks, away from the main beryl pegmatite bodies.

To conclude on a more light-hearted note, we observe that blue 'octahedral' beryls have much in common with emeralds, both in their octahedral substitution (e.g. analysis 3, Table 2) and their occurrence in schists and sediment-hosted veins (e.g. Keller, 1981). Had our beryl developed in ultramafic surroundings, and not in a quartz conglomerate, then perhaps the Emerald Isle would now be boasting its first true emeralds. Instead Ireland will have to content herself, not inappropriately considering the influence of the Atlantic Ocean on her weather, with having the wettest beryl on record.

#### Acknowledgements

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### Addendum

While this paper was in press, Dr P. F. Zanazzi kindly carried out X-ray single crystal structural refinements of the blue beryl. He studied two fragments taken from a single rock specimen. The results he obtained, and our joint observations on them, follow. For the experimental procedures and calculation details see Aurisicchio *et al.* (1988). Cell constants (Å) are, for fragment A,  $a = 9.2577(12)$ ,  $c = 9.1780(15)$  refined to  $R = 2.4\%$ , and for fragment B,  $a = 9.2624(12)$ ,  $c = 9.1714(15)$  refined to  $R = 3.3\%$ .

Since the results from the two fragments were found to be similar, only details for fragment A (which gave the best agreement factor) are given here. For fragment A, bond distances (Å), are Si–O<sub>1</sub> 1.601(2) and 1.604(2), Si–O<sub>2</sub> 1.611(2) × 2, mean Si–O 1.607, Be–O<sub>2</sub> 1.647(2) × 4, Al–O<sub>2</sub> 1.946(2) × 6. The number of independent reflections was 428.

Na was assigned to the 0.0, 1/4 (2a) site, and H<sub>2</sub>O to the 0, 0, 0 (2b) site. Fragment A yielded an electron density of 15.7 e<sup>−</sup> at 2a and of 11.5 e<sup>−</sup> at 2b. A better agreement factor ( $R = 2.2\%$ ) was obtained by reversing the assignment of Na and H<sub>2</sub>O. This yielded electron densities of 17.3 e<sup>−</sup> on 2a (H<sub>2</sub>O) and 9.7 e<sup>−</sup> on 2b (Na). These electron densities are remarkably consistent with the chemical analysis (Table 1). Assuming 0.90 Na and 1.90 H<sub>2</sub>O (per 36 oxygens) one can calculate electron densities of 9.9 e<sup>−</sup> for Na and 19 e<sup>−</sup> for H<sub>2</sub>O. This observation favours the hypothesis (Hawthorne and Černý, 1977) that Na is located at 2b and H<sub>2</sub>O at 2a. It contrasts with the location of Na at 2a in the red, water-free beryl from Utah reported by Aurisicchio *et al.* (1988), and suggests that the location of Na in beryl may be either 2a or 2b depending on whether water is abundant or deficient, respectively.

Concerning the octahedral site, excellent agreement was found between the observed electron density (56.6 e<sup>−</sup>) and that calculated on the basis of the chemical analysis (54.6 e<sup>−</sup>).

The cell constants measured by Dr Zanazzi are lower than those we obtained from X-ray powder data. The discrepancy is tentatively attributed to differences in the two X-ray methods, and possibly to compositional variation in the beryl from one part of the rock outcrop to another. To our knowledge, the *c*-cell dimensions for both fragments are lower than any value previously reported. We postulate that the reduced *c* cell edge, which reflects the correspondingly short Be–O bond distance, is caused by the substitution of Si for Be on the T' site. A broad inverse correlation between the Be–O distance and excess Si in the analysis is also apparent in the data of Aurisicchio *et al.* (1988).