Reports

Rhodizite: Structure and Composition

Abstract. *The mineral rhodizite could not be assigned a chemical formula on the basis of chemical analyses. The solution of the crystal structure reported here reveals that* $CsB_{12}Be_4Al_4O_{28}$ *is the ideal formula. The oxygen atoms occupy all but four sites per cell of cubic close packing whose period is* ½a. *The boron, beryllium, and aluminum atoms occupy interstices of this array, the first two in tetrahedral coordination, the last in octahedral coordination. Together these atoms form a continuous network whose composition is* $B_{12}Be_4Al_4O_{28}$, *which should be neutral. The alkali atom is enclosed in a cage in this network and presumably is not behaving as an ion.*

In some crystals the atomic sites permit such a wide range of replacements that it is difficult to establish a rational chemical formula from the chemical analyses. This is particularly true of certain minerals, among which sphalerite and tourmaline are notorious. Indeed the analyses of tourmaline are so variable that, until the arrangement of atoms in the crystal structure became known, the composition could only be generally described as a complex boroaluminum silicate of iron, magnesium, and the alkalis. But as soon as its crystal structure was solved, a typical ideal composition was obvious, and its chemical analyses then became interpretable.

The mineral rhodizite appears to offer a somewhat parallel case, for its composition has been problematical ever since it was first described from the Ural Mountains by Rose (*1*) in 1834. Over a hundred years after its discovery, Strunz (*2*), aided by a knowledge of its cell and symmetry, as well as a guess as to its structure, suggested that its formula might be represented as $NaKLi_4Al_4B_3Al_{10}O_{27}$. The 1951 edition of Dana's System (*3*) gives its composition as a complex borate of beryllium, aluminum, and the alkalis, and quotes Strunz's formula.

Well-crystallized specimens collected by Frondel in Manjaka, Madagascar, have been examined and analyzed by Frondel and Ito (*4*). They describe their material as strongly piezoelectric and pyroelectric, density 3.44 ± 0.01, isometric, space group $P\bar{4}3m$ with $a = 7.317$ Å. Aided by a knowledge of the space group, Frondel and Ito gave a different interpretation of the composition from that of Strunz, as indicated by the following comparison of the content of one cell:

Strunz:

$$NaKLi_4Al_4Be_3B_{10}O_{27}$$

Frondel and Ito:

$$(Cs_{.44}K_{.31}Rb_{.16}Na_{.03})Al_4Be_4B_{11}O_{25}(OH)_4$$

Frondel and Ito (alternative):

$$(Cs_{.44}K_{.31}Rb_{.16}Na_{.03})Al_4Be_4B_{12}O_{27}(OH)_3$$

The alternative formula was discounted by Frondel and Ito on the basis of density. The measured density was 3.44 g/cm², which compares well with 3.47, the density calculated for the preferred formula, but poorly with that calculated for the alternative formula, namely 3.59.

Some of the new Manjaka rhodizite was made available to us by C. Frondel for the purpose of a study of its crystal structure. We confirmed the isometric optics of the material, and found from precession photographs that its diffraction symbol is *m3mP---*. Taken together with its positive piezoelectric and pyroelectric response, as well as the presence of tetrahedral faces on the crystal, this fixes the space group as $P\bar{4}3m$. The cell edge, determined from precession photographs, was 7.32 Å, and this was refined with the aid of a precision back-reflection Weissenberg photograph to $a = 7.319 \pm 0.001$ Å. Our space group and cell thus confirm the data of Strunz as well as those of Frondel and Ito.

We based our crystal-structure analysis of rhodizite, reported here, on intensities diffracted by a sphere ground to a radius of 0.097 mm (*5*). The intensities were measured with a single-crystal diffractometer operated with equi-inclination geometry. In our preliminary work, intended to establish the structure, we used filtered $MoK\alpha$ radiation and a scintillation detector. The asymmetric Friedel unit in the $MoK\alpha$ sphere contains about 760 reciprocal-lattice points. Of these, we observed 504 reflections with measurable intensities. These were corrected for Lorentz, polarization, and absorption effects. Our initial step was to prepare a three-dimensional Patterson function with these data.

The composition of the Manjaka rhodizite deduced by Frondel and Ito implies that there is one atom of alkali, of average atomic number 36, and average atomic weight 90.5, per cell. Because of the large size of this alkali, it would appear not to be involved in substitution for the smaller nonalkali atoms, so that it is natural to assign the one alkali atom to an equipoint of multiplicity one, of which two are available in space group $P\bar{4}3m$, namely *1a* at 0 0 0 and *1b* at ½ ½ ½. The steps in solving the structure are unaffected by which choice is made; we chose *1a*. In this case we are dealing with a heavy-atom problem with the heavy atom at the origin. The peaks of the Patterson function might then be expected to be dominated by an image of the structure as seen from the origin.

Unfortunately this circumstance does not necessarily lead directly to the correct structure. We expected that our most reasonable route lay in the direction of first finding peaks in the Patterson function which corresponded to the oxygen atoms that immediately coordinated with the alkali at the origin, of then calculating a trial electron density whose phases were based upon the alkali and these surrounding oxygen atoms, of then seeking to interpret new peaks appearing in the electron-density function, and of continuing this iterative process until all atoms were found. This quickly led us to a structure which had the virtue of containing an odd number of oxygen atoms per cell, as required by Frondel and Ito's preferred formula. Unfortunately, the structure could not be refined below about R equal to 27 percent.

The key to the correct structure was found in the incorrect one, in which the odd oxygen at ½ ½ ½ in *1b* had been surrounded tetrahedrally by Be atoms in *4e* at approximately ⅝ ⅝ ⅝. All Fourier maps, however, showed an additional peak in the complimentary tetrahedral position at about ⅜ ⅜ ⅜. This required a set of eight atoms at the vertices of a cube, surrounding the center of the cell. The edge of this cube is approximately $\frac{1}{4}a \approx 1.8$ Å. Since this is an acceptable Al-O distance, the set of eight atoms could be interpreted as part of four octahedra of oxygen surrounding four Al atoms in equipoint 4*e* at ⅜ ⅜ ⅜. If this interpretation were correct, there should be 12 additional oxygen atoms in equipoint 12*i* at about ⅜ ⅜ ⅛. This central cluster would comprise four octahedra about the four Al atoms, each sharing three edges with its neighboring octahedra to form a tight cluster whose composition would be Al_4O_{16}. Since this provides the correct number of Al atoms for the Strunz as well as for the Frondel and Ito formulas, we began anew by assuming this cluster at the center of the cell, and with the alkali atom at the origin. We computed structure factors and three-dimensional electron-density functions which revealed other atoms, and iterated this cycle until all atoms other than hydrogen were accounted for. The ideal structure, and our preliminary refinement of it to *R* equal to 12½ percent, which was based upon 495 non-zero reflections, is described in Table 1. A projection of the lower half of the cell is shown in Fig. 1, with atoms labeled in the asymmetric unit bounded by two mirrors of $P\bar{4}3m$ and one cell edge. Bond distances will be published after further refinement.

In the rhodizite structure the oxygen atoms are arranged in cubic close packing whose period parallel to *a* is ½*a*. If all close-packed sites were occupied, 32 oxygen atoms would be required, but four sites are unoccupied, in a manner described below, so that the cell contains only 28 oxygen atoms, namely, 4 O(1) + 12 O(2) + 12 O(3).

The metal atoms occupy octahedral and tetrahedral voids between oxygen atoms. Each Al atom is surrounded by six oxygen atoms in octahedral coordination, namely, 3 O(1) + 3 O(2). Each of the four octahedra shares three edges with the other octahedra to form a tight central cluster of composition $Al_4O_{16}{}^{-20}$.

Each of the Be atoms is surrounded by four oxygen atoms in tetrahedral coordination, namely O(1) + 3 O(3). The four Be atoms thus augment the central cluster to form a larger cluster of composition $Be_4Al_4O_{28}{}^{-36}$. This cluster is bordered by 24 oxygen atoms, namely 12 O(2) + 12 O(3), and all atoms of this cluster are entirely within the cell boundaries.

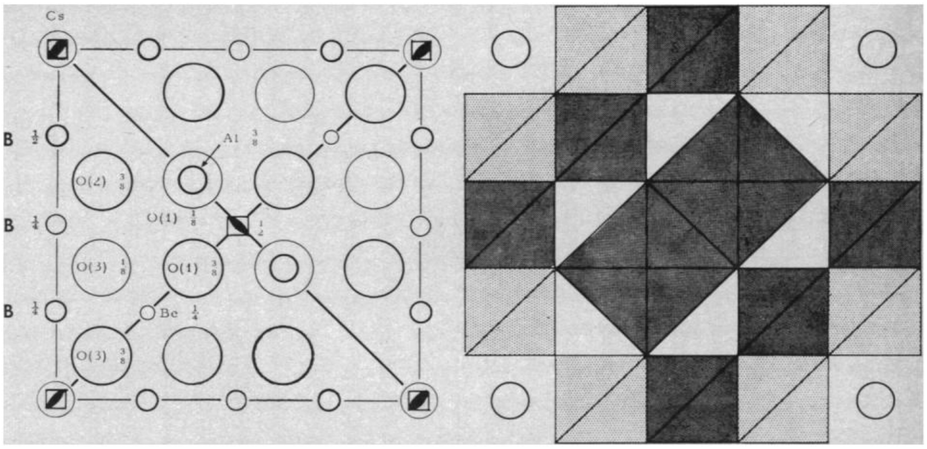

Fig. 1. Arrangement of atoms in the mineral rhodizite. (Left) Atom locations in the lower half of the ideal structure, showing some of the symmetry elements of space group $P\bar{4}3m$ which repeat the labeled atoms. (Right) The network in the upper half of the cell represented as coordination polyhedra. The tetrahedra in the heavily shaded diagonal bands have their centers on level $z \approx \frac{3}{4}$. In these the metal is alternately B and Be, with Be on the mirror in the middle of the band. The more lightly shaded tetrahedra have their centers at $z = \frac{1}{2}$ and contain B only. The central pair of heavily shaded octahedra contain Al at level $z \approx \frac{5}{8}$. The circles represent the alkali atoms at level $z = 1$.

Table 1. Coordinates of the rhodizite structure (space group $P\bar{4}3m$, $a = 7.319$Å).

Atom	Equipoint	Coordinates of representative point	Parameters	
			Ideal	$R = 12.7\%$ unweighted 7.1% weighted
Cs	1*a*	000		
B	12*h*	*x*½0	$x = \frac{1}{4}$	0.245 ± .002
Be	4*e*	*xxx*	$x = \frac{3}{4}$	.755 ± .003
Al	4*e*	*xxx*	$x = \frac{3}{8}$	.3575 ± .0005
O(1)	4*e*	*xxx*	$x = \frac{5}{8}$	.6195 ± .0009
O(2)	12*i*	*xxz*	$x = \frac{3}{8}$ $z = \frac{1}{8}$	.3635 ± .0006 .1017 ± .0006
O(3)	12*i*	*xxz*	$x = \frac{1}{8}$ $z = \frac{5}{8}$	.1339 ± .0008 .6019 ± .0008

Each B atom is surrounded by four oxygen atoms in tetrahedral coordination, namely, 2 O(3) + 2 O(2). The Be atoms lie in the cell faces, four to a face, and connect the enlarged clusters with one another. In this way the entire structure, except for the alkali atoms, comprises a connected network of composition $(B_{12}Be_4Al_4O_{28})^0$ per cell.

The oxygen atoms of the connected network are in cubic close packing which would be complete except for four missing oxygen atoms which would tetrahedrally surround the origin. The resulting hole at the origin is occupied by an alkali atom, whose immediate environment consists of 12 O(3) atoms, each at a distance of about 3.24 Å. These oxygen atoms do not uniformly surround the alkali, but occur as four tetrahedrally located clusters of three, each three outlining a face of a tetrahedron of oxygen atoms surrounding Be.

The structure reported here has the formula $CsB_{12}Al_4Be_4O_{28}$, which differs from the Frondel and Ito formula in that (i) it has 12 B instead of 11, (ii) it has 28 O instead of 29, and (iii) it does not appear to need any hydrogen atoms, as suggested by the following argument. All oxygen atoms of rhodizite are exactly satisfied by electrostatic valency bonds, provided that the alkali atom is ignored and no oxygen atoms are regarded as hydroxyls. The electrostatic valency summations are as follows:

$$\begin{aligned} O(1)&: \quad 3\cdot\tfrac{1}{2}(Al) + \tfrac{1}{2}(Be) = 2 \\ O(2)&: \quad \tfrac{1}{2}(Al) + 2\cdot\tfrac{3}{4}(B) = 2 \\ O(3)&: \quad \tfrac{1}{2}(Be) + 2\cdot\tfrac{3}{4}(B) = 2 \end{aligned}$$

Because of this, it seems reasonable to suppose that the hydrogens reported in Frondel and Ito's analysis are, in fact, absent from the structure, and that in the recorded analysis the loss on ignition was due rather to a loss of some of the other constituents, especially B and alkali. The density computed for the ideal formula, $CsB_{12}Be_4Al_4O_{28}$ (except that the alkali mixture found by Frondel and Ito was used instead of pure Cs), in an isometric cell of edge $a = 7.319$ Å, is 3.478 g/cm^3. This is essentially the same as that of Frondel and Ito's preferred formula which requires 3.47, as compared with a measured density of 3.44. The small excess in calculated density could readily be attributed to a small error in the proportions of the several alkalies making up the alkali site.

The ideal formula $CsB_{12}Be_4Al_4O_{28}$ appears to be unbalanced in the amount of one excess positive charge. In other words, the alkali appears to behave formally as a neutral atom. It also appears to be held, clathrate fashion, within the large hole at the origin. For the Manjaka rhodizite, the composition of the alkali in the hole is $Cs_{.47}Rb_{.17}K_{.33}Na_{.03}$. It is evident that these various atoms, whose radii vary from about 1.7 Å down to 1 Å for ionic radii, or about 2.4 Å to 1.6 Å for metallic radii, cannot all fit the same-sized void. The occurrence of neutral Na in the clathrate structure Na_8Si_{46} and Na_xSi_{136} has just been discovered and discussed by Kasper *et al.* (*6*). Rhodizite appears to offer another example of a neutral alkali in a cage.

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References and Notes

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5. We thank Dr. C. T. Prewitt for preparing several spheres in his diamond-impregnated grinder.
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7. We thank W. Dollase for discussions of many of the problems arising in the course of this investigation, as well as help with the computations, which were carried out at the MIT Computation Center. Supported by an NSF grant.

24 January 1966

Shaping of the Continental Rise by Deep Geostrophic Contour Currents

Abstract. *Geostrophic contour-following bottom currents involved in the deep thermohaline circulation of the world ocean appear to be the principal agents which control the shape of the continental rise and other sediment bodies.*

The continental rise is a broad, uniform, gently sloping and smooth-surfaced wedge of sediments, 100 to 1000 km wide and 1 to 10 km thick which, wherever trenches are absent, lies at the base of the continental slope. It is normally covered with, and probably is largely composed of, monotonously homogeneous fine gray lutites. These "hemipelagic" or "terrigenous" sediments were deposited at comparatively high rates. Postglacial rates ranged from 5 to 50 cm per 1000 years, and even higher rates predominated during the Pleistocene (*1*). In most instances seismic refraction investigations reveal that the wedges of sediment are thickest beneath the upper continental rise and gradually thin seaward (*2*). It has been suggested that these modern geosynclines lie in ancient deep-sea trenches and that they were filled in large measure by turbidity currents. However, recognizable turbidites constitute a small proportion of the glacial and postglacial sediments of the continental rise (*1*). Since hemipelagic lutites are derived almost entirely from denudation of land, a seaward diffusion of lutite is generally assumed, but the transporting mechanisms and directions of transport are difficult to infer because of the lack of sediment variability.

The continental rise off eastern United States merges south of Cape Hatteras with the broad, southeasterly plunging Blake-Bahama Outer Ridge. Seismic investigations (*3*) indicate that this southerly extension of the continental rise is an undeformed sediment wedge similar in seismic velocity and geological structure to the normal continental rise sediment wedge found further north.

The outer ridge is separated from the continent by the Blake-Bahama Basin and by the broad Blake Plateau (Fig. 1). Terrigenous sediments derived from southeastern United States are barred from the eastern Blake Plateau, the Blake Escarpment, and the western Blake-Bahama Basin by the vigorous northerly transport of the Gulf Stream which flows at velocities of 100 to 300 cm/sec along the western margin of the Blake Plateau. Thus the existence of the accumulation of a continental-rise-type sediment 1000 km seaward of Florida suggests a north-to-south abyssal transport of terrigenous sediments.

Agassiz concluded that the Blake Plateau is "swept clean of slime and ooze." He did not specify the destination of the detritus, but Stetson concluded that much of the finest material is transported with the Gulf Stream far into the northern North Atlantic (*4*).

The growing Gulf Stream draws over 12 million m^3/sec of the Antilles Current (*5*) across the Blake Plateau. Transportation by this westerly flow may account for the relatively thin veneer of Recent sediments and the frequent exposure of Tertiary and Mesozoic marls on the Blake Plateau and Blake Escarpment. Numerous unconformities were encountered in the reduced Tertiary carbonate section penetrated by JOIDES (Joint Oceanographic Institutions' Deep Earth Sampling Program) (*6*) drill holes, which suggests that a vigorous but fluctuating westerly transport had persisted throughout the Tertiary. Some of this detritus, including all of the bedload, must be deposited somewhere near Cape Hatteras where the Gulf Stream flows into the deep Atlantic, but there is no obvious topographic feature directly east of Cape Hatteras which might represent a pile of detritus. Although the Gulf Stream apparently has locally eroded the Blake Plateau, its main effect has been to prevent terrigenous deposition seaward of the stream and to inhibit deposition of the normally thin pelagic carbonate oozes.

Slope water off northeastern North America is bluish or grayish green, while the Gulf Stream and Sargasso Sea are a clear deep ultramarine. Slope water, which north of Hatteras lies at the surface between the Gulf Stream and the continental slope and laps up on the continental shelf, not only supports a much richer biota than the Sargasso Sea, but also contains at least an order of magnitude more suspended matter and is, therefore, a potentially