

# ZANAZZIITE

## A NEW MINERAL FROM MINAS GERAIS, BRAZIL

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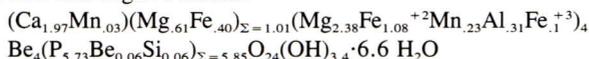
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### ABSTRACT

Zanazziite is a new magnesium beryllium phosphate closely related to roscherite. It occurs as barrel-shaped crystals and crystal rosettes up to 4 mm, with colorless quartz, rose quartz crystals, and eosphorite in pockets in the Lavra da Ilha pegmatite, near Taquaral, in northeastern Minas Gerais, Brazil. Specimens, labeled "roscherite," are widely distributed. The mineral is named for Dr. Pier F. Zanazzi of the Università degli Studi di Perugia, in recognition of his studies of the crystal structures and crystal chemistry of minerals.

Analysis gave  $P_2O_5$  39.27,  $SiO_2$  0.36,  $Al_2O_3$  1.54,  $Fe_2O_3$  0.76, CaO 10.65, MgO 11.66, FeO 9.63, MnO 1.77, BeO 9.81,  $H_2O$  13.32, total 98.77 with BeO by atomic-absorption spectrophotometry;  $H_2O$  by H analyzer; FeO by titration; and other elements, including total Fe, by microprobe. Crystals show considerable zoning with respect to FeO and MgO. Formula:



or, ideally:  $Ca_2Me^{+2}Me_4^{+2}Be_4(PO_4)_6(OH)_4 \cdot 6H_2O$ , where  $Me^{+2}$  indicates Mg, Fe, and Mn, with  $Mg > Fe$ . Monoclinic space group C2/c.  $a = 15.874(4)\text{\AA}$ ,  $b = 11.854(3)\text{\AA}$ ,  $c = 6.605(1)\text{\AA}$ ,  $\beta = 95^\circ 21'(2)'$ ,  $V = 1237\text{\AA}^3$ ,  $Z = 2$ . Strongest X-ray diffraction lines, in  $\text{\AA}$ , with intensities and indices: 9.50 (90) (110), 5.91 (100) (020), 3.16 (70) (330), 3.05 (50) (510), 2.766 (50) (240), 2.682 (40b) (600), 2.208 (40), 1.642 (50b). Crystals are prismatic to bladed, generally rough to barrel-shaped, with the forms {100}, {110} and {001}.

Zanazziite is pale to dark olive-green, with a vitreous to slightly pearly luster. Cleavages are on {100} good, and {010} distinct. The mineral is nonfluorescent. Density = 2.76 measured, 2.77 calculated; Mohs hardness is about 5. Optically biaxial +,  $\alpha = 1.606$ ,  $\beta = 1.610$ ,  $\gamma = 1.620$ ,  $2V_z = 72^\circ$  ( $65^\circ$  calc)  $X = b$ ,  $Z:[100] = 3^\circ$  in obtuse  $\beta$ ; cleavage fragments give an almost perfectly centered BXA figure.  $1 - K_p/K_c = 0.0067$ .

### INTRODUCTION

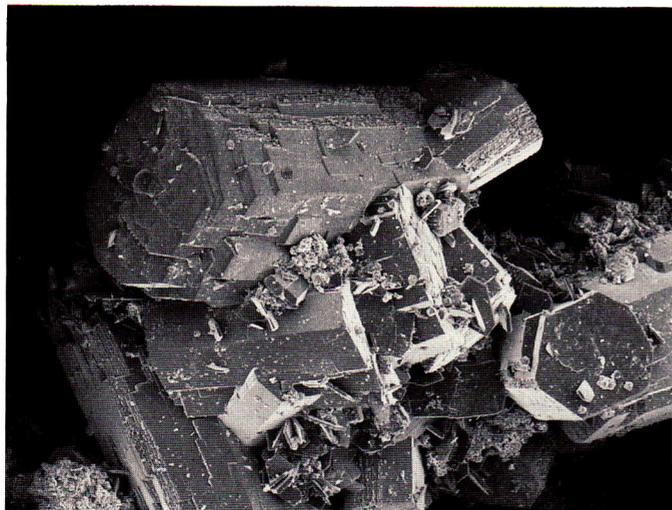
A mineral identified as roscherite on the basis of X-ray diffraction data was reported from the Lavra da Ilha pegmatite in Minas Gerais, Brazil, by Cassedanne and Cassedanne (1973). A crystal of this mineral was used by Fanfani *et al.* (1975) for a crystal structure determination. Although roscherite is a Mn/Fe mineral (Lindberg, 1958), Fanfani *et al.* (1975) concluded that the Lavra da Ilha mineral contains mostly Mg with less Fe and just a little Mn, as well as substantial Al. They obtained the most satisfactory structural refinement with a Mg:Fe ratio of 7:3. Our investigations, described in this paper, show that the Lavra da Ilha mineral is an essentially Al-free Mg mineral related to roscherite, and is thus a new species. It is named zanazziite, after Dr. Pier F. Zanazzi of the Università degli Studi di Perugia, in recognition of his substantial studies of the structural crystallography and crystal chemistry of many minerals, including this one. The name and description have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. The holotype specimen, #R17847, is preserved at the Smithsonian Institution. This specimen also provided the crystal on which Fanfani *et al.* (1975) made their structure determination. Numerous specimens of zanazziite have been collected and are widely distributed in public and private mineral collections throughout the world.

### OCCURRENCE

The Lavra da Ilha pegmatite and its minerals have been described by Cassedanne and Cassedanne (1973). The pegmatite outcrops in the bed of the Jequitinhonha River, in Itinga municipio, near Taquaral, in northeastern Minas Gerais, Brazil. The pegmatite appears structurally simple, with a wall zone rich in feldspar and muscovite, and a quartz core. Near the core margin are small pockets and fissures which contain quartz crystals and a number of phosphate minerals.

The quartz crystals are large and colorless but cloudy, with faces commonly covered with a thin, milk-white to rose-colored film of drusy quartz. It is usually upon this film and on rose quartz crystals that zanzaziite has grown in pale to dark olive-green, translucent crystals which tend to resemble pyromorphite in habit, although showing inclined terminal faces as a consequence of being monoclinic. Individual crystals of zanzaziite are barrel-shaped, up to 4 mm long and 1 to 2 mm in diameter. Multiple crystals vary from simple groups of subparallel individuals to divergent sprays resulting in hemispherical forms. The faces making up the sides of the "barrels" are glassy and curved; the ends are dark green, frosted in appearance, and consist of a complex mosaic of terminal faces. Zanzaziite also occurs in bladed crystals of similar morphology, but these are less common.

In addition to the large, cloudy quartz crystals, other minerals earlier than zanzaziite in the pockets are albite, muscovite, rose quartz in crystals, and wardite. Eosphorite is roughly contemporaneous with zanzaziite; even after careful study, the temporal relationship remains obscure. Eosphorite occurs in crystals, usually similar to those of zanzaziite in size, but sometimes much larger. They are elongate, transparent and golden brown in color, and occur in individual crystals, sprays, and druses. Other late minerals include apatite crystals in small radial clusters, pyrite, which forms minute druses on zanzaziite and tiny isolated crystals and crystal groups on eosphorite, albite, and Mn oxides in thin films and smudges.



**Figure 1.** SEM photograph of zanzaziite crystals, showing the common pseudo-hexagonal morphology. The largest crystal is about 0.4 mm in length. NMNH #R17847.

## CHEMISTRY

Zanzaziite, NMNH specimen #R17847, was analyzed with an ARL-SEMQ microprobe, operating at 15Kv and 0.15  $\mu$ A, with an electron beam approximately 1 micron in diameter. Corrections were made using a modified version of the Magic IV program. The standards were Durango apatite for P, Rockport fayalite for Mn, and Kakanui hornblende for all others. Background corrections were included. Beryllium was determined on a separate sample of 84.93 mg by atomic-absorption spectrophotometry. Water was determined using an H analyzer on duplicate samples of about 25 mg. A microprobe analysis was made on a different (cotype) specimen, NMNH #154805, supplemented with an FeO determination by titration. Spectroscopic analysis and a general microprobe scan showed that no elements other than the ones reported were present in other than trace amounts.

The analytical results are presented in Table 1. The analysis of the type specimen represents the average of a total of 25 spot analyses made on four grains. Fe is divided between ferrous and ferric states

**Table 1.** Chemical analyses of zanzaziite and roscherite.

Oxide	Zanzaziite NMNH #R17847	Zanzaziite NMNH #123018	Zanzaziite NMNH #154805	Roscherite NMNH #C6719
P <sub>2</sub> O <sub>5</sub>	39.27	38.36	38.30	39.09
SiO <sub>2</sub>	0.36	—	0.22	0.01
Al <sub>2</sub> O <sub>3</sub>	1.54	1.03	1.45	0.47
Fe <sub>2</sub> O <sub>3</sub>	0.76	—	0.8**	—
CaO	10.65	10.11	10.05	10.63
MgO	11.66	9.85	8.80	6.99
FeO	9.63	8.91*	9.40**	20.52*
MnO	1.77	2.26	3.66	1.32
BeO	9.81	—	—	—
H <sub>2</sub> O	13.32	—	—	—
Total	98.77			

— Indicates not determined.

\* Total Fe.

\*\* By titration.

based on Fe<sup>2+</sup>:Fe<sup>3+</sup> ratio of 14:1 determined by titrimetric analysis. The second analysis in Table 1 is of another (cotype) specimen of zanzaziite in the Smithsonian collection (NMNH #123018). Although there are differences between the analyses of this specimen and of the holotype (NMNH #R17847), these differences are not greater than the variations within the holotype sample itself.

## ZONING

Four traverses with the microprobe were made over a single zanzaziite crystal mounted in section parallel to the long direction (*c* axis). These were run across the crystal in two directions at four different locations as shown in Figure 3. The *c* axis is parallel to scans 1 and 2. As is the case with associated eosphorite (White, this issue, p. 418–422), zanzaziite is dramatically and complexly zoned, and a number of interesting observations can be made from the results of the analyses:

(1) The first part of the crystal that grew, near the start of scans 1, 2, and 3, contains the least iron. The analyzed crystal contained approximately 4% iron oxide upon initial crystallization. (All Fe is calculated as FeO.)

(2) The FeO content quickly climbed to about 10%, from which level it varied somewhat, reaching a maximum of about 13.5% and dropping to nearly 4%. MgO varies between 8 and 12%. Magnesium and iron show a strongly but not perfectly inverse relationship. This pattern is supportive of the model that the two elements substitute extensively for each other but do have some preference for different sites in the structure.

(3) There is very little variation in the other metals in zanzaziite. Al<sub>2</sub>O<sub>3</sub> is slightly enriched at the outset of growth, where the iron is at its least, beginning at about 3.3% and falling to a rather consistent 1.5 to 2% from there on. CaO and MnO are remarkably consistent at about 10% and 1.75%, respectively. Al, Ca and Mn analyses were included in all of the traverses but the results were so similar that they are shown in Fig. 2 for 1-1' only.

## FORMULA

Deriving the formula of zanzaziite was a complex task. For their structural analysis, Fanfani *et al.* (1975) had only partial chemical data, which suggested that the mineral has significant Al. They thus interpreted their electron density information to derive the formula:

Ca<sub>2</sub>(Al<sub>1.33</sub>□<sub>0.67</sub>)(Mg,Fe)<sub>4</sub>Be<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>6</sub>·4H<sub>2</sub>O  
with Mg:Fe = 7.3 and Al randomly occupying <sup>2</sup>/<sub>3</sub> of a site of rank 2, called M(2) in this paper. The □ indicates that <sup>1</sup>/<sub>3</sub> of the M(2) site is vacant. In a later paper on a triclinic roscherite, Fanfani *et al.* (1977)

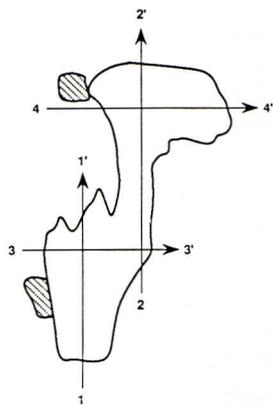
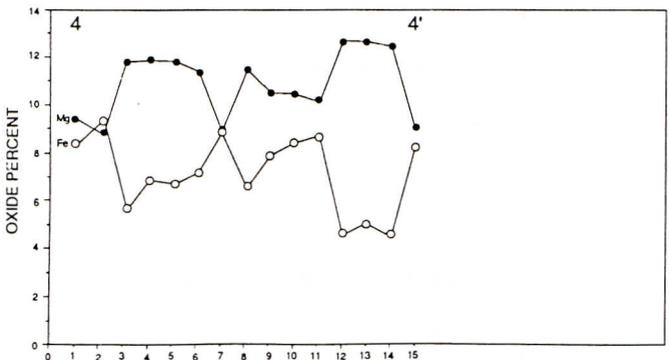
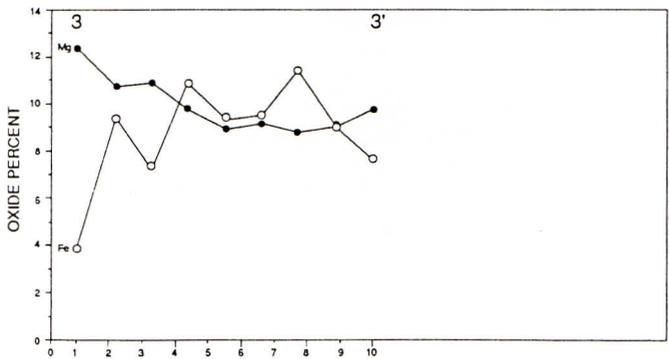
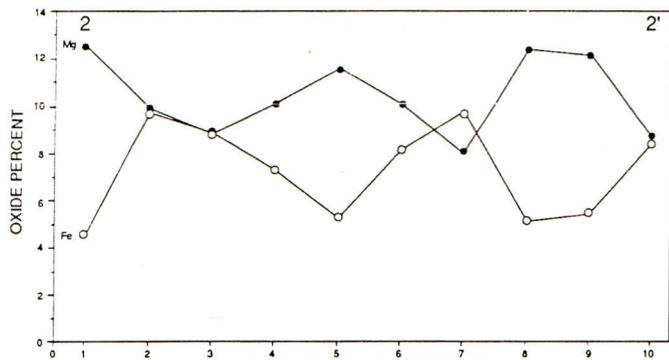
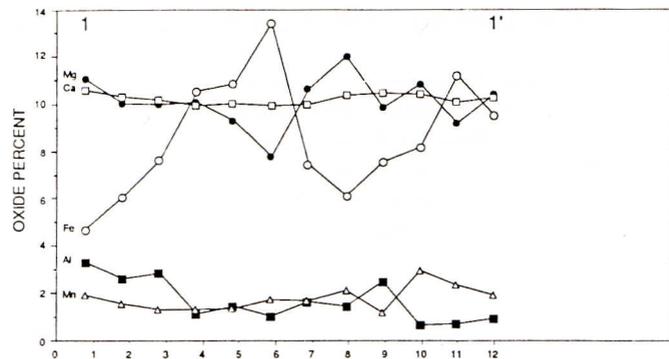


Figure 2. Graph showing results of microprobe scans for Ca, Mg, Fe, Mn and Al across a zanzaziite crystal, NMNH #R17847.



Figure 3. Zanzaziite crystal, 4 mm, on rose quartz, from Brazil. USNM #154810. Dan Behnke photo.



Figure 4. Zanzaziite crystal aggregate, 2.8 mm across, from Brazil. USNM #155707. Dan Behnke photo.

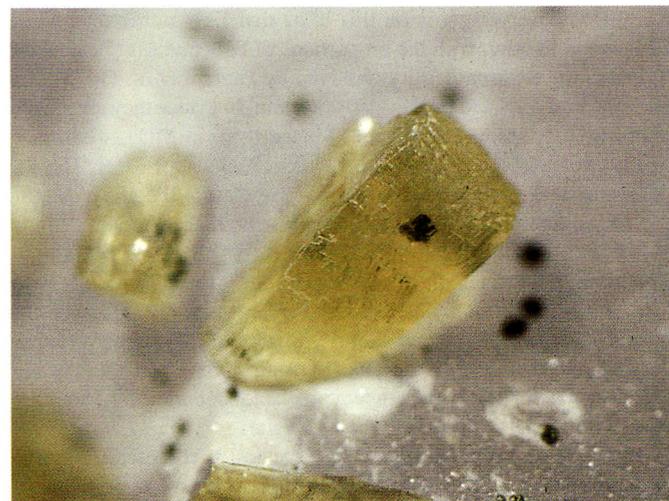
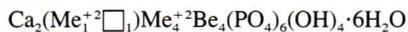
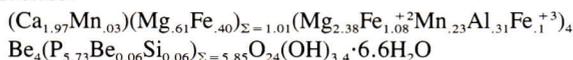


Figure 5. Zanzaziite crystal, 1.4 mm, from Brazil. NMNH #155707. Photo by Dan Behnke.

concluded that roscherite might also contain only divalent cations (indicated by  $\text{Me}^{+2}$ ) in M(2) and proposed a possible roscherite-type formula:



In fact, zanazziite contains little  $\text{Al}^{+3}$  and the Fe is almost entirely divalent  $\text{Fe}^{+2}$ , as shown by the chemical analysis. In a structure analysis, the actual atoms cannot be resolved. The X-rays are scattered by the electrons of the atoms, and the structure analysis derived from the X-ray scattering or diffraction data provides an estimate of the number of electrons associated with each atomic site. The formula proposed by Fanfani *et al.* (1975) is equivalent to 17.3 electrons in M(2) and 64.8 electrons in the general Mg-Fe site or M(1). If we assume that M(1) is fully occupied by four atoms, we can derive the formula for NMNH #R17847, based on 34 oxygen atoms on the structure:



This provides a number of electrons in M(1) and M(2) close to that determined by Fanfani *et al.* (1975) and the number of H ions to match the chemical analysis for H as well as providing charge balance. The sum of the analysis is a bit low, and there are some minor problems with the derived formula, notably with the tetrahedral site occupied by P. There are some vacancies indicated in the site, since the atoms should add to six, and the substitution of Be and Si for P is very unusual. The vacancies could be eliminated by putting some Al in the site, but although Al substitutes commonly for Si in silicates, it is not known to substitute for P in phosphates.

There is also some uncertainty about the distribution of the various cations between the M(1) and M(2) sites. The M(2) site is highly distorted, with two Me-O distances about 2.27 Å, two about 2.53 Å, and the two Me-OH bonds 1.73 Å. This would suggest that only very small or highly distorted atoms could fit in the site. However in triclinic roscherite, the M(2) site is split in two, with one half being largely occupied and the other vacant. The splitting of the M(2) site causes the change to triclinic symmetry. In the triclinic roscherite, the occupied site has distances of 2.20, 2.48, and 2.00 Å, much less distorted, and suitable for  $\text{Fe}^{+2}$ , which is compatible with somewhat distorted octahedral sites of about this size. The distances observed in monoclinic roscherite may be an average for the occupied and unoccupied sites. Such an average would give a "fuzzy" picture of that part of the structure, which would appear as a high temperature factor for the OH involved in the site. This is in fact what Fanfani *et al.* (1975) observed. It is on this basis that  $\text{Fe}^{+2}$  rather than Mn is assigned to the site, with the proportions of  $\text{Fe}^{+2}$  and  $\text{Mg}^{+2}$  calculated to match the electron density observed by Fanfani *et al.* (1975). The placement of  $\text{Al}^{+3}$  and  $\text{Fe}^{+3}$  is also uncertain, but since they are smaller than  $\text{Mg}^{+2}$ , it seems reasonable to place them in M(1), the smaller of the two sites.

Despite these minor problems, the formula fits the chemical data and the structure well. The ideal formula for zanazziite is:



where  $\text{Me}^{+2}$  indicates divalent Mg, Fe, and Mn; with  $\text{Mg} > \text{Fe}$  or Mn. This is the formula suggested by Fanfani *et al.* (1977) as possible for a roscherite-type mineral. Some variation in the number of atoms in M(2) and therefore in the OH:H<sub>2</sub>O ratio is likely. This may also help account for the high temperature factor reported by Fanfani *et al.* (1975) for OH adjacent to the M(2) site.

Ironically, the relationship of this species to roscherite is a little uncertain because no authentic roscherite specimen has been studied in such chemical and structural detail as zanazziite. Zanazziite may be the magnesium analog of roscherite, which is rich in manganese or iron, or it may differ in the occupancy of M(2), the amount of  $\text{Fe}^{+3}$ , or the amount of OH and H<sub>2</sub>O. The X-ray powder diffraction patterns of zanazziite and roscherite are very similar. The roscherite group minerals require further study.

## ROSCHERITE AT THE TYPE LOCALITY

Not all of the specimens from Lavra da Ilha that give roscherite-type X-ray diffraction patterns are zanazziite. A remarkable spray of pale green crystals which approach 2 cm in length is in the Smithsonian collection. It was hoped that the specimen would be zanazziite because the great size of the mass of crystals would make it very easy to separate absolutely clean samples for analysis and measurement of physical properties. Unfortunately, in spite of its pale color, this sample (NMNH #C6719) is an Fe-dominant triclinic roscherite (see Fanfani *et al.*, 1977). The microprobe analysis is given in Table 1. The crystals are complexly and irregularly zoned. Some sectors contain as much as 8% MgO and approach the zanazziite composition field. The minerals associated with this roscherite are earlier-crystallized albite and muscovite, along with later eosphorite and another generation of albite in very small and sharply developed crystals scattered sparsely over the roscherite.

Table 2. X-ray powder diffraction data for zanazziite; Gandolfi camera,  $\text{CuK}_\alpha$  radiation.

d	I	hkl
9.50	90	110
5.91	100	020
4.82	20	310
4.43	10	021
3.35	20	13 $\bar{1}$
3.16	70	330
3.05	50	510
2.945	20b	040
2.852	10	33 $\bar{1}$
2.766	50	240
2.682	40b	600
2.208	40	15 $\bar{1}$ , 710
2.159	20	350, $\bar{7}11$
2.031	20	351, $\bar{2}23$
1.974	20	800, 060
1.917	20	
1.769	20	
1.746	10	
1.692	10	
1.642	50b	
1.517	10	
1.490	10	
1.461	10	
1.430	10	

## CRYSTALLOGRAPHY

Fanfani *et al.* (1975) determined the space group and unit cell of zanazziite as well as its crystal structure. Their results are summarized here. Zanazziite is monoclinic, space group C2/c.  $a = 15.874(4)\text{Å}$ ,  $b = 11.854(3)\text{Å}$ ,  $c = 6.605(1)\text{Å}$ ,  $\beta = 95^\circ 21'(2)'$ ,  $V = 1237\text{Å}^3$ ,  $Z = 2$ .

X-ray powder diffraction data for zanazziite are given in Table 2; they are very close to the data given for roscherite by Lindberg (1958) and published on Powder Diffraction File Card 11-355. Least-squares refinement of these data gives the lattice parameters  $a = 15.850(13)\text{Å}$ ,  $b = 11.850(6)\text{Å}$ ,  $c = 6.652(7)\text{Å}$ ,  $\beta = 95^\circ 55'(4)'$ , in fairly good agreement with the parameters determined by Fanfani *et al.* (1975).

Single crystals of zanazziite are too uneven to permit satisfactory measurement of the interfacial angles and morphological relationships; however, morphologies appear similar to those reported by Lindberg (1958) for roscherite. Crystals of zanazziite are most commonly barrel-shaped and have major {100} and {110}. Faces of {001} are irregular and rounded. Less common bladed crystals have major {100}, minor {110}, and irregular, rounded {001}.

## PHYSICAL PROPERTIES

Zanazziite is pale to dark olive-green, with a white streak. Its luster is vitreous but may be slightly pearly on cleavage surfaces. Its cleavage is {100} good, {010} distinct, in the orientation of Lindberg (1958) for roscherite. Zanazziite is nonfluorescent in longwave or shortwave ultraviolet light. Its measured density is 2.76 g/cm<sup>3</sup>, calculated 2.77 g/cm<sup>3</sup>. The Mohs hardness is about 5, judging from its resistance to scratching and breakage by a steel needle.

Optically, zanazziite is biaxial positive,  $\alpha = 1.606$ ,  $\beta = 1.610$ ,  $\gamma = 1.620$ , all  $\pm 0.002$ , as measured with the Becke line method in Na light using a spindle stage.  $2V_z = 72^\circ$  (65° calc.),  $X = b$ ,  $Z:[100] = 3^\circ$  in obtuse  $\beta$ . Cleavage fragments give an almost perfectly centered BXA figure. Calculation of the specific refractive energies, with the analysis recalculated to 100%, using the Gladstone-Dale constants of Mandarino (1976), indicates good internal agreement of the data;  $1 - K_p/K_c = 0.0067$ .

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uate at the University of Delaware. Dr. J. A. Mandarino of the Royal Ontario Museum, Dr. Donald Peacor of the University of Michigan, and Dr. Richard Erd, U.S.G.S. at Menlo Park made many helpful suggestions.

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