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Minasgeraisite, a new member of the gadolinite group from Minas Gerais, Brazil

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ABSTRACT

Minasgeraisite, ideally $Y_2CaBe_2Si_2O_{10}$, is a new member of the gadolinite group, occurring in the form of 0.2- to 1.0-mm-diameter rosettes coating and intergrown with milarite, albite, quartz, and muscovite in a late-stage complex granitic pegmatite. The empirical formula, on the basis of 10 oxygen atoms, is $(Y_{0.72}REE_{0.41}Ca_{0.56}Bi_{0.31})_{2.00}(Ca_{0.45}Mn_{0.20}Mg_{0.08}Fe_{0.05}Zn_{0.02}Cu_{0.01}\square_{0.19})_{1.00}(Be_{1.55}B_{0.21}Si_{0.24})_{2.00}(Si_{1.95}P_{0.08})_{2.03}O_{10}$. Only several hundred milligrams are known to exist. The mineral is lavender to lilac purple and has a sheaflike habit, with a grain size of less than 3–5 μm. It is not magnetic and not fluorescent under either SW or LW ultraviolet radiations; Mohs hardness is estimated at 6 to 7 D_{meas} is greater than 4.25, D_{calc} = 4.90 g/cm³, luster is earthy to subvitreous, and the streak is pale purple. Minasgeraisite is slowly soluble in common acids. The mineral has one excellent cleavage, {100} by analogy with gadolinite, and another good cleavage, {001}. Minasgeraisite is biaxial (+), with $\alpha = 1.740(4)$, $\beta = 1.754(4)$, $\gamma = 1.786(4)$, $\gamma - \alpha = 0.046$, $2V_z = 68°$ (average), X = colorless, Y = pale grayish yellow, Z = lavender purple, with $Z > Y > X$. Dispersion is $r > v$, very weak. Least-squares refinement of 114-mm-diameter Gandolfi film data gives $a = 9.833(2)$ Å, $b = 7.562(1)$ Å, $c = 4.702(1)$ Å, $\beta = 90.46(6)°$, $V = 349.60(14)$ Å³. Z = 2. Space group is $P2_1/a$.

INTRODUCTION

In 1980, fine milarite crystals were found at the Jaguaracu pegmatite in the state of Minas Gerais, Brazil. R. V. Gaines collected about eight small matrix specimens of drusy material which contained small amounts of a lilac-colored mineral which could not be readily identified. E. E. Foord further studied the mineral and associated species. Initial investigation consisted of an emission spectrographic analysis and powder X-ray diffraction analysis. A diffraction pattern similar to that of gadolinite was obtained, but the chemistry was significantly different from that of gadolinite and other structurally related minerals. The new material contained major Y and Y-group REE, Bi, Ca, and Mn and almost no Fe. The mineral has been named minasgeraisite in honor of the state of Minas Gerais, Brazil, which is noted for its complex granitic pegmatites and for the many new pegmatite-hosted mineral species that have been found there. Pronunciation of the name is mi′ nas ger′ ais ite. The mineral and name (83–90) were approved prior to publication by the IMA Commission on New Minerals and New Mineral Names. Only several hundred milligrams of minasgeraisite are known to exist. Holotype material has been deposited with the U.S. National Museum.

OCCURRENCE, MORPHOLOGY, AND PHYSICAL PROPERTIES

Minasgeraisite occurs as a sparse, accessory, late-stage mineral in small druses in a zoned, complex, granitic pegmatite. The pegmatite body, known as the Lavra de Sr. Jose Pinto, is located at Jaguaracu, adjacent to a soccer field, Municipo de Timoteo (near Coronel Fabriciano), Minas Gerais, Brazil. The pegmatite as exposed is lenticular, with a strike length of at least 100 m and a maximum width of 20 m. It crops out on a steep hillside, and, at the uppermost end, pinches out to less than 1 m in width. This pegmatite was first exploited approximately 20 years ago for industrial beryl. More recently it was mined by Jose Pinto for mineral specimens, mainly tourmalinated quartz crystals and cleavelandite druses. The principal

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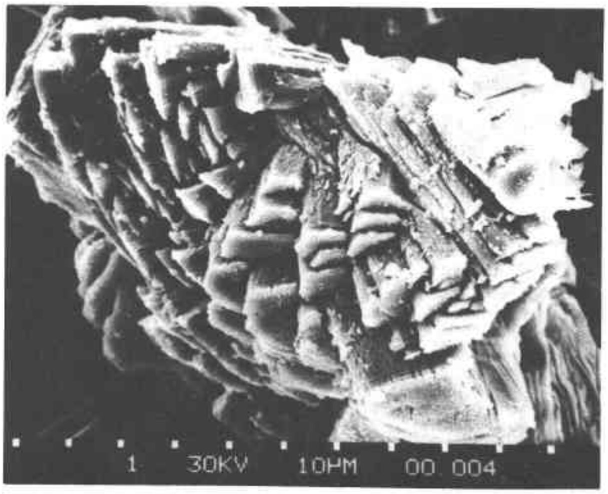

Fig. 1. Part of a spherical aggregate of growth-zoned minasgeraisite crystals showing elongation along **a** and simple pedion terminations. Distance between tic marks is 10 μm.

Table 1. Chemical analyses of minasgeraisite in weight percent

Oxide	Bulk sample	Bi-richest portion
SiO_2	26.37**	24.5 (electron microprobe)
Al_2O_3	0.32 (deducted as mica)	0.0 " "
FeO*	0.69	0.7 (from ICP analysis of bulk sample)
MgO	0.61	0.6 " "
CaO	11.47	8.1 (electron microprobe)
Na_2O	<0.1	<0.1 " "
TiO_2	0.02	0.0 (from ICP analysis of bulk sample)
MnO	2.83	3.5 (from electron microprobe)
P_2O_5	1.21	1.2 (from ICP analysis of bulk sample)
B_2O_3	1.45	1.5 " "
BeO	7.8	7.8 " "
Bi_2O_3	14.7	28.5 (from electron microprobe)
CuO	0.14	0.1 (from ICP analysis of bulk sample)
ZnO	0.35	0.3 " "
ZrO	<0.02	0.0 " "
La_2O_3	0.25	0.2 (from electron microprobe)
Ce_2O_3	0.20	0.0 " "
Pr_2O_3	0.13	0.1 " "
Nd_2O_3	0.50	0.2 " "
Sm_2O_3	0.26	0.1 " "
Eu_2O_3	0.00	n.d.
Gd_2O_3	0.32	0.2 " "
Tb_2O_3	0.23	0.1 " "
Dy_2O_3	1.26	1.3 (from ICP analysis of bulk sample)
Ho_2O_3	0.37	0.3 (from electron microprobe)
Er_2O_3	1.94	1.3 " "
Tm_2O_3	0.75	0.6 " "
Yb_2O_3	7.86	5.9 " "
Lu_2O_3	1.71	1.5 (calculated from CNR distribution)
Y_2O_3	16.38	11.3 (from electron microprobe)
Totals	99.8	99.9

*Fe expressed as FeO.
**After deduction of 0.6 wt.% as mica. Analysis of bulk sample done on 10.6 mg by J. G. Crock, using the ICP method. Bi_2O_3 was determined using AAS, also by J. G. Crock. Sum of REE = 32.2 wt.% for bulk sample.

workings are reached through an adit that slopes gently downward at the foot of the hill. Most of the workings are underground, and the pegmatite is at present abandoned and flooded. A replacement zone containing adularia, albite, hematite rosettes, muscovite, quartz, and milarite has produced a typical "Alpine-cleft" type environment (Stalder et al., 1973). The largest milarites found were tan, more than 30 mm in length and 12 mm in diameter, implanted on druses of albite. Greenish-yellow and pale-tan milarite crystals were also found associated with druses of muscovite and tourmalinated quartz. Additional minerals present include amazonite, which has been replaced locally along cleavages by pink adularia; almandine-spessartine garnet crystals as much as 1 cm across; magnetite in irregular masses as much as 25 cm across; churchite, $YPO_4 \cdot 2H_2O$; sky-blue elbaite in rare small irregular masses; pyrite in microscopic crystals; and nodules, as much as several centimeters or more across, consisting of a mixture of cerussite and pyromorphite, which represent the replacement of a pre-existing lead- and possibly bismuth-bearing mineral. Also present are numerous round and ocherous spots of light-yellow and powdery anatase. The spots of anatase are especially common embedded in the surface of some of the late quartz crystals and on adularia druses.

Minasgeraisite coats and is intergrown with the milarite, muscovite, quartz, albite, and rarely other minerals. The muscovite on which most of the minasgeraisite occurs is an iron- and lithium-bearing variety and is colored yellowish bronze. All of the associated minerals are euhedral, as is the minasgeraisite. Minasgeraisite occurs as single and multiple rosettes ranging from 0.2 to approximately 1.0 mm across. Individual matrix specimens containing the mineral range from 2 to 7.5 cm across. The minasgeraisite was one of the latest minerals to form, and only quartz completely encloses it. Individual rosettes of minasgeraisite are concentrically zoned with medium-purple rims and pale-purple cores. Figure 1 shows the curved sheaflike habit of the mineral and growth zoning, manifested by light and dark zones. Individual crystals are usually less than 3–5 μm across. Under the polarizing microscope, a strong mosaic texture made up of individual grains is present.

Minasgeraisite is not magnetic, has an earthy to subvitreous luster, has a faint pale-purple streak, and is not fluorescent under either SW or LW ultraviolet light. Mohs hardness is estimated at 6–7, and D_{meas} is greater than 4.25 g/cm³ (density of pure Clerici solution). A Berman microbalance determination of the density was not possible. D_{calc}, using determined cell volume and molecular weight, is 4.90 g/cm³. The mineral is soluble and gelatinizes in hot H_2SO_4 or HCl. It has one excellent cleavage, which should be {100} by analogy with gadolinite, and a second good cleavage, {001}.

Optically, minasgeraisite is biaxial (+), with α = 1.740(4), β = 1.754(4), γ = 1.786(4), $\gamma - \alpha = 0.046$, $2V_z$ = 68° (average). The measured range of $2V$ is from 50 to 72°, and $2V_z$ (calc.) = 68°. The mineral is moderately pleochroic with X = colorless, Y = pale grayish yellow, and Z = lavender purple. Dispersion is very weak, $r > v$.

Table 2. Gadolinite group and structurally related minerals

$A_2\ B\ \ C_2\ L_2\ O_{10}$	a (Å)	b (Å)	c (Å)	b (°)	Z	Reference
Gadolinite-$Y_2Fe^{2+}Be_2Si_2O_{10}$	10.00	7.565	4.768	$90^{\circ}19'$	2	Miyawaki et al., 1984
Gadolinite-(Ce)$(Ce,La,Nd,Y)_2Fe^{2+}Be_2Si_2O_{10}$	10.01	7.58	4.82	$90^{\circ}47'$	2	JCPDS 29-1408
Minasgeraisite-$Y_2CaBe_2Si_2O_{10}$	9.833	7.562	4.702	$90^{\circ}26'$	2	This paper
Homilite-$Ca_2(Fe,Mg)B_2Si_2O_{10}$	9.67	7.57	4.74	$90^{\circ}22'$	2	JCPDS 17-211
Datolite-$Ca_2(\square)B_2Si_2O_8(OH)_2$	9.62	7.60	4.84	$90^{\circ}09'$	2	JCPDS 11-70
Bakerite-$Ca_2(\square)B_2(Si_{1.5}B_{0.5})_2O_8(H_2O)_{0.5})_{10}$	9.60	7.60	4.82	$90^{\circ}12'$	2	JCPDS 14-68
Herderite-$Ca_2(\square)Be_2P_2O_8F_2$	9.82	7.70	4.81	$90^{\circ}06'$	2	JCPDS 6-338
Hydroxyl-herderite-$Ca_2(\square)Be_2P_2O_8(OH)_2$	9.805	7.648	4.813	$90^{\circ}10''$	2	JCPDS 29-1408
Bergslagite-$Ca_2(\square)Be_2As_2O_8(OH)_2$	10.13	7.81	4.88	$90^{\circ}10'$	2	Hansen et al., 1984
´Calciogadolinite´-$Ca_2Fe^{2+}Be_2Si_2O_8(OH)_2$	9.97	7.56	4.69	$90^{\circ}00'$	2	Povarennykh, 1972
Synth. calciogad.-$CaYFe^{3+}Be_2Si_2O_{10}$	9.988	7.566	4.696	$90^{\circ}01'$	2	Ito and Hafner, 1974
´Yberisilite´=hingganite $Y_2(\square)Be_2Si_2O_8(OH)_2$	10.20	7.80	4.90	$92^{\circ}00'$	2	Povarennykh, 1972
Hingganite-(Yb)=$(Yb,Y)_2(\square)Be_2Si_2O_8(OH)_2$	9.888	7.607	4.740	$90^{\circ}27'$	2	Voloshin et al., 1983
´Calcibeborosilite´-$CaY(\square)(Be,B)_2Si_2O_8(OH)_2$ or possibly $Y(\square)Ca(Be,B)_2Si_2O_8(OH)_2$	9.86	7.48	4.66	$91^{\circ}30'$	2	Povarennykh, 1972
Euclase group: related to gadolinite group with $\underline{a}_e = \underline{a}_g/2$, $\underline{b}_e = \underline{b}_g x2$						
Euclase-$Al_2(\square)Be_2Si_2O_8(OH,F)_2$	4.763	14.29	4.618	$100^{\circ}15'$	2	JCPDS 14-65
Vayrynenite-$Mn_2(\square)Be_2P_2O_8(OH,F)_2$	5.411	14.49	4.73	$102^{\circ}45'$	2	JCPDS 12-707

Optical orientation could not be determined because of the small grain size and mosaic texture.

CHEMISTRY

Minasgeraisite was analyzed by inductively coupled plasma (ICP) and AAS (atomic absorption spectrometry) methods, as well as by electron microprobe (Table 1). The electron-microprobe analytical conditions were fully automated 6-spectrometer ARL SEMQ instrument, 15-kV accelerating voltage, 10 nA on brass sample current, 2-μm spot size, 40-s count times on peak positions for samples and standards, 4-s count times on background positions, natural and synthetic bismuthinite, diopside, albite, and rhodonite, and synthetic REE NBS glass standards were used, and data reduction was done using MAGIC IV. About 1 wt% muscovite remained in the 10.6-mg minasgeraisite concentrate that was purified in Clerici solution. The muscovite was subtracted before calculation of the empirical formula. Insufficient material was available for a water determination, and because the analytical total was so nearly 100%, it was deemed unnecessary. The empirical formula, calculated on the basis of 10 oxygen atoms and assignment of the amount of Ca necessary to fill the A site with the remainder being assigned to the B site, is $(Y_{0.72}REE_{0.41}Ca_{0.56}Bi_{0.31})_{2.00}(Ca_{0.45}Mn_{0.20}Mg_{0.08}Fe_{0.05}Zn_{0.02}Cu_{0.01}\square_{0.19})_{1.00}(Be_{1.55}Si_{0.24}B_{0.21})_{2.00}(Si_{1.95}P_{0.08})_{2.03}O_{10}$. The simplified and ideal formula of minasgeraisite, $Y_2CaBe_2Si_2O_{10}$, is compared with other members of the gadolinite group in Table 2. A refinement of the crystal structure of gadolinite suggests that the B site is partially vacant and that partial substitution of a hydroxyl for oxygen compensates for the lack of positive charge at the B site (Miyawaki et al., 1984). A six-step semiquantitative emission spectrographic analysis of 1.5 mg (N. M. Conklin, U.S. Geological Survey, analyst) is in good agreement with the ICP and AAS analyses. The presence of major Bi, from approximately 10 to 28.5 wt% Bi_2O_3, was confirmed by four methods: electron microprobe, ICP, AAS, and emission spectrography. Bi in major quantities has not been reported previously in members of the gadolinite group. In a spectrochemical study of 29 gadolinites, an average content of 63 ppm Bi was determined (Gurney and Ahrens, 1969). The environment, which was rich in Be with some Bi and containing available divalent cations such as Ca and Mn, favored the formation of minasgeraisite. The depletion of Fe and Mg and related enrichment of Ca and Mn is well documented in closed or nearly closed complex pegmatite systems (e.g., Staatz et al., 1955; Foord, 1976).

Using the electron-microprobe analytical results for the Bi-richest and REE-poorest area found (Bi_2O_3 = 28.5 wt%, total REE_2O_3 = 23.06 wt%) in a radiating aggregate, and the results for the other elements from both ICP and electron-microprobe determinations (Table 1), an A-site occupancy of $(REE_{0.86}Bi_{0.65}Ca_{0.49})_{2.00}$ is calculated. A Bi-dominant member of the gadolinite group may exist, but cannot be presently confirmed.

Cores of radiating sheaves of minasgeraisite are richer in Ca (12.5 wt% CaO) and the REEs (total REE_2O_3 = 35.2 wt%) and poorer in Mn (2.6 wt% MnO), whereas the rims contain more Mn (3.5 wt% MnO) and Bi (28.5 wt% Bi_2O_3), and lower Ca (8.1 wt% CaO) and REEs (total REE_2O_3 =

Table 3. Indexed X-ray powder diffraction data for minasgeraisite

hkl	d(A) calc	d(A) obs	I/I_o
110	5.99	5.99	30
001	4.70	4.70	20
210	4.12	4.12	10
$\bar{1}11$	3.71	3.71	30
120	3.53	3.53	15
$\bar{2}01$	3.41	3.41	30
$\bar{2}11$	3.11	3.11	100
220, 310	2.997	3.000	15
021	2.946	2.945	15
$\bar{1}21$	2.826	2.830	100
$\bar{3}11$	2.542	2.540	90
400	2.458	2.460	10
002	2.351	2.350	15
012	2.245	2.250	30
$\bar{1}12$	2.192	2.190	30
$\bar{4}11$	2.100	2.100	7
420	2.061	2.060	7
$\bar{2}31$	2.027	2.030	20
$\bar{1}22$	1.959	1.960	25
$\bar{2}22$	1.854	1.855	30
$\bar{5}11$	1.769	1.768	35
$\bar{1}32$	1.695	1.695	10
$\bar{4}12$	1.664	1.665	30
$\bar{2}32$	1.626	1.625	30
$\bar{4}22$	1.555	1.555	15
620	1.504	1.504	10
$\bar{2}13$	1.468	1.468	10
$\bar{6}21$	1.435	1.435	30
$\bar{2}23$	1.392	1.392	10
$\bar{4}03$	1.326	1.326	20
052, $\bar{6}22$	1.272	1.272	20
160	1.250	1.250	10
$\bar{7}12$	1.195	1.195	15
$\bar{8}11$	1.177	1.177	15
+ additional lines			

114 mm diameter Gandolfi camera used with CuKa (1.54178A) radiation. 35 kV, 18 ma, 22 hrs. Data for a cell with a = 9.833(2)A, b = 7.562(1)A, c = 4.702(1)A, β = 90.46(6)°, V = 349.60(14)A^3.

23.1 wt%). Light- and dark-colored zones shown in Figure 1 correlate with the chemical zonation.

CRYSTALLOGRAPHY AND X-RAY DIFFRACTION DATA

The curved, sheaflike habit of minasgeraisite and the small grain size precluded single-crystal study; however, minasgeraisite has a gadolinitelike X-ray diffraction pattern with sharp peaks. All lines are indexed in space group $P2_1/a$ (Table 3). Refined cell data are $a = 9.833(2)$, $b = 7.562(1)$, $c = 4.702(1)$ Å, $\beta = 90.46(06)°$, $V = 349.60(14)$ Å^3. Z = 2. These cell data are similar to those reported for synthetic gadolinite-group phases described by Ito and Hafner (1974). The powder pattern is similar to JCPDS card no. 18-220. In order to directly confirm the similarity of the powder patterns for minasgeraisite and gadolinite, a few crystals of nonmetamict gadolinite from Liberty Bell Mountain, near Washington Pass, Golden Horn batholith, Okanogan County, Washington, were obtained from Mr. R. C. Boggs for study. A 114-mm Gandolfi film gave a pattern closely resembling the minasgeraisite and JCPDS card no. 18-220.

DISCUSSION AND MINERALS RELATED TO MINASGERAISITE

Minasgeraisite belongs to the gadolinite group (Table 2). The high CaO content, 11.47 wt%, in minasgeraisite is noteworthy. Unlike the "calciogadolinite" described by Nakai (1938) which contained 11.91 wt% CaO, 11.24 wt% FeO, 7.65 wt% Fe_2O_3, and 29.16 wt% REE_2O_3, the minasgeraisite contains 11.47 wt% CaO, 0.69 wt% FeO, 14.7 wt% Bi_2O_3, and 32.2 wt% REE_2O_3. While having a similar content of CaO to that of "calciogadolinite," minasgeraisite does not contain appreciable Fe. The REEs and Bi occupy about three-quarters of the A site with Ca making up the remaining one-fourth of the site. However, Ca is the single most abundant cation in the divalent B site, and this fact distinguishes minasgeraisite from all other members of the gadolinite group or minerals structurally related to this group. In the case of Nakai's (1938) "calciogadolinite," considering the iron to be present in the B site, the analytical results indicate that the Ca is dominantly in the trivalent A site. A Ca-rich gadolinite was described by Oftedal (1972), but it is not known if it is a true "calciogadolinite" because of the only partially determined chemistry. "Calciogadolinite" is not considered to be a valid mineral species by Fleischer (1983), but the name has been widely used in the literature. A calculation of the empirical formula from Nakai's analysis indicates that the total REE cation fraction is still greater than the Ca cation fraction: $(Y_{0.95}Ce_{0.12}Ca_{0.93})_{2.00}(Fe^{2+}_{0.68}Fe^{3+}_{0.42}Mn_{0.05}Mg_{0.02}Th_{0.01})_{1.18}(Be_{1.87}Al_{0.14})_{2.01}(Si_{1.74}\square_{0.26})_{2.00}O_{10}$. The presence of 1.45 wt% B_2O_3 indicates some solid solution toward homilite. The presence of about 0.2 atom vacancy in the 6-coordinated divalent B site is analogous to the major vacancies shown in datolite (Ito and Mori, 1953), "calcibeborosilite" (after Semenov et al., 1963, quoted in Povarennykh, 1972), herderite, hydroxyl-herderite, hingganite, and hingganite-(Yb) (Voloshin et al., 1983) as shown in Table 2. Hingganite-(Y) is the same species as "yberisilite" (after Semenov et al., 1963, in Povarennykh, 1972). The gadolinite-(Ce) described by Segalstad and Larsen (1974) indicates the existence of a Ce-group-dominant gadolinite. The purple color of minasgeraisite may be due to the presence of Mn in the virtual absence of Fe, substituting for Ca in the divalent B site. Synthesis studies (Ito, 1967; Ito and Hafner, 1974) have shown that Fe^{3+} may substitute in the B site. Cation vacancies are also known to be present in the C site, which contains divalent or trivalent cations in fourfold coordination.

A chondrite normalized ratio (CNR) plot for minasgeraisite resembles those of other normal gadolinites, e.g., Vainshtein et al. (1958) and Bonshtedt-Kupletskaya and Smolyaninova (1972). As indicated by Vainshtein et al. (1960), the REE distribution in gadolinites strongly depends on the environment of their formation. This type of phenomenon is found in many other REE-bearing minerals, e.g., davidite (Foord et al., 1984).

CONCLUSIONS

Minasgeraisite is a new member of the gadolinite group with Ca the dominant cation in the sixfold B site, and is distinct from end-member "calciogadolinite" which is characterized by having Ca dominant in the eightfold A site. The mineral is a product of crystallization in a granitic pegmatite environment from a Be-, Bi-, REE-, Ca-, and Mn-rich fluid in the absence of elements such as Fe, Mg, and Ti. Other minerals of the gadolinite group, such as the Bi-dominant member, should exist in nature.

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Mr. Russell C. Boggs (University of Eastern Washington) provided several crystals of nonmetamict gadolinite from Liberty Bell Mountain, Washington, for comparison. Dr. Akira Kato assisted in the recognition of minasgeraisite as a new member of the gadolinite group and initiated processing of the mineral through the IMA Commission on New Minerals and New Mineral Names.

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