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Liddicoatite, a new calcium end-member of the tourmaline group

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Abstract

Liddicoatite, a new calcium end-member of the tourmaline group, ideally $Ca(Li,Al)_3Al_6B_3Si_6O_{27}(O,OH)_3(OH,F)$, is rhombohedral, $R3m$, with a = 15.867(4), c = 7.135(4)A, and cell volume V = 1555.6(9)A^3. Liddicoatite is the calcium analog of elbaite. It is a common mineral in the detrital soils of Antsirabe, Madagascar.

Introduction

During a systematic search for compositional variation in natural tourmalines, we noted that many large, multi-colored tourmalines from Madagascar have an unusually high calcium content. A comprehensive investigation of 75 Madagascar tourmalines resulted in the discovery of a new end-member in the tourmaline group. This new mineral is the calcium analog of elbaite. We have named the mineral liddicoatite in honor of Mr. Richard T. Liddicoat, President of the Gemological Institute of America, in recognition of his contributions to gemological knowledge and education. The mineral and the name were approved in advance of publication by the Commission on New Minerals and New Mineral Names, IMA. Holotype material is deposited in the National Museum of Natural History, Smithsonian Institution, Washington, D.C., under catalog #135815. Additional holotype material has been deposited in the British Museum (Natural History), London, England, the Royal Ontario Museum, Toronto, Ontario, Canada, and the Geological Survey of Canada, Ottawa, Ontario, Canada. The pronounciation is lidd′–i–coat–ite.

Previous work

The tourmalines from the pegmatites of Madagascar were first described by Lacroix (1893, p. 102–105), and the beautiful zoning of these crystals was initially noted by him. Duparc *et al.* (1910), in their comprehensive investigation of the pegmatites of Madagascar, described these tourmalines in great detail and presented optical, morphological, and analytical data. A further description was by Lacroix (1922, p. 411–432). Of special interest is the analysis of a pale pink crystal from Maroando with 2.58 percent CaO, and a crystal from Antaboko with 4.10 percent CaO (Duparc *et al.*, 1910). These are the only extant prior analyses of this new mineral. Their significance was not apparent at the time they were made, because the extent of solid solution in the tourmaline group was not well understood.

Locality

The locality of liddicoatite can be stated only in general terms. The crystals occur as detritus in the soils near Antsirabe in Madagascar, and a specific site for the occurrence of the type material is not known.

Morphology

Liddicoatite is found as large well-formed crystals of obvious trigonal symmetry, displaying the common tourmaline morphology. The crystals are stout, prismatic, and range in size up to 25 × 10 cm. The crystals are deeply striated parallel to *c*. There are no obvious or distinguishing differences in the morphology of liddicoatite when compared with elbaite; the forms present are typical of tourmalines in general.

Color zoning

The most striking feature of some liddicoatite, but not all, is the extremely beautiful symmetrical color zoning (Fig. 1). The most beautiful specimens are zoned green, pink, and red, but browns, blues, and many hues are frequently observed. The orientation of the zoning is of particular interest, inasmuch as most gemmy zoned elbaite is either zoned parallel to

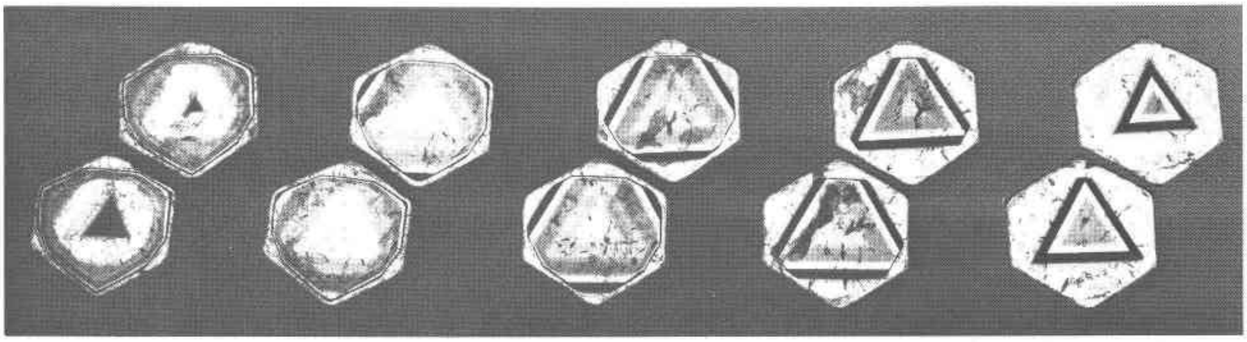

Fig. 1. Symmetrical color zoning in Madagascar liddicoatite.

{0001} or {10$\bar{1}$0}, {11$\bar{2}$0}, or both of the latter forms. In most liddicoatite, however, the predominant zoning is parallel to a pyramid. This causes a slight blurring of zone margins when cross-sections of the crystal are viewed parallel to *c*, but the effect is nonetheless beautiful. The calcium/sodium ratio remains almost constant from zone to zone. Color is of no use in the determination of the species. Both elbaite and liddicoatite come in all the previously noted colors. Although the specimen chosen for type material and described herein is brown in color, this is not a characteristic or diagnostic feature of liddicoatite.

Table 1. Chemical analysis of liddicoatite, holotype specimen NMNH #135815

	Wt. %
SiO_2	37.7
Al_2O_3	37.9
TiO_2	0.38
FeO	0.83
MnO	0.27
MgO	0.11
CaO	4.21
Na_2O	0.88
Li_2O	2.48
F	1.72
B_2O_3	10.89
H_2O^+	2.69
Total	100.06
O= F	0.72
Total	99.34

analyst: Joseph Nelen

Structural formula based on 31 anions (O^{2-}, OH^-, F^-) : $(Ca_{0.72}Na_{0.27})(Li_{1.59}Al_{1.13}Fe_{0.11}Ti_{0.05}Mn_{0.04}Mg_{0.03}\square_{0.05})Al_{6.00}B_{3.00}Si_{6.02}(O_{27.27}(OH)_{2.73})(F_{0.87}(OH)_{0.13})$, for the general formula $X\,Y_3\,Z_6\,B_3\,Si_6(O,OH)_{30}(OH,F)$.

Physical and optical properties

The type liddicoatite is brown, transparent, and has a vitreous luster on fracture surfaces. Cleavage is weak parallel to {0001} or absent. The streak is very light brown. The mineral is not fluorescent in either short or long wave ultraviolet radiation.

Liddicoatite is uniaxial negative with $\epsilon = 1.621$, $\omega = 1.637$ in sodium light. Birefringence is moderate (0.016). The mineral is strongly pleochroic ($\omega > \epsilon$) with ϵ = light brown, ω = dark brown. The density, determined by Berman balance with temperature correction, is 3.02 g/cm³, which is in reasonable agreement with the calculated value of 3.05 g/cm³. Application of the Gladstone-Dale relationship, based on the constants of Mandarino (1976) and the chemical analysis of Table 1, yields a calculated average index of refraction $\bar{n} = 1.636$ when the observed density is used. This gives better agreement with the observed $\bar{n} = 1.632$ than does the calculated density.

The hardness of liddicoatite is about 7½ (Mohs). Liddicoatite has physical and optical characteristics too similar to elbaite to permit characterization without analysis. The above refractive indices and density apply to the holotype specimen only. The refractive indices of liddicoatite vary with the iron and manganese content, as do the indices of most tourmalines (Deer *et al.*, 1962, p. 300–319).

Chemical analysis

Initial chemical study of liddicoatite was done by electron microprobe analysis, using an ARL SEMQ electron microprobe and NMNH microprobe standards. Because microprobe results are inadequate to characterize in detail the complex solid-solution relationships in tourmalines, it was decided to perform complete wet-chemical analyses on some representative Madagascar specimens. The analysis of the holotype material is given in Table 1. In consideration of the rarity of good wet-chemical analyses of tourmalines in the literature, the procedures we used are outlined in some detail.

Analytical procedures

Reduction of sample size was done first in an iron percussion mortar to −40 mesh; removal of metal contamination with a magnet was followed by further grinding in a tungsten carbide mill to −100 mesh. Moisture, SiO_2, Al_2O_3, FeO, CaO, and MgO were determined on 0.5 g portions by classical chemical methods (Peck, 1964). Prior to filtration of silica, boron was volatilized by repeated dehydration with an HCl–methanol mixture (Hillebrand *et al.,* 1953). Iron in the R_2O_3 portion was determined using 0-phenanthroline; titanium as the tiron complex; aluminum was precipitated with 8-hydroxyquinoline (Jarosewich, 1966). Using a separate sample the MnO was dissolved by fusion with Na_2CO_3, acidified, oxidized to permanganate and determined colorimetrically. For total water the Penfield method (Peck, 1964) was used, the H_2O^+ being the difference between total water and moisture. For fluorine 0.5 g samples were fused with ZnO–Na_2CO_3 flux and filtered (Grimaldi *et al.,* 1955). The fluorine in the filtrate was distilled using a constant-temperature distilling apparatus (Huckabay *et al.,* 1947), precipitated as the lead chlorofluoride complex, filtered off, and dissolved in 5 percent nitric acid. The fluorine in the lead chlorofluoride complex was determined indirectly by precipitating the chloride-equivalent with excess silver and titrating the excess silver by the Volhard method (Hillebrand *et al.*, 1953). Alkali content was determined flame-photometrically after sample decomposition according to the J. Lawrence Smith method. Boron was titrated with NaOH and mannitol after removal of interfering substances and neutralization. Precision of method was ± 0.2 percent B_2O_3 on NBS 93 (a 12.76% borosilicate glass).

Crystallography

Liddicoatite from the holotype specimen was studied by single-crystal and powder X-ray diffraction techniques. Like all other tourmalines, liddicoatite is rhombohedral, with space group *R3m*. The cell dimensions were obtained from a refinement of the powder diffraction data using the program of Appleman and Evans (1973). They are: a = 15.867(4), c = 7.135(4)A, cell volume V = 1555.6(9)A^3, Z = 3. Silicon was used as an internal standard.[1] Liddicoatite is indistinguishable from elbaite by X-ray powder-diffraction techniques, and the cell dimensions fall within the range of reported values for lithium–aluminum tourmalines (Epprecht, 1953). We do not think that cell dimensions alone are reliable criteria for determining this species. Although c/a of liddicoatite is close to the c/a of some dravite/schorl solid solutions, if one has true c and true a from X-ray studies, it is clear from the charts of Epprecht (1953) that liddicoatite is a lithium–aluminum tourmaline. Although cell dimensions can be used to differentiate between elbaite, dravite, and schorl, there is insufficient evidence to indicate that the cell dimensions can be used, with reliability, to differentiate between sodium/calcium analogs such as elbaite/liddicoatite and dravite/uvite (Dunn *et al.,* 1977).

Table 2. Structural comparison between liddicoatite and elbaite

Site and Multiplicity	Ideal Elbaite Donnay & Barton, 1972	Ideal Liddicoatite (Present Study)
18c	Si	Si
9b	B	B
18c (Z)	Al	Al
9b (Y)	(Al,Li)	(Li,Al)
3a (X)	Na	Ca
3a	O_1(F,OH)	O_1(F,OH)
9b	O_2	O_2
9b	O_3(O,OH)	O_3(O,OH)
9b	O_4	O_4
9b	O_5	O_5
18c	O_6	O_6
18c	O_7	O_7
18c	O_8	O_8

Crystal chemistry

Liddicoatite is a calcium lithium aluminum tourmaline end-member. It is the direct structural analog of elbaite, the sodium lithium aluminum end-member. This analogy is illustrated in Table 2, which

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[1] Powder-diffraction data for liddicoatite may be obtained from D. E. Appleman.

compares the idealized structure of elbaite (Donnay and Barton, 1972) with that postulated for ideal end-member liddicoatite on the basis of its chemical composition, its crystallographic similarity to elbaite, and the probable continuous solid solution which this study suggests between the two species. Note that the only significant difference is the substitution of calcium for sodium in position *X*, with a concomitant change in the Al:Li ratio in the disordered position *Y*. Thus end-member elbaite can be written, for example: $Na(Al_{1.68}Li_{1.32})\ B_3Al_6Si_6O_{27.36}(OH)_{2.64}(F,OH)$, using the actual Al:Li ratio of the crystal studied by Donnay and Barton. By analogy, end-member liddicoatite can be written: $Ca(Li_{1.74}Al_{1.26})B_3Al_6Si_6O_{27.52}(OH)_{2.48}(F,OH)$, using the actual Al:Li ratio found in our crystals. Neither the elbaite studied by Donnay and Barton nor our type liddicoatite are pure end-members, but both indicate that calcium can be substituted for sodium in *X* without any major chemical or structural change except to the Al:Li ratio in *Y*. The necessary large charge-balance adjustment is almost completely effected in this way, rather than by a change in the $O^{2-}:(OH)^-$ ratio.

The existence of similar Ca-Na substitution in Mg tourmalines has previously been demonstrated by Dunn *et al.*, (1977) for the series uvite–dravite. These authors showed that complete solid solution exists in nature between uvite, ideally $CaMg_3(Al_5Mg)B_3Si_6(O,OH)_{30}(F,OH)$, and dravite, ideally $NaMg_3Al_6B_3Si_6(O,OH)_{30}(F,OH)$. Reference to the crystal-structure determination by Buerger *et al.* (1962) on uvite from DeKalb, New York, and to the data of Dunn *et al.* (1977) indicates that in this series also, Ca–Na substitution is compensated by a change in cation ratios. In this case it is the Mg:Al ratio in the *Y* position which is affected (Table 2).

Microprobe data obtained in this study suggest that there is complete solid solution between liddicoatite and elbaite, analogous to that between uvite and dravite. However, complete solid solution apparently does not occur between liddicoatite and uvite, probably for the same reasons outlined by Donnay and Barton (1972) for immiscibility between elbaite and dravite.

Conclusions

Liddicoatite, the newly-recognized calcium analog of elbaite tourmaline, is a moderately abundant species represented in most major mineral collections. Microprobe analyses of a large number of multiply-zoned Madagascar tourmalines show that most specimens are liddicoatite, although some are elbaite.

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