

MANGANESE-RICH RED TOURMALINE FROM THE FOWLER TALC BELT, NEW YORK

ROBERT A. AYUSO AND C. ERVIN BROWN

U.S. Geological Survey, Mail Stop 954, Reston, Virginia 22092, U.S.A.

ABSTRACT

Red uvite from the Arnold talc mine contains up to 4.34 wt. % MnO as determined by microprobe analyses. The manganese content is unusually high for a lithium-poor tourmaline and is in great contrast with the abundant, manganese-poor dravite and uvite that occur elsewhere in the Gouverneur area. The red uvite occurs with manganese-bearing tremolite (hexagonite), braunite Mn_7SiO_{12} and quartz in a carbonate-rich sequence in the Balmat-Edwards synform. Manganese-rich dravite is precluded in pegmatitic areas but specialized environments consisting of evaporitic rocks possibly represented in this area contain bulk compositions that could have led to the formation of manganese-rich minerals.

Keywords: uvite, manganese, tourmaline, evaporitic rocks, Arnold mine, New York.

SOMMAIRE

L'uvite rouge de la mine de talc d'Arnold (état de New York, E.-U.) contient jusqu'à 4.34% de MnO en poids (analyses à la microsonde). Pour une tourmaline pauvre en lithium, une telle teneur en manganèse est anormalement élevée, excédant fortement celle de la dravite et de l'uvite d'autres localités de la région de Gouverneur. L'uvite rouge est accompagnée de trémolite manganifère (hexagonite), braunite Mn_7SiO_{12} et quartz, dans une série carbonatée du synforme de Balmat-Edwards. Des roches évaporitiques, dont on soupçonne la présence dans ce socle fortement métamorphisé, posséderaient le chimisme approprié pour expliquer pareille association d'espèces manganifères.

(Traduit par la Rédaction)

Mots-clés: uvite, manganèse, tourmaline, roches évaporitiques, mine Arnold, New-York.

INTRODUCTION

Tourmaline is a common accessory mineral in most rocks of the Precambrian Grenville Complex in St. Lawrence County, New York. As part of a study of tourmaline compositions in tourmaline-bearing rocks found mainly northwest of Gouverneur, the authors also analyzed red tourmaline from the Arnold talc mine in the talc belt near Fowler (Fig. 1). Our purpose here is to present microprobe data for the unusually manganese-rich tourmaline from the Arnold mine, and to compare its composition with that of other varieties of tourmaline (excluding Li-rich elbaite).

The talc belt includes a sequence of layered rocks composed mainly of talc and tremolite and containing significant amounts of serpentine and anorthophyllite. This belt is part of a thick, carbonate-rich metasedimentary sequence exposed in the overturned limb of the Balmat-Edwards synform (Brown & Engel 1956). Locally within the talc belt are thin, discontinuous layers containing manganese-bearing minerals. Local concentrations of manganese minerals, forming pods, also occur in the nearby Balmat mining district (Brown *et al.* 1979).

Engel (1962) first described the manganese-rich zone of the Fowler talc belt and the occurrence of wine-red tourmaline coexisting with pink to lavender manganese-bearing tremolite (hexagonite). He also reported the composition of red tourmaline forming large (2-3 cm) crystals in quartz-rich veins in the Woodcock mine (Fig. 1). In contrast to our results, Engel's data (Table 1) pertain to tourmaline that is not manganese-rich but that contains significant amounts of iron.

Tourmaline disseminated in a rock composed mainly of hexagonite is exposed in a rib of unmined waste-rock in the Arnold open-cut talc mine and can be found on the waste pile of the nearby Wight mine. C. E. B. collected specimens of tourmaline-bearing rock from the Arnold mine in 1969; the authors and J.F. Slack collected additional specimens in 1980 and 1981 from the dump at the Wight mine.

MICROPROBE ANALYSES

Microprobe analyses were obtained on 2-to-10- μ m spots along closely spaced traverses by combining wavelength-dispersion and energy-dispersion techniques in an automated three-channel microprobe having an operating voltage of 15 kV and a current of 0.150 nA.

Synthetic and natural minerals used as standards include: plagioclase for Al, Na and K, biotite for Ti, pyroxene for Si and Mg, synthetic tephroite for Mn, fayalite for Fe, garnet for Ca, and synthetic chlorapatite for Cl. Checks on the standardization were made against well-characterized minerals, including buergerite, calcic amphibole, phlogopite and anorthoclase. Corrections and data reduction were made according to the method of Bence & Albee (1968).

The formula for tourmaline was calculated on the

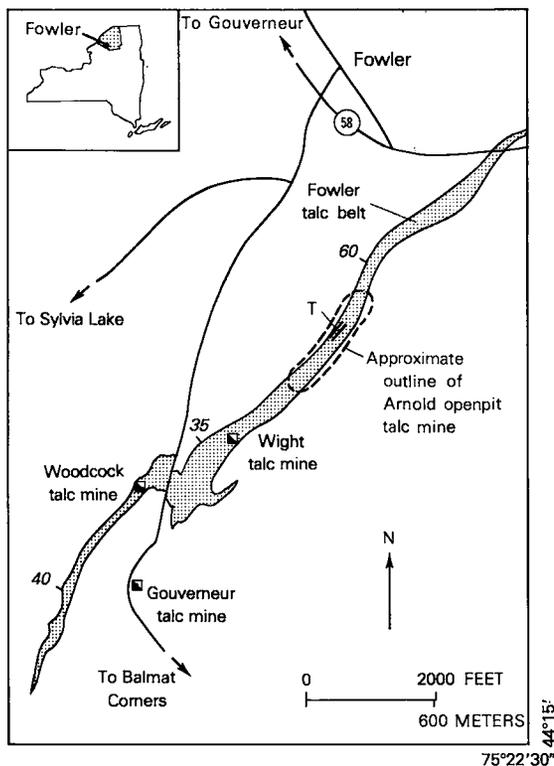


FIG. 1. Talc belt near Fowler, New York, showing location of tourmaline-hexagonite occurrence (T) in Arnold mine, and location of other mines that also have similar occurrences. Adapted from Brown & Engel (1956).

basis of 29 oxygen atoms, assuming three boron atoms per formula unit. Averages and approximate variations at 2σ are given where appropriate (Tables 1, 2).

DESCRIPTION OF TOURMALINE-BEARING ROCKS

The tourmaline-bearing rocks are predominantly grey to pale lavender and consist of Mn-tremolite (hexagonite), braunite (Mn-rich opaque phase) and talc. Tourmaline comprises less than 5% of the rock. Red tourmaline from the Arnold mine forms poikiloblastic, subhedral to anhedral grains as much as 3 mm in diameter arranged along discontinuous bands parallel to layering. Tourmaline also forms scattered clusters surrounded by euhedral tremolite. The poikiloblastic tourmaline is generally crowded with randomly oriented euhedral tremolite and anhedral braunite (Fig. 2). This sieve-like texture suggests that the tourmaline grew late in the paragenetic sequence. The red tourmaline from the Arnold mine shows moderate absorption, and dichroism from rose to red. No optical zoning is evident.

COMPOSITION OF TOURMALINE

The red tourmaline from the Arnold mine is significant in that although it contains substantial amounts of manganese, it falls within the uvite-dravite series. The ideal formula for uvite is $\text{CaMg}_3(\text{Al}_3\text{Mg})\text{B}_3\text{Si}_6(\text{O},\text{OH})_{30}(\text{OH},\text{F})$, as documented by Dunn *et al.* (1977b), and that for dravite is $\text{NaMg}_3\text{Al}_6\text{B}_3\text{Si}_6(\text{O},\text{OH})_{30}(\text{OH},\text{F})$ as given in Walenta & Dunn (1979). Along this series, the X site is occupied in the ideal formula by Na and Ca, the Y site by Mg, and the Z site by Al and Mg (Walenta & Dunn 1979).

Typical traverses across individual grains indicate substantial compositional homogeneity from core to rim, in agreement with the lack of optical zoning. However, slightly higher contents of Mn but lower Al are found along the rim of some grains, relative to the core. In a total of 66 analyzed spots, the range of the $\text{Na}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$ ratio is 0.323 to 0.358, that of the $\text{FeO}/(\text{FeO} + \text{MgO})$ ratio is 0.125 to 0.138, and that of the $\text{MnO}/\text{Al}_2\text{O}_3$ ratio is 0.158 to 0.180.

The calcium content in the red tourmaline is high, averaging 2.78 wt. % (Table 1), resulting in a relatively low Na/Ca ratio and a composition of 51% uvite. This composition recurs throughout the Gouverneur area; it corresponds to the middle of the uvite-dravite series (Dunn *et al.* 1977b). The Arnold specimen is substantially enriched in Mn compared to uvite tabulated by Dunn *et al.* (1977b) and to the reddish brown tourmaline (61% uvite) from Ontario, which contains no trace of Mn or Li (Bruce 1917).

Although microprobe analyses of tourmaline cannot yield data to completely characterize the site occupancies in the structure, it seems reasonable to suggest that the composition of the red manganese uvite from the Arnold mine generally conforms to the ideal formula of uvite given by Dunn *et al.* (1977b). The low Al content in the red uvite is in agreement with the addition of Mg in the Z site to compensate for the substitution of Na for Ca in the X position and to maintain charge balance (Dunn *et al.* 1977a, b). According to Manning (1969, 1973), Mn^{3+} may occupy both the Y and Z sites and is the cation responsible for the pink color in tourmaline. However, charge balance in the red uvite can be accomplished by varying the Mg/Al ratio without resorting to the addition of Mn^{3+} in the Z site. Furthermore, the analytical data obtained by electron microprobe cannot be used to adequately and precisely determine the $\text{Mn}^{3+}/\text{Mn}^{2+}$ ratio and its relation to color. Thus, available microprobe data for this red uvite are insufficient to properly assess the importance of Mn^{3+} in producing the red color.

Throughout the area northwest of Gouverneur, tourmaline compositions can be directly correlated with the bulk composition and type of host rock

TABLE 1. COMPOSITION AND FORMULA OF TOURMALINE FROM THE ARNOLD MINE, THE WOODCOCK MINE, AND FROM NORTH OF GOUVERNEUR, NEW YORK

Location	1 Arnold†	2 Woodcock	3	4 North Gouverneur	5				
Sample #	80-1	Wo-To-1	67-37	67-51	67-90				
SiO ₂	36.41 (1.08)	36.44	37.73 (0.47)	37.24 (0.29)	34.34 (0.34)				
Al ₂ O ₃	25.79 (1.04)	25.88	30.05 (0.10)	28.90 (0.16)	24.88 (0.74)				
TiO ₂	1.02 (0.21)	1.68	1.77 (0.08)	0.23 (0.03)	1.13 (0.11)				
FeO	2.02 (0.13)	n.d.	0.69 (0.19)	2.34 (0.34)	12.36 (0.19)				
Fe ₂ O ₃	n.d.	n.d.	n.d.	n.d.	n.d.				
MnO	4.34 (0.27)	0.01	0.01 (0.01)	0.02 (0.02)	0.04 (0.04)				
MgO	12.95 (0.38)	11.77	12.52 (0.13)	12.86 (0.25)	7.83 (0.30)				
CaO	2.78 (0.09)	1.61	1.26 (0.13)	3.55 (0.03)	2.22 (0.10)				
Na ₂ O	1.44 (0.02)	n.d.	2.31 (0.02)	0.98 (0.04)	1.66 (0.13)				
K ₂ O	0.03 (0.11)	n.d.	0.02 (0.03)	0.04 (0.01)	0.12 (0.03)				
Total	86.78	84.69	86.36	86.51	84.58				
Si	5.99	8.99	—	6.00	9.00	6.02	9.02	6.06	9.06
B	3.00			3.00		3.00			
Al	5.00	5.13	—	5.63	5.84	5.50	5.53	5.17	5.32
Ti	0.13			0.21		0.03		0.15	
Fe	0.28	4.05	—	0.09	3.06	0.32	3.42	1.82	3.89
Mn	0.60			0		0		0.01	
Mg	3.17			2.97		3.10		2.06	
Ca	0.49	0.96	—	0.22	0.93	0.61	0.87	0.42	1.02
Na	0.46			0.71		0.25		0.57	
K	0.01			0		0.01		0.03	

* Data for tourmaline in columns 1 and 3-5 are derived by electron microprobe. All iron is shown as FeO. Average composition along traverses are given $\pm(2\sigma)$. Formulas were calculated for 29 oxygen atoms, and assume 3 atoms of boron per formula unit.

† Spectrographic analysis shows Li 20 ppm, Ba, Cr and Cu 30 ppm each, Ni 5 ppm, Pb 15 ppm and Sr 700 ppm.

(Brown & Ayuso 1982). For example, tourmaline in granite pegmatites is iron-rich (schorl), whereas the calcic and magnesian varieties (dravite-uvite) occur in magnesium-rich metasediments (Table 1). However, major compositional differences exist between red uvite from the Arnold mine and brown uvite-dravite from the metasediments north of Gouverneur; the brown tourmaline contains manganese only as a trace constituent, whereas uvite from the Arnold mine contains up to 4.34 wt. % MnO (Table 1). Similarly, the compositions of dravite summarized by Epprecht (1953) are manganese-poor (< 0.2 wt. % MnO). An additional occurrence of a red magnesian tourmaline (dravite) occurs in Kenya (Dunn *et al.* 1973), but this tourmaline is characterized by high content of iron and a very small amount of manganese (0.03 wt. % MnO). Reddish orange tourmaline (dravite-uvite) containing only a trace of Mn (300 ppm) has also been found at the Black Hawk mine, Maine (J.F. Slack, oral comm. 1982). Thus it would seem that a red color in tourmaline does not necessarily imply a manganese-rich composition.

Iron-rich tourmaline enriched in Mn (5.39 wt. % MnO) from Chester County, Pennsylvania, was cited by Doelter (1915). However, this tourmaline is low in Na (0.36 wt. % Na₂O) and Ca (1.96 wt. % CaO), and very high in Fe (14.73 wt. % FeO), and thus not

TABLE 2. COMPOSITION OF TREMOLITE AND BRAUNITE FROM THE ARNOLD TALC MINE, NEW YORK*

Mineral	Tremolite**			Braunite
	80-1	9	15	80-1
Sample #				
SiO ₂	56.20 (1.24)	57.83	57.76	9.35 (0.13)
TiO ₂	0.04 (0.06)	0.03	0.05	0.49 (0.06)
Al ₂ O ₃	0	0.57	0.64	0.37 (0.04)
FeO	0.13 (0.01)	0.11	0.14	2.77 (0.14)
Fe ₂ O ₃	n.d.	0.20	0	n.d.
MnO	1.17 (0.09)	2.81	0.06	74.22 (0.34)
MgO	24.43 (0.11)	24.25	24.73	0.28 (0.34)
CaO	11.80 (0.10)	11.42	13.26	0.28 (0.06)
K ₂ O	0.08 (0.03)	0.14	0.09	n.d.
Na ₂ O	0.40 (0.17)	0.17	0.28	n.d.
Cl	0	0.01	0.02	n.d.
F	n.d.	0.41	0.26	n.d.
H ₂ O ⁻	n.d.	0.06	0.13	n.d.
H ₂ O ⁺	n.d.	2.09	2.38	n.d.
O ⁻ = F, Cl	—	0.17	0.11	—
Total	94.25	99.93	99.70	87.76

* Data for tremolite and braunite in sample 80-1 are derived by electron microprobe. All iron shown as FeO. Total manganese reported as MnO. Average compositions are given $\pm(2\sigma)$. ** Data for samples 9 and 15 are from Rose *et al.* (1968).

analogous to the Mn-rich uvite from the Arnold mine. Other examples of manganiferous tourmaline have MnO contents of up to 5.85 wt. %, but have less than 0.25 wt. % MgO. Thus, none of the examples cited by Doelter (1915) have compositions equivalent to the one discussed here.

The occurrence of Mn-rich tremolite and braunite in the Arnold mine is compatible with our sugges-

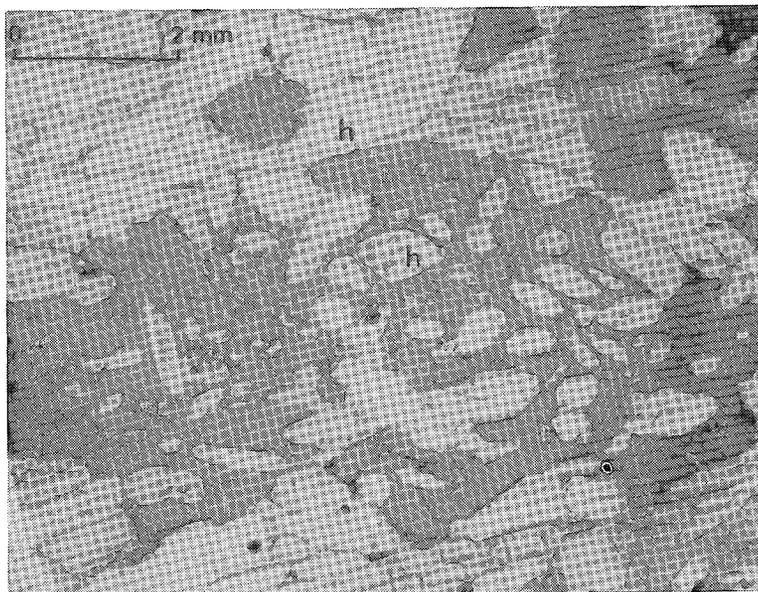


FIG. 2. Poikilitic red tourmaline (t) with hexagonite (h) and braunite (b).

tion that Mn-rich tourmaline is an integral part of this manganese-rich metamorphic assemblage. An abundance of manganese in the geochemical environment is also indicated by the occurrence, in the Arnold mine, of white tremolite that has exsolved manganese-rich lamellae oriented along the $(10\bar{1})$ plane (Bown 1966, Ross *et al.* 1968). Compositions of white tremolite given by Engel (1962) and recalculated by Ross *et al.* (1968) are here supplemented by new microprobe data (Table 2) that confirm the general enrichment in manganese. The assemblage also contains braunite Mn_7SiO_{12} , a manganese-rich opaque phase; it typically is anhedral in habit and shows feathery or irregular boundaries with manganese-rich tremolite and red tourmaline (Fig. 2). Braunite is also present as a fine dusting in all other phases. Compositionally, braunite from the Arnold mine (Table 2) is similar to that from metamorphosed manganese-rich sediments studied by Dasgupta & Manickavasagam (1981).

DISCUSSION

In general, many metasedimentary rocks in the Balmat area show geological attributes characteristic of an evaporite environment (Lea & Dill 1968). For example, phase assemblages may consist of scapolite, anhydrite, dolomite, talc, phlogopite and tremolite. Manganese-rich minerals have also been identified in the nearby Balmat mine and include rhodonite (Peacor *et al.* 1978) and a manganese-rich pyroxene

(Gordon *et al.* 1981). Tirosite, the manganese-rich amphibole, is also present there in Mn-rich pods (Brown *et al.* 1979).

Provided that no crystal-chemical barriers exist, bulk composition and geochemical environment seem to be the most important factors affecting the composition of tourmaline. Shimoda (1957, cited in Howie 1975) noted that the abundances of manganese and magnesium in tourmaline are inversely correlated in pegmatitic rocks. Slivko (1961) concluded that the occurrence of substantial amounts of manganese-rich magnesian tourmaline is geochemically precluded by the contrasting nature of the environments required for the formation of dravite and manganese-rich tourmaline. He also suggested that dravite forms in manganese-poor environments. In his view, environments necessary for the formation of manganese-rich tourmaline should be found principally in pegmatites saturated in lithium and sodium. In contrast, the manganese-rich uvite in the Arnold mine probably reflects the vital but stratigraphically limited effect of bulk composition in controlling tourmaline occurrence and variety. From this preliminary study, we can reasonably suggest that the series uvite-dravite may accommodate substantial amounts of Mn, and that Mg and Mn do not necessarily behave antipathetically.

ACKNOWLEDGEMENTS

The authors thank George E. Erdman, Vice Presi-

dent, Gouverneur Talc Co., for allowing C.E.B. to visit and collect specimens from the Arnold Mine, and Kenneth Totten, mining engineer, for pointing out the mineral occurrence. We also acknowledge J.F. Slack, D.D. Hogarth and G.D. Robinson, Jr. for their many constructive suggestions that resulted in a much improved report.

REFERENCES

- BENCE, A.E. & ALBEE, A.L. (1968): Empirical correction factors of the electron microanalysis of silicates and oxides. *J. Geol.* **76**, 382-403.
- BOWN, M.G. (1966): A new amphibole polymorph in intergrowth with tremolite: clino-anthophyllite. *Amer. Mineral.* **51**, 259-260 (abstr.).
- BROWN, C.E. & AYUSO, R.A. (1982): Magnesian tourmaline-rich metasediments in the Grenville lowlands of New York: potential for occurrence of massive sulfide deposits. *Geol. Soc. Amer. Abstr. Programs* **14**, 8.
- BROWN, J.S. & ENGEL, A.E.J. (1956): Revision of Grenville stratigraphy and structure in the Balmat-Edwards district, northwest Adirondacks, New York. *Geol. Soc. Amer. Bull.* **67**, 1599-1622.
- BROWN, P.E., ESSENE, E.J. & PEACOR, D.R. (1979): Phase relations inferred from field data for Ca-Mg-Mn pyroxenes and pyroxenoids. *Amer. Geophys. Union Trans.* **60**, 422-423 (abstr.).
- BRUCE, E.L. (1917): Magnesian tourmaline from Renfrew, Ontario. *Mineral. Mag.* **18**, 133-135.
- DASGUPTA, H.C. & MANICKAVASAGAM, R. (1981): Chemical and X-ray investigation of braunite from the metamorphosed manganeseiferous sediments of India. *Neues Jahrb. Mineral. Abh.* **142**, 149-160.
- DOELTER, C. (1915): *Handbuch der Mineralchemie*. II (10). T. Steinkopff, Dresden, Germany.
- DUNN, P.J., APPLEMAN, D.E. & NELEN, J.E. (1977a): Liddicoatite, a new calcium end-member of the tourmaline group. *Amer. Mineral.* **62**, 1121-1124.
- _____, _____, _____ & NORBERG, J. (1977b): Uvite, a new (old) common member of the tourmaline group and its implications for collectors. *Mineral. Record* **8**, 100-108.
- _____, AREM, J. & SAUL, J. (1973): Red dravite from Kenya. *J. Gemm.* **14**, 386-387.
- ENGEL, A.E.J. (1962): The Precambrian geology and talc deposits of the Balmat-Edwards district, northwest Adirondack Mountains, New York. *U.S. Geol. Surv. Open-File Rep.*
- EPPRECHT, W. (1953): Die Gitterkonstanten der Tourmaline. *Schweiz. Mineral. Petrog. Mitt.* **33**, 481-505.
- GORDON, W.A., PEACOR, D.R., BROWN, P.E. & ESSENE, E.J. (1981): Exsolution relationships in a clinopyroxene of average composition $\text{Ca}_{0.43}\text{Mn}_{0.69}\text{Mg}_{0.82}\text{Si}_2\text{O}_6$: X-ray diffraction and analytical electron microscopy. *Amer. Mineral.* **66**, 127-141.
- HOWIE, R.A. (1975): Tourmaline. *Proc. Ussher Soc.* **3**, 209-213.
- LEA, E.R. & DILL, D.B. (1968): Zinc deposits of the Balmat-Edwards district, New York. In *Ore Deposits of the United States, 1933-1967*. The Graton-Sales volume. 1. (J.D. Ridge, ed.). Amer. Inst. Mining, Metallurgical and Petroleum Engineers, New York.
- MANNING, P.G. (1969): An optical absorption study of the origin of color and pleochroism in pink and brown tourmaline. *Can. Mineral.* **9**, 678-690.
- _____. (1973): Effect on second-nearest-neighbour interaction on Mn^{3+} absorption in pink and black tourmalines. *Can. Mineral.* **11**, 971-977.
- PEACOR, D.R., ESSENE, E.J., BROWN, P.E. & WINTER, G.A. (1978): The crystal chemistry and petrogenesis of a magnesian rhodonite. *Amer. Mineral.* **63**, 1137-1142.
- ROSS, M., SMITH, W.L. & ASHTON, W.H. (1968): Triclinic talc and associated amphiboles from Gouverneur mining district, New York. *Amer. Mineral.* **53**, 751-769.
- SHIMODA, N. (1957): Geochemical studies on the pegmatite minerals. V. Tourmalines from pegmatite of Sakihama, Iwate. *Nippon Kagaku Zasshi* **77**, 1001-1003 (in Jap.).
- SLIVKO, M.N. (1961): Manganese tourmalines. *Int. Geol. Rev.* **3**, 195-201.
- WALENTA, K. & DUNN, P.J. (1979): Ferridravite, a new mineral of the tourmaline group from Bolivia. *Amer. Mineral.* **64**, 945-948.

Received November 18, 1982, revised manuscript accepted July 12, 1983.