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A unique manganese-rich silicic edenite in the Grenville marble, Fowler, New York

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Abstract

A manganiferous pod in the Grenville marble of the Arnold open pit of the Gouverneur Talc Company at Fowler, New York, consists of alternating layers composed mostly of polycrystalline braunite and a chemically unique Mn-rich silicic edenite which has the chemical formula $[(Na_{0.47}K_{0.01}Ca_{0.03})(Ca_{1.03}Mn_{0.97})(Mg_{4.55}Mn_{0.31}Al_{0.10}Fe_{0.04})(Si_{7.49}Al_{0.51})O_{22.13}(OH)_{1.87}]$, based on electron microprobe analyses. This amphibole belongs to space group $C2/m$ and has unit-cell edges $a = 9.802(2)$ Å, $b = 18.025(4)$ Å, $c = 5.281(1)$ Å; $\beta = 104.39(1)°$. The measured density is 3.28 g/cm³; the calculated density is 3.114 g/cm³. The difference is attributed to about 10% by volume of braunite that occurs as minute inclusions in the edenite. The optical properties of this edenite are $\gamma = 1.642$, $\beta = 1.632$, $\alpha = 1.620$, all ± 0.002; $2V_{calc} = 84°$; weakly pleochroic with Z = pale pinkish brown, Y = pale orange brown, X = colorless. Electron microprobe analyses of the garnet (82 mol% spessartine) and the braunite associated with the manganoan silicic edenite are presented.

Introduction

Peterson et al. (1984) reported the occurrence of donpeacorite, braunite, and tirodite in a manganiferous pod in the Grenville Marble on the 2500-foot level of the no. 4 Zn mine at Balmat, New York. In 1982, we found another Mn-rich pod in the Grenville Marble of the Arnold open pit, which is operated by the Gouverneur Talc Company as a source of industrial talc (talc-tremolite). Mn-rich pods are not uncommon in the 1.1 Ga, highly deformed, and regionally metamorphosed Grenville marble, which consists of a sequence several thousand meters thick of alternating units of dolomitic and silicate-bearing marbles with intercalated anhydrite-bearing evaporite beds (Dill et al., 1978; Swanson and Sclar, 1984) that are associated with paragneisses (Engel and Engel, 1953a, 1953b, 1958a, 1958b). Mn-bearing amphibole was reported earlier from the Arnold pit (Ross et al., 1969), but it is not equivalent to the Mn-rich amphibole described in this paper. Probably the best-known Mn-bearing mineral from these manganiferous pods is the attractive lavender manganoan tremolite known to mineral collectors as "hexagonite." The peak physical conditions to which the Grenville Marble sequence was subjected during regional metamorphism at Balmat (Brown et al., 1978) were 625 ± 25°C (calcite-dolomite geothermometry) and 6.5 ± 0.5 kbar (sphalerite-pyrite-pyrrhotite geobarometry).

Field occurrence and mineral associations

The manganiferous pod in the Arnold open pit consists of layered rock (Fig. 1), in which layers containing mostly polycrystalline braunite ranging in thickness from 0.5–3.5 mm alternate with pale pinkish brown layers composed mostly of calciferous Mn-rich amphibole (Benimoff et al., 1987) and subordinately of garnet $[(Sp_{81.8}Py_{8.8}Gr_{8.1}Al_{1.3})]$ and talc. The braunite layers define minor folds (Fig. 1) and are composed of essentially monomineralic aggregates of braunite which show 120° grain boundaries in polished section and are clearly part of the metamorphic assemblage. The grain size of the amphibole is 0.2–0.5 mm.

Electron microprobe analyses

Electron microprobe analyses of the Mn-rich amphibole (Table 1), garnet (Table 2), and braunite (Table 3), were obtained with a JEOL 733 electron microprobe at Lehigh University. The data were corrected using a Tracor-Northern adaptation of the Bence-Albee procedure. The standards used were Kakanui hornblende (USNM 143965) for Si, Fe, Mg, Al, Ca, Na, K, Ti; Ilmen Mts ilmenite

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(USNM 96189) for Mn; and Tiebaghi Mine chromite (USNM 117075) for Cr. Operating conditions of the electron microprobe were 15 kV, 20 nA, ca. 1 μm beam diameter; counting times 30 s; background 100–200 counts.

Amphibole and braunite chemistry

A formula for the Mn-rich amphibole based on the general formula of Leake (1978), $A_{0-1}B_2{}^{[6]}C_5{}^{[4]}T_8O_{22}(OH)_2$, was calculated for the average (AVE.) of the analyses in Table 1, assuming the difference between the oxide sum and 100% is the wt% of H_2O and allocating all cations except H^+ on the basis of ionic size as follows: T < C < B < A. The charge-balanced formula with OH + O = 24 that results is $[(Na_{0.47}K_{0.01}Ca_{0.03})(Ca_{1.03}Mn_{0.97})(Mg_{4.55}Mn_{0.31}Al_{0.10}Fe_{0.04})(Si_{7.49}Al_{0.51})O_{22.13}(OH)_{1.87}]$. The calculated density based on this formula is 3.114 g/cm³. The measured density using a pycnometer and a 200-mg hand-picked sample of amphibole containing about 10% by volume of braunite in the form of observed disseminated minute inclusions (<20 μm) is 3.28 g/cm³. Taking the average reported density of braunite (4.75; range 4.7–4.8), the calculated percent of braunite as inclusions is 10.2, which is similar to the estimated content of inclusions. The difference is attributed to the braunite inclusions in the edenite.

The amphibole is characterized by a very high Mg-Fe ratio, a high Mn content, and a low Al content. F and Cl were sought using energy-dispersive X-ray spectroscopy. A trace of Cl was detected; F was not detected. The results indicate that the concentration of each halogen is probably less than 0.05 wt%.

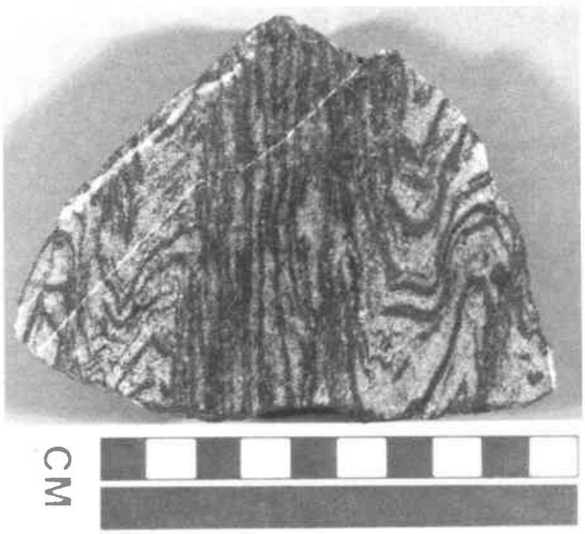

Fig. 1. Photograph of Mn-rich assemblage from Arnold pit. Black layers are dominantly braunite; light layers are dominantly Mn-rich calciferous amphibole.

The average of the braunite analyses in Table 3 gives the calculated charge-balanced formula $[(Mn^{2+}{}_{0.94}Mg_{0.04}Na_{0.02}Ca_{0.01})(Mn^{3+}{}_{5.62}Fe^{3+}{}_{0.36}Ti_{0.02})(Si_{0.94}Al_{0.06})O_{12}]$ based on the end-member $Mn^{2+}Mn^{3+}{}_6SiO_{12}$.

Table 1. Analyses of Mn-rich amphibole

Oxide	1	2	3	4	5	6	7	AVE.
SiO_2	49.65	54.49	53.09	53.45	52.84	53.54	53.59	52.95
TiO_2	0.11	0.06	0.07	0.04	0.04	0.06	0.03	0.06
Al_2O_3	6.20	2.53	3.42	2.91	4.59	3.01	2.76	3.63
Cr_2O_3	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00
FeO*	0.64	0.22	0.28	0.26	0.48	0.27	0.22	0.33
MnO	9.13	11.73	11.09	11.45	9.76	10.85	10.81	10.69
MgO	20.20	21.90	21.82	21.51	21.17	21.66	22.87	21.59
CaO	7.84	6.34	6.88	6.49	7.52	7.00	6.84	6.99
Na_2O	2.64	1.35	1.64	1.50	1.98	1.48	1.42	1.71
K_2O	0.12	0.05	0.06	0.04	0.12	0.04	0.04	0.07
LOI								1.95**
Total	96.56	98.67	98.35	97.64	98.50	97.91	98.57	99.97

Note: AVE. = Average of seven amphibole grains.
* Fe_{tot} reported as FeO.
** LOI determined on a 15-mg, hand-picked sample of amphibole heated in air 6 h at 140 °C and then heated in air 6 h at 1000 °C.

Table 2. Analyses of garnet associated with manganoan silicic edenite

Oxide	1	2	3	4	5	6	7	8
SiO_2	37.04	36.18	35.61	35.28	36.69	36.01	35.13	36.16
Al_2O_3	20.28	20.89	20.99	20.68	20.68	20.87	20.49	20.78
FeO*	0.47	0.55	0.53	0.57	0.64	0.64	0.61	0.63
MnO	36.82	37.17	37.82	36.83	37.51	39.89	40.30	38.05
MgO	2.83	2.75	2.41	2.57	2.74	1.57	1.25	2.41
CaO	3.29	3.06	3.01	2.99	3.32	2.68	2.59	2.90
Total	101.23	100.60	99.87	98.92	101.57	101.67	100.37	100.93

* Fe_{tot} reported as FeO.

TABLE 3. Analyses of braunite associated with manganoan silicic edenite

Oxide	1	2	AVE.
MnO*	83.52	81.76	82.64
FeO**	4.62	4.55	4.59
MgO	0.32	0.28	0.30
Al_2O_3	0.52	0.54	0.53
Cr_2O_3	0.00	0.01	0.01
SiO_2	10.15	9.87	10.01
TiO_2	0.28	0.28	0.28
CaO	0.04	0.06	0.05
Na_2O	0.05	0.13	0.09
K_2O	0.00	0.00	0.00
Total	99.50	97.48	98.50

* Mn_{tot} reported as MnO.
** Fe_{tot} reported as FeO.

CELL DIMENSIONS AND OPTICAL PROPERTIES

Single-crystal X-ray studies of the amphibole with a Picker FACS-1 diffractometer show that it is monoclinic with space group $C2/m$ and unit-cell dimensions a = 9.802(2) Å, b = 18.025(4) Å, c = 5.281(1) Å; β = 104.39(1)°. Exsolution lamellae of the type reported by Ross et al. (1969) were not found.

The amphibole has a very pale, pinkish-brown color in thick crushed grains and is weakly pleochroic with Z = pale pinkish-brown, Y = pale orange brown, and X = colorless; $Z \wedge c$ = 33°; $2V_{calc}$ = 84°. The indices of refraction are γ = 1.642, β = 1.632, α = 1.620, all ±0.002 as determined by the immersion method in white light.

CONCLUSIONS

The calciferous amphibole in the manganiferous pod in the northwest corner of the Arnold open pit at Balmat, New York, is rich in Mn and low in Fe and Al. The sedimentary precursor of the manganiferous pod was a thin-bedded sedimentary deposit composed of alternating layers of manganese oxide intercalated with calcareous siliceous mud that was rich in manganese oxide.

The reported occurrence of Mn-bearing amphibole with a wide range of composition in the Grenville marble at this locality, augmented by the occurrence of this Mn-rich edenite of unique composition in association with braunite and spessartine, provides evidence for the close control on the chemistry of metamorphic minerals in these rocks by the bulk chemistry of the original individual beds in the Grenville sedimentary sequence. Evidence for long-range diffusion and transport perpendicular to bedding is lacking. Each bed appears to have been an isochemical system that developed a unique equilibrium assemblage of metamorphic minerals with a unique mineral chemistry for each solid-solution series, in accord with the pressure and temperature impressed on the entire sedimentary package.

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