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Kutnahorite, a rare Mn Mineral from Piz Cam (Bergell Alps)

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Abstract

This note describes a new occurrence of Mn minerals in quartzite layers which are interbedded in a massive sequence of chlorite-muscovite-clinozoisite-albite schists and marbles of the Suretta nappe (Upper Pennine). Mn minerals which have been identified include spessartine, rhodonite, piemontite, rhodochrosite and veins of the rare Mn dolomite kutnahorite. They are thought to represent oceanic deposits, recrystallized during greenschist grade Tertiary metamorphism.

Riassunto

In questo lavoro descriviamo minerali di manganese che si trovano in quarziti intercalate in scisti di clorite-muscovite-clinozoisite-albite e calcescisti della falda Suretta (Pennidico superiore). Minerali identificati includono spessartite, rodonite, piemontite, rodocrosite e vene di rara dolomite manganesifera, kutnahorite. Sembra che rappresentino depositi del fondo oceanico, ricristallizzati durante un metamorfismo Terziario di grado degli scisti verdi.

The distribution of manganese minerals in the Rhetic Alps was subject of studies by Geiger (1948), Stucky (1960), Trommsdorff *et al.* (1970), and Peters *et al.* (1973, 1978). Assemblages of Mn-carbonates and silicates are thought to have crystallized during Tertiary regional metamorphism at conditions of zeolite and greenschist facies. Recently we came across a new occurrence of a mineral assemblage different from those described previously and found it worthwhile to report some mineralogic and chemical data especially since it includes *kutnahorite*, a rare mineral which is new for Switzerland.

In 1969 one of us (R. M.) found pink minerals in quartzite layers a few meters W of the summit of Piz Cam, Bergell. Coordinates of the Swiss National Map for this locality are 767.1/137.7. A second visit showed that these quartzites which are interbedded in chlorite-muscovite-clinozoisite schists and calcite

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marbles are folded and extend over several hundred meters. Typical metamorphic index minerals in the associated rocks are albite and chloritoid (WENK, 1974). We collected specimens, several of which could not be identified by visual inspection. Since many of the minerals are fine-grained and show similar optical properties also determinations with the petrographic microscope were often ambiguous. We relied on microprobe analyses to identify carbonates and on Debye-Scherrer photographs of crushed single crystals picked from thin sections for pyroxenoids. Some samples were also investigated by transmission electron microscopy. Microprobe analyses were recalculated into mineral formulas and are listed in Table 1 (complete analyses are available from H. R. W. on request).

Table 1. Mn-minerals Piz Cam. Chemical formulas. (Averages of microprobe spot analyses, all Fe expressed either as Fe^{2+} or Fe^{3+})

	Mg	Mn	Fe^{2+}	Ca	CO_3			Sample No.
Rhodochrosite	0.02	0.86	0.14	0.10				1
	0.02	0.84	0.08	0.12				6
	0.02	0.81	0.04	0.13				7
	0.00	0.80	0.01	0.13				8
Kutnahorite	0.21	0.20	0.07	0.52				2
Calcite	0.00	0.00	0.00	0.99				8
	Mg	Mn	Fe^{2+}	Ca	Si	Al	O_3	
Rhodonite	0.01	0.87	0.02	0.08	1.01			1
	0.01	0.86	0.02	0.08	1.02			1
	0.02	0.92	0.05	0.10	0.94	0.04		6
	0.01	0.80	0.05	0.08	1.03			7
	Mg	Mn	Fe^{2+}	Ca	Al	Si	O_{12}	
Spessartine	0.02	2.38	0.18	0.46	1.99	2.99		2
	0.04	1.96	0.56	0.71	1.88	2.96		2
	0.01	2.45	0.41	0.55	1.67	3.04		6
	0.02	2.26	0.42	0.43	1.93	3.01		8
	Mg	Ca	Mn^{3+}	Fe^{3+}	Al	Si	$O_{12.5}$	
Piemontite	0.01	1.88	0.43	0.58	2.18	2.94		5

Sample description

1. Rhodochrosite – rhodonite – spessartine quartzite.
2. Spessartine – rhodonite – Mn – dolomite schist.
3. Piemontite – quartzite.
6. Rhodochrosite – rhodonite – spessartine quartzite.
7. Hematite (with alteration to Mn_2O_3) bearing rhodochrosite – rhodonite quartzite.
8. Quartzbearing spessartine – rhodochrosite rock with calcite veins, oxidized.

In our samples we identified five Mn-minerals but cannot be sure that these are the only ones present at the locality. Below is a short description of each.

We found three carbonates. The most common is *rhodochrosite*. Crystals are heavily twinned on $e = (01\bar{2}1)$ due to deformation (associated quartz shows deformation bands). 10–13 atomic percent Ca substitute for Mn. Some rhodochrosite layers are crosscut by veins of *calcite* which does not contain manganese, others by veins of the Mn-dolomite *kutnahorite* (FRONDEL and BAUER, 1955). The grain size of this rare carbonate is larger than the groundmass rhodochrosite (0.5–1 mm). Kutnahorite is moderately twinned. Crystals are homogeneous and show sharp and intensive ordering reflections $h\bar{h}0l : l = 2n$ in selected area electron diffraction patterns.

Rhodonite identified by Debye-Scherrer patterns of single grains form lenticular aggregates, generally within rhodochrosite masses. Crystals show frequent lamellar twinning. About 10 atomic percent of Mn is replaced by Ca. In these samples which we analyzed with X-ray methods we could not find any pyroxmangite which is a common Mn silicate at other localities in the Rhetic Alps (PETERS *et al.*, 1973).

Spessartine is common in most Mn-mineral assemblages. Its composition is variable (Table 1) which may be due to partial alteration which is often observed. In hand specimens spessartine is colored brown, in thin sections it appears green.

Spectacular *piemontite* occurs at the base of the outcrop as bladed crystals up to 1 cm long and is associated only with quartz.

Textures are complicated and there is no evidence for chemical equilibrium of the various phases. There are retrograde alterations and secondary veins which indicate that crystallization occurred at different stages. The most likely equilibrium assemblage is rhodonite-rhodochrosite-quartz. It does not seem justified to use phase relations (e.g. ALBRECHT and PETERS, 1975; MARESCH and MOTTANA, 1976; PETERS *et al.*, 1973) to predict quantitatively metamorphic conditions for this locality. PETERS *et al.* (1973) observed with increasing grade a change from rhodochrosite-quartz to rhodochrosite-pyroxmangite and rhodochrosite-tephroite assemblages. Rhodochrosite-rhodonite may represent the higher temperature equivalent (MARESCH and MOTTANA, 1976). For stratigraphic arguments the metamorphism has to be post-Jurassic. In their description of lamprophyric dikes at nearby Piz Lizun, NIEVERGELT and DIETRICH (1977) suggest that it may have been very early Tertiary of Cretaceous.

It is of interest to find concentrations of manganese in the rather monotonous gneiss series of the Suretta nappe. It was proposed by FERRARIO and MONTRASIO (1976) that the Mn deposits and associated amphibolites in the contact zone of the Bergell granite represent relics of oceanic crust. Mn-silicates occurring with tonalite may constitute the same unit (WENK *et al.*, 1977) and recently NIEVERGELT and DIETRICH (1977) followed the suggestion of WENK (1973) that greenstones at Piz Cam and Piz Lizun and amphibolites in V. Forno may both belong to the Suretta nappe. Clearly Mn-mineralization cannot be used as a tectonic indicator but reflect chemical and physical conditions in the ocean (e.g. BURNS and BURNS, 1975; THOMIS and BURNS, 1975). It points nevertheless to a similar early history and perhaps depositional proximity of higher Pennine and lower Austroalpine nappes.

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Note added in proofs: In a recent publication PETERS et al. (1978) discuss occurrences of Mg-free manganese calcites with up to 50% $MnCO_3$ in similar assemblages. The relationship between Mg-bearing kutnahorite and manganese calcite in metamorphic rocks emerges now as a crucial mineralogic problem especially in comparison with the enigmatic low temperature dolomite.

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