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Goldmanite from the black slates of the Ogcheon belt, Korea

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ABSTRACT

Goldmanite, the vanadium analogue of grossular and andradite, was found as subrounded green porphyroblasts ranging from 0.1 to 1.7 mm in size in the carbonaceous black slates from the Deokpyeong area of the Ogcheon belt in Korea. A radiating aggregate of slightly curved blades of goldmanite crystals displays birefringence and replaces the fine-grained black matrix. The V_2O_3 content ranges from 21.9 to 26.6 wt.% (24.0 wt.% average), higher than previously reported values. The calculated mole % of the goldmanite end-member ranges from 72 to 91. Its cell dimension was calculated to be 12.04 Å from X-ray diffraction. The black slate in the Deokpyeong area is the richest known accessible source of relatively pure goldmanite.

KEYWORDS: black slate, garnet, goldmanite, vanadium.

Introduction

GOLDMANITE ($Ca_3V_2Si_3O_{12}$) is the vanadium analogue of grossular and andradite. Moench and Meyrowitz (1964) described the mineral from a metamorphosed uranium-vanadium deposit in sandstone in New Mexico and gave it the name goldmanite. Subsequently, several occurrences were reported from the skarn deposits in Western Siberia (Shepel' and Karpenko, 1970); the metamorphosed Cambrian carbonaceous shale from Northern Kazakhstan (Filippovskaya *et al.*, 1972); the calcareous metapelites and skarns in France (Benkerrou and Fonteilles, 1989); and the Palaeocene sandstone of the North Sea (Hallsworth *et al.*, 1992). In this paper, we report goldmanite from the black slates of the Ogcheon belt in Korea.

The Ogcheon belt is located between the Precambrian Ryeongnam and Gyeonggi massifs and consists of highly deformed Late Proterozoic to Palaeozoic metasedimentary rocks such as metapsammite, metapelite, marble, and diamictite, and Jurassic and Cretaceous granites (Koh and Kim, 1995). Although many geological studies of the Ogcheon belt have been carried out, its stratigraphic framework has not been established due to the lack of identifiable fossils and the complex transposition of its strata. In particular, black slates in the Munjuri Formation attract much economic interest due to their anomalously high content of rare elements (Lee *et al.*, 1981; Lee, 1986; Lee *et al.*, 1986; Kim, 1989). In an extensive geochemical analysis of 369 samples, the black slates contain on average 245 ppm U, 3200 ppm V, 2080 ppm Cu, 360 ppm Mo, 1700 ppm Zn, and 620 ppm Ni (Kim, 1989). The black slates are also rich in graphitic carbon (20% average), and are exploited in some parts for anthracitic coal. During a study of uranium mineralization, vanadian garnet was found in the black slate of Munjuri Formation in the Deokpyeong area in the northeast of the Ogcheon belt (Fig. 1).

Mineralogy

A specimen of the black slate was collected from a road cut in the Deokpyeong area. Mineralogical analysis shows that the slate consists mainly of graphite, clinochlore, pyrite, tremolite, celsian and quartz with minor amounts of baryte, goldmanite, uranocircite, uraninite, ph'ogopite, apatite, titanite and talc. Goldmanite occurs as subrounded grains scattered in the fine-grained matrix. The green goldmanite contrasts with the black matrix. The grain sizes range from 0.1 to 1.7 mm (0.6 mm average). The volume fraction is estimated at 1.3%. In petrographic observations of thin sections, goldmanite appears to be a radiating

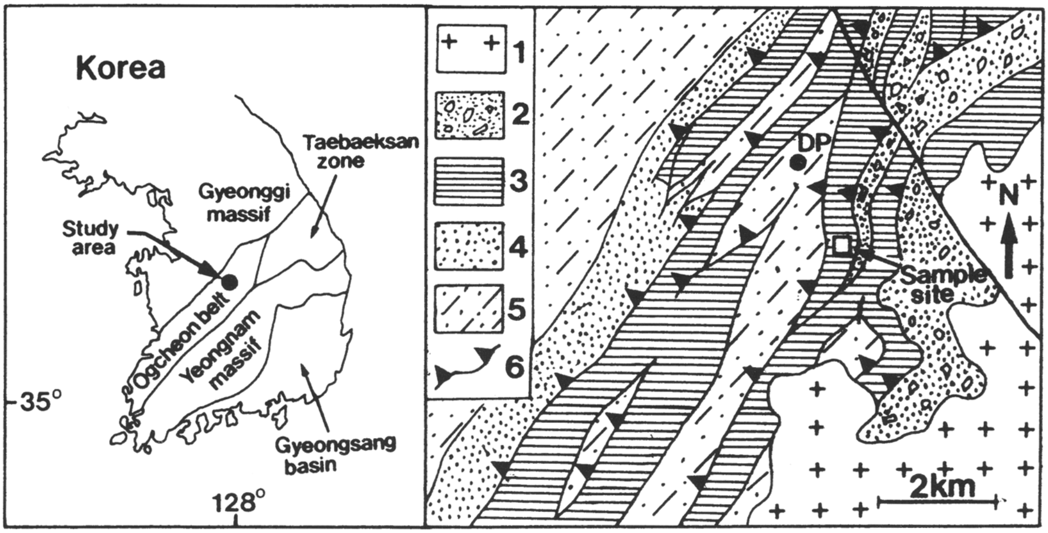

FIG. 1. Geological map and location of the Deokpyeong area in the northeast of the Ogcheon belt (after Koh and Kim, 1995). 1, Cretaceous granite; 2, Hwanggangni Formation (pebble-bearing phyllite); 3, Munjuri Formation (mica schist, black slate, phyllite, marble); 4, Taehyangsan Formation (quartzite); 5, Unkyori Formation (garnet-biotite schist, metapsammite); 6, Thrust faults. DP: Deokpyeong.

aggregate of slightly curved blades of various thickness that replaces the black fine-grained matrix (Fig. 2). Goldmanite displays birefringence under crossed nicols.

The chemical composition of goldmanite was determined using a wavelength-dispersive X-ray spectrometer attached to a CAMECA SX51 electron microprobe under the following conditions: 15 kV, 10 nA, 20 s counting time, and 10 μm beam diameter. The standards used were Si, albite; Al, corundum; V, vanadinite; Ca, wollastonite; Mn and Ti, $MnTiO_3$; Fe, hematite; Mg, periclase; and Cr, Cr_2O_3. The V_2O_3 content ranges from 21.9 to 26.6 wt.% (24.0 wt.% average) (Table 1). Detailed analyses for a selected single grain showed a random compositional variation between 23.2 and 25.1 wt.%. The composition can be described as a solid solution of two end-members, goldmanite and grossular. The calculated mole% of the goldmanite end-member ranges from 72 to 91, whereas that of grossular ranges from 5 to 23. The bulk V_2O_3 content of the slate as determined by a Jovin Yvon 138Ultrace inductively-coupled plasma atomic emission spectrometer was 0.7 wt.%. X-ray diffraction analysis was carried out on powder using a Philips X'PERT X-ray diffractometer. Measured *d*-spacings match well with those in JCPDS file No. 16-714. From the *d*842 line, the cell dimension was calculated to be 12.04 Å, which is consistent with the variation of the cell dimensions in the grossular–goldmanite solid solution series (Benkerrou and Fonteilles, 1989).

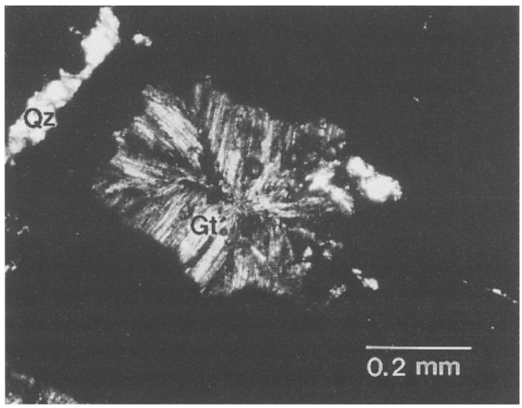

FIG. 2. Photomicrograph of a thin section under crossed Nicols showing goldmanite (Gt) in fine-grained matrix (black). Qz: quartz.

TABLE 1. Electron microprobe analyses of goldmanite

	1	7(r)**	7(m)**	7(c)**	12	13	45	46	62
SiO_2	33.53	35.99	36.14	36.04	36.05	35.67	35.83	35.44	36.18
Al_2O_3	1.84	2.83	3.86	3.17	3.10	2.69	3.32	2.65	5.10
TiO_2	0.48	0.91	1.32	1.19	0.93	0.68	0.81	0.99	0.78
Cr_2O_3	0.03	0.02	0.00	0.05	0.03	0.07	0.02	0.08	0.03
V_2O_3	26.55	24.58	23.46	24.53	24.15	25.48	24.34	25.27	21.89
MnO	0.17	0.30	0.49	0.50	0.68	0.67	0.97	0.41	0.88
FeO*	0.71	0.86	0.65	0.77	0.29	0.18	0.47	0.71	0.47
MgO	0.00	0.00	0.01	0.00	0.01	0.03	0.02	0.01	0.03
CaO	33.78	33.60	33.51	33.57	33.97	34.31	34.07	34.24	34.21
Total	99.08	99.09	99.45	99.81	99.22	99.76	99.86	99.79	99.57
Number of cations on the basis of 12 oxygens									
Si	2.962	2.980	2.966	2.961	2.978	2.945	2.949	2.930	2.958
Al	0.181	0.276	0.374	0.307	0.302	0.261	0.322	0.258	0.491
Ti	0.030	0.057	0.082	0.074	0.058	0.042	0.050	0.062	0.048
Cr	0.002	0.001	0.000	0.003	0.002	0.005	0.002	0.005	0.002
V	1.775	1.632	0.544	1.616	1.559	1.687	1.606	1.674	1.435
Mn	0.012	0.021	0.034	0.034	0.048	0.047	0.068	0.029	0.061
Fe	0.049	0.060	0.044	0.053	0.020	0.012	0.032	0.049	0.032
Mg	0.000	0.000	0.001	0.000	0.001	0.003	0.003	0.001	0.004
Ca	3.018	2.981	2.948	2.955	3.005	3.035	3.004	3.032	2.998
Garnet end-members (mole %)									
Goldmanite	91.0	83.8	78.5	82.4	82.5	84.5	81.1	83.7	72.6
Grossular	5.3	10.5	14.7	10.8	12.2	11.1	13.0	10.4	21.7
Schorlomite	1.5	2.9	4.2	3.7	3.0	2.1	2.5	3.1	2.4
Uvarovite	0.1	0.1	–	0.2	0.1	0.2	0.1	0.3	0.1
Spessartine	0.4	0.7	1.1	1.1	1.6	1.5	2.2	0.9	2.0
Almandine	1.6	2.0	1.5	1.7	0.6	0.4	1.0	1.6	1.0
Pyrope	–	–	–	–	–	0.1	0.1	–	0.1

* Total Fe as FeO.
** Analyses from rim (r), middle (m) and core (c) of a single grain

The V_2O_3 content of goldmanite in the black slate is higher than previously reported values except that of a detrital goldmanite (28.7 wt.%) extracted from a drill core in the North Sea. Since the North Sea locality is not accessible, the black slate in the Deokpyeong area is the richest known accessible source of relatively pure goldmanite.

Black shale, a precursor of black slate, is well known to be enriched with trace metals relative to normal shales (Wignall, 1994). The most important process of metal enrichment is complexation with organic matter under the anoxic conditions of sedimentation. In the Ogcheon basin, vanadium possibly originated from chemical weathering of the Precambrian Ryeongnam and Gyeonggi massifs. The vanadium was complexed with organic matter under a reducing euxinic environment. Subsequent burial diagenesis and orogenic events metamorphosed the black shale into slate. Regional metamorphism *P–T* conditions of the Ogcheon belt in the Deokpyeong area are estimated at 4.2–8.2 kbar and 490–540°C respectively, which are sufficient for the crystallization of garnet (Kim *et al.*, 1995). During metamorphism, the dispersed vanadium associated with amorphous carbon mobilized to form goldmanite with the graphitization of amorphous carbon. The high vanadium content of the black shales favoured the formation of goldmanite instead of other end-member garnets.

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