

GOLDMANITE, A VANADIUM GARNET FROM LAGUNA,
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ABSTRACT

Goldmanite, $\text{Ca}_3(\text{V,Fe,Al})_2\text{Si}_3\text{O}_{12}$, is a new garnet that occurs as a constituent of a metamorphosed uranium-vanadium deposit in the Laguna uranium mining district, about 45 miles west of Albuquerque, New Mexico. The garnet is sparsely to abundantly disseminated in thin dark vanadium-rich layers in a small uranium-vanadium deposit in the Entrada Sandstone within a few feet of the base of a thick diabase sill. Viewed in thin section, the garnet is seen to occur as minute anhedral grains and euhedral dodecahedral crystals that are embedded in vanadium clay and calcite. Goldmanite is free from impurities, dark green to brownish green, and weakly anisotropic; measured $G=3.74 \pm .03$, $n=1.821 \pm .001$, and probable $a=12.011 \text{ \AA}$.

The calculated density is 3.737. The three strongest x-ray powder pattern lines with indices and intensities are 2.688 \AA (420) (100), 3.005 \AA (400) (65), and 1.607 \AA (642) (49). Microchemical analysis showed: CaO 33.3, MnO 0.3, MgO 0.7, V_2O_5 18.3, Fe_2O_3 5.4, Al_2O_3 4.9, SiO_2 36.6, sum 99.5 per cent, or:



The mineral is therefore the vanadium analogue of grossular and andradite garnet. Goldmanite is named in honor of Marcus I. Goldman, sedimentary petrologist of the U. S. Geological Survey.

INTRODUCTION

Goldmanite, $\text{Ca}_3(\text{V, Fe, Al})_2\text{Si}_3\text{O}_{12}$, a new mineral, has been identified as a constituent of a metamorphosed uranium-vanadium deposit in the Laguna uranium mining district, about 45 miles west of Albuquerque, New Mexico. The garnet occurs in one of several small uranium-vanadium deposits in the Sandy (or South Laguna) mine area, about 4 miles southeast of Laguna, New Mexico. The mine area may be reached via jeep road about 3 miles southwest of U. S. Highway 66 from the Mesita village turnoff (Fig. 1).

The Sandy mine area, studied in 1955 and 1956 as part of a comprehensive investigation of the geology and uranium deposits of the Laguna district by the U. S. Geological Survey, contains many small but very interesting uranium-vanadium deposits in the Entrada Sandstone and Todilto Limestone (Hilpert and Moench, 1960, p. 457-460). The largest deposit, in the sandstone, yielded about 900 tons of low-grade ore that had a uranium-vanadium ratio of about 1:1. The deposits are of Colorado Plateau type, obscure in origin, but definitely older than the diabase noted in the following discussion.

¹ Publication authorized by the Director, U. S. Geological Survey.

The rocks of the Sandy mine area have been intruded and metamorphosed by numerous interconnecting diabase dikes and sills. The dikes are generally less than 10 feet thick, but the sills are as much as 75 feet thick and have extensively metamorphosed the country rocks and some of the uranium-vanadium deposits. Sills that are about 20 feet thick have metamorphic envelopes that are about 5 feet thick. As the intruded

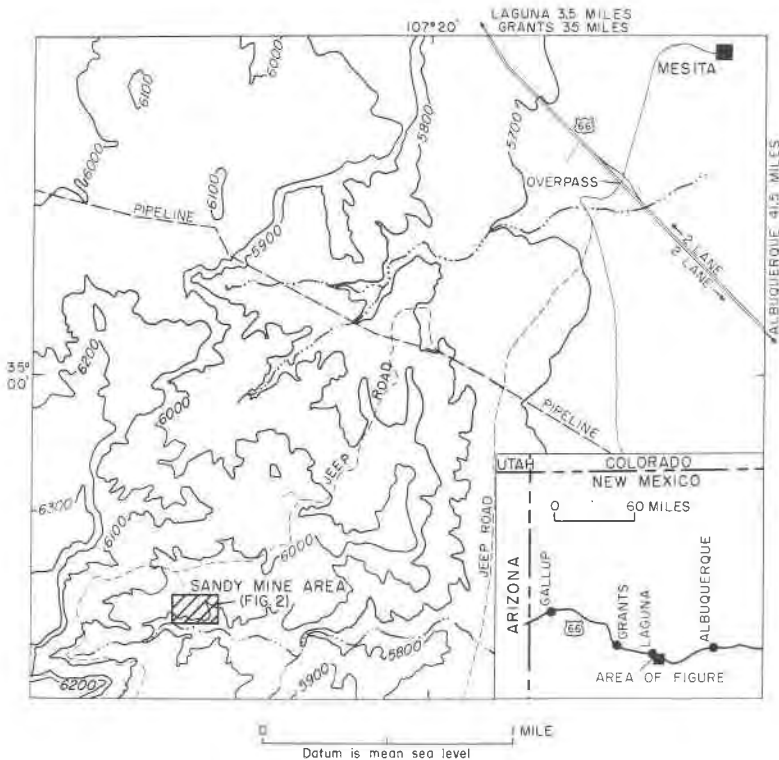


FIG. 1. Index map showing location of Sandy mine area.

rocks are limestone and calcite-cemented sandstone, a variety of calc-silicate minerals was produced, including diopside, idocrase, wollastonite, epidote and grossular-andradite; the garnet is most abundant. Other metamorphic minerals are biotite, spinel, plagioclase and pyrrhotite; the pyrrhotite occurs locally within an inch or two of the sill contacts.

While studying thin sections of metamorphosed uranium-vanadium deposits, it was noted that garnet in relatively unmineralized sandstone was colorless, whereas garnet in dark well-mineralized rock, con-

taining abundant vanadium clay and uranium minerals, was deep green or brownish green. This difference was noted within a single thin section. To confirm the opinion that the green color might be due to vanadium, two small samples of garnet were separated from dark ore, analyzed spectrographically by Nancy M. Conklin, U. S. Geological Survey, and found to be rich in vanadium (Moench, 1962).

The presence of vanadium in garnet was previously reported by Doelter (1916), who classed V_2O_3 as a rare component of calcium garnet and reported 0.09 and 0.24 per cent V_2O_3 in 2 chemical analyses. According to his formula ($Ca_3V_2Si_3O_{12}$), trivalent vanadium substitutes for aluminum and trivalent iron in the calcium garnet series. More recently, Badalov (1951) described a vanadium-rich grossular that contained 4.52 per cent V_2O_3 , the highest vanadium content reported in garnet to date. This garnet was associated with vanadium-bearing tourmaline in the contact zone between quartz veins and vanadiferous graphitic hornfels. Badalov reported that the garnet occurred in zoned dodecahedral crystals, 1.5 to 2 millimeters in diameter, that were almost colorless near their surfaces, and commonly were darker green in their central parts. The central parts were especially rich in vanadium and chromium, as shown by spectrographic analysis. Lee, Coleman, and Erd (1963) reported as much as 0.75 per cent V_2O_3 in garnet from parts of the Franciscan glaucophane schists of the Cazadero area, California.

OCCURRENCE

The goldmanite described here was obtained from the prospect pit shown near the center of Fig. 2. Similar garnet was seen in thin sections of mineralized sandstone and limestone from two other localities indicated on Fig. 2, and from several other places outside the area of Fig. 2. Garnet from the prospect pit was chosen for detailed study because the garnet is more abundant there, more homogenous, and more readily separable from the sandstone. The small uranium-vanadium deposit exposed in the prospect pit is in the Entrada Sandstone, overlain by relatively unmineralized Todilto Limestone 2 to 3 feet thick, which is overlain by a diabase sill about 20 feet thick (Fig. 2).

The uranium-vanadium deposit in the prospect pit is characterized by paper-thin to half-inch-thick layers of dark brownish gray ore-bearing sandstone that alternate with somewhat thicker layers of light tan relatively unmineralized sandstone. Quartz forms about 85 per cent of the detrital fraction of the sandstone; microcline and fragments that are too altered for identification form the remaining 15 per cent. The dark sandstone is solidly cemented by vanadium clay and subordinate calcite, whereas the light sandstone is solidly cemented by calcite. Vanadium clay

from the mine area is composed of interstratified mica (probably roscoelite) and montmorillonite; it contains 7 or 8 per cent vanadium. (*X*-ray analysis by John C. Hathaway; spectrographic analyses by Nancy M. Conklin). Uraninite and coffinite, the uranium-bearing minerals in the unoxidized ore of the Sandy mine area, have been oxidized at this locality and much uranium evidently has been leached from the deposit. Vanadium clay, in contrast, has resisted oxidation. A selected specimen of representative banded sandstone had 0.09 per cent U and 0.87 per cent V_2O_5 .

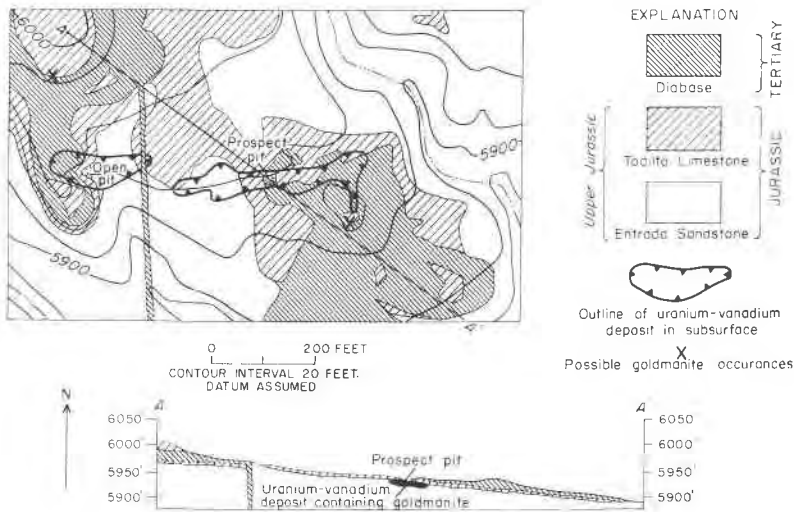


FIG. 2. Geologic map and section of part of the Sandy mine area, Valencia County, New Mexico.

Common garnet is sparsely to abundantly disseminated through the sandstone and encrusts joint surfaces, but goldmanite is confined to the dark layers rich in vanadium clay. Garnet that encrusts joint surfaces contains little vanadium (analyzed spectrographically) and is probably andradite-grossular. Viewed in thin section, the garnet in the light colored layers is nearly colorless and is probably andradite-grossular, whereas goldmanite, associated with vanadium clay, is deep green to brownish green.

Goldmanite in the prospect pit is fine-grained, rarely exceeding 0.1 millimeter and averaging about 0.02 millimeters in diameter. Viewed in thin section, it is generally free of impurities, and unzoned. Where associated with vanadium clay, goldmanite is anhedral and locally may com-

pletely fill the interstices between 3 or 4 small detrital quartz and feldspar grains. Where embedded in calcite, goldmanite is euhedral; many small crystals of separated goldmanite exhibit sharply defined dodecahedral faces.

SEPARATION

Owing to its fine grain size and the solidly cemented character of the rock, goldmanite was difficult to separate. First, more than a pound of dark vanadium-rich rock was broken from the paler sandstone. The dark material was then crushed, screened into 3 size classes ranging downward from somewhat less than that of the largest garnet grains, and further disaggregated and cleaned, using an ultrasonic vibrator. Quartz, feldspar, calcite, vanadium clay, and other relatively light minerals were removed with bromoform and methylene iodide. The heavy concentrates contained goldmanite, detrital ilmenite, and possibly some spinel. Goldmanite was further concentrated using a Frantz electromagnetic separator, and then hand picked under a microscope until 60 milligrams of goldmanite without visible impurities were obtained. A 55-milligram sample of the final separate was submitted to Robert Meyrowitz for microchemical analysis.

PROPERTIES

The approximate density, G , of goldmanite was determined by finding the density ($3.74 \pm .03$) of diluted Clerici solution in which small fragments remained suspended. Because of fine grain size, more accurate determination of the density was not attempted. The calculated density (3.737) agrees with the measured value.

The index of refraction, n , was found by immersion to be $1.821 \pm .001$, using sodium light and correcting for small temperature changes. Like many calcium garnets, goldmanite is weakly anisotropic.

The probable cell edge of goldmanite is 12.011 \AA , determined by x-ray powder diffraction analysis, using halite as an internal standard, and projecting the computed cell edges for the .8863 and smaller d spacings (Table 1) to $90^\circ \theta$. The peaks were indexed using data on synthetic end member andradite, the pattern of which is similar in spacings and intensities to that of goldmanite. The intensities reported in Table 1 were averaged from two separate diffractometer runs.

In Table 2 the properties of natural goldmanite described in this report are compared with Skinner's (1956) values for synthetic end member garnets. Although the cell edge of goldmanite, which is not an end member, is close to Skinner's value for synthetic end member andradite, the value of the density and the refractive index of goldmanite are

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR GOLDMANITE

Cu radiation, $\lambda = 1.54050$; Ni filter			
hkl	$2\Phi(\text{CuK}\alpha_1)$	$d(\text{\AA})$	Intensity (approximate)
220	20.86	4.255	12
400	29.69	3.005	65
420	33.30	2.688	100
332	34.95	2.565	9
422	36.60	2.453	38
510	38.15	2.357	16
521	41.10	2.194	16
611	46.51	1.951	22
620	47.80	1.901	8
444	52.70	1.735	8
640	55.04	1.667	18
642	57.30	1.607	49
800	61.69	1.502	10
840	69.85	1.345	9
842	71.91	1.312	10
664	73.83	1.282	4
10·4·0	87.21	1.117	9
10·4·2	89.12	1.098	9
880	92.91	1.063	6
12·0·0	100.43	1.002	3
12·2·0	102.40	.9883	3
12·2·2	104.33	.9753	9
12·6·0	118.56	.8960	5
12·6·2	120.70	.8863	3
14·2·0	130.01	.8498	1
12·8·0	135.15	.8333	7
14·4·0	137.95	.8252	6
14·4·2	140.83	.8176	12
14·4·2	141.62 (CuK α_2)	.8176	7

distinctly lower, as might be expected in view of the fact that vanadium has a smaller atomic weight than iron and that 6-coordinated, 3-valent vanadium has a larger radius than structurally equivalent iron (Ahrens, 1952, Table 16). Thus, the cell edge and refractive index of goldmanite plot outside the diagrams of Sriramadas (1957) and Winchell (1958) for the common garnets. However, as the cell edge, refractive index, and density of goldmanite are all within the grossular-andradite range, it is conceivable that large amounts of vanadium in calcium garnets would escape detection except by chemical or spectrochemical analysis. As vanadium is not an uncommon minor constituent of metamorphic rock,

TABLE 2. PROPERTIES OF GOLDMANITE AND THE COMMON END MEMBER GARNETS

Garnet	Goldmanite ¹	Grossular ²	Andradite ²	Pyrope ²	Almandite ²	Spessartite ²
Cell edge (Å)	12.011	11.851	12.048	11.459	11.526	11.621
Refractive index	1.821	1.734	1.887	1.714	1.830	1.800
Density (measured)	3.74	—	—	—	—	—
Density (calculated)	3.737	3.594	3.859	3.582	4.318	4.190

¹ Goldmanite of this report.

² Skinner (1956)

it may be in calcium garnets more commonly than has been recognized to date.

COMPOSITION

The microchemical analysis is given in Table 3, and microspectrochemical analysis in Table 4.

Spectrographic analyses of two samples by Nancy M. Conklin have been reported (Moench, 1962). One sample (G-2a) had 21 per cent vanadium in the quantitative analysis, which is excessive inasmuch as the sample also gave about 7 per cent aluminum and 4.3 per cent iron. Conceivably this sample was contaminated by vanadium-rich spinel, for Mary E. Mrose (written communication, 1958) found lines close to those of a spinel-type mineral as well as garnet in one *x*-ray powder pattern. The other sample (G-2b) had 14 per cent vanadium, which is more nearly commensurate with the 18.3 per cent V₂O₃ (12.5 per cent V) reported in

TABLE 3. MICROCHEMICAL ANALYSIS OF GOLDMANITE

Analyst: Robert Meyrowitz

Constituent	Weight per cent
SiO ₂	36.6
Al ₂ O ₃	4.9
Fe ₂ O ₃	5.4
V ₂ O ₃	18.3
CaO	33.3
MgO	0.7
MnO	0.3
Total	99.5

Table 3. In addition to the elements listed in Table 3, Conklin's semi-quantitative spectrographic analysis of sample G-2b (Moench, 1962) showed .15 per cent titanium, .007 per cent barium, .03 per cent chromium, and .007 per cent copper. None of these four elements was found by C. L. Waring in the microspectrochemical analysis of the chemically analyzed sample.

Because the garnet formed in a uranium-vanadium deposit, one might expect it to contain uranium as well as vanadium, but none was detected. The usual sensitivity of uranium in spectrographic analysis is about 0.05 per cent, but as Conklin used a dilution technique in the semi-quantita-

TABLE 4. MICROSPECTROCHEMICAL ANALYSIS OF GOLDMANITE
Analyst: C. L. Waring, U. S. Geological Survey

Per cent ¹	Elements
>10	Ca, Si, V
3	Al, Fe
0.1	Mg

¹ For methods and ranges reported see Waring and Worthing (1961) and Waring (1962).

tive analyses because of the small size of the samples, somewhat more than 0.1 per cent uranium might have escaped detection.

ANALYTICAL PROCEDURES

The selection of methods for the chemical analysis of goldmanite was guided by the microspectrochemical analysis of the mineral (Table 4). Microchemical procedures were used for the various determinations upon separate splits of 49 milligrams of the 55 milligram sample. One portion (approximately 10 milligrams) was used for the determination of total iron, total vanadium, CaO, MgO and MnO; a second portion (approximately 4 milligrams) was used for the determination of SiO₂ and Al₂O₃.

The first portion of the sample was decomposed in a mixture of H₂SO₄ and HF. Aliquots of the sulfuric acid solution were used for the total iron, total vanadium, MgO, MnO, and CaO determinations.

Total iron was determined spectrophotometrically by the o-phenanthroline procedure and calculated as Fe₂O₃. Total vanadium was determined spectrophotometrically by the hydrogen peroxide procedure and calculated as V₂O₃. Total MgO plus CaO was determined by photometric microtitration with approximately 0.001 M standard disodium ethylene diamine tetra-acetate (Versene) using Eriochrome Black T as the indicator. MgO was determined spectrophotometrically by the "Clayton-

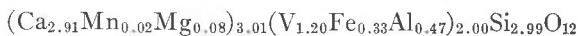
Yellow" (Thiazole Yellow) procedure. Because the amount of magnesium present in the aliquot of the solution taken for the determination of total MgO plus CaO was very small, a known amount of magnesium was added. CaO was then computed by difference between the MgO and the total MgO plus CaO determinations.

The second portion was decomposed by fusion with NaOH in a 3 milliliters size gold crucible. The melt was dissolved in dilute HCl and aliquots of the resulting solution were used for the determination of SiO₂ and Al₂O₃.

SiO₂ was determined spectrophotometrically by the molybdenum blue procedure, with 1-amino-2-naphthol-4 sulfonic acid-sulfite solution as the reducing agent. Al₂O₃ was determined spectrophotometrically using Alizarin Red S. with calcium. The aliquot of the solution used for the determination of Al₂O₃ was oxidized by boiling with (NH₄)₂S₂O₈ to insure that all the vanadium was in the V⁵⁺ state before the determination was made. A standard curve was made using known Al₂O₃ solutions containing the same concentrations of iron and V⁵⁺ present in the aliquot of the sample taken for the determination of Al₂O₃. Ferric iron was reduced by hydroxylamine hydrochloride and then the ferrous iron was complexed by the addition of thioglycolic acid and potassium ferri-cyanide.

FORMULA

The formula of goldmanite, as computed from the microchemical analysis, is:



This formula conforms to the general garnet structural formula A₃^{VIII}B₂^{VI}X₃^{IV}O₁₂, and the garnet is the vanadium analogue of grossularite and andradite. In terms of end members, the analyzed garnet contains 59.8 mole per cent Ca₃V₂Si₃O₁₂, 20.1 mole per cent grossular, 16.7 mole per cent andradite, 2.7 mole per cent pyrope, and 0.7 mole per cent spessartite.

The small amounts of magnesium and manganese present are assumed to be 8-coordinated, and the good 1:4 balance between silicon and oxygen virtually precludes the possibility of substitution of iron, aluminum, or vanadium in the 4-coordinated sites. Though the valences of vanadium and iron could not be determined chemically, the assumption that both are trivalent and 6-coordinated is most reasonable.

According to Hans H. Adler (writt. comm., July 12, 1963), the infrared spectrum of goldmanite is similar to that of andradite, but with ν₃ vibrations (11-12 microns) of the silicate ions shifted to slightly lower frequencies. The absence of absorption corresponding to the ν₃ vibra-

tions of vanadate ions, which occur characteristically in the range of 12–14 microns, is evidence against the presence of such ions in substitution for SiO_4^{4-} groups. The spectral shift and absence of vanadate absorptions support the conclusion that vanadium occurs in 6-coordinated positions.

DISCUSSION

Goldmanite is merely one of a host of new synthetic and natural garnets (Geller *et al.*, 1960; Milton *et al.*, 1961). Indeed, further possibilities seem almost inexhaustible. Goldmanite is of geologic interest, however, because of the bearing it has on the age of the uranium-vanadium deposits of the Laguna district relative to the emplacement of diabase, as well as for the bearing it may have on the mineralogic distribution of elements in metamorphic terranes.

In his study of the distribution of elements in some metamorphic minerals in the gneisses of southwestern Quebec, Kretz (1959, p. 382–386) noted that the vanadium content of garnet relative to the vanadium contents of coexisting biotite or hornblende increased with the calcium content of the garnet. He suggested that the presence of calcium in garnet increased the affinity of the structure for vanadium, and noted that iron, magnesium and manganese did not have the same influence. This is perhaps attributable to the relatively larger unit cell size of calcium garnets, facilitating the substitution of the relatively large, trivalent vanadium (Ahrens, 1952, Table 16) in the octahedral positions. None of the garnets listed by Kretz (1959, Table 4) is close to the andradite-grossular series in composition (maximum $\text{CaO} = 7.1$ per cent), and vanadium is present only in trace amounts (maximum $\text{V}_2\text{O}_3 = 0.032$ per cent). True calcium garnet, however, might be expected to act as a “blotter” for the available vanadium in a metamorphic rock.

The diabase sills and dikes of the Laguna district have been inferred from structural evidence to be younger than the uranium-vanadium deposits (Hilpert and Moench, 1960; Moench, 1963). The presence of goldmanite in the contact metamorphic envelope also indicates this age relation, for the garnet must have formed at the expense of vanadium-bearing minerals in the ore. As vanadium clay is the only identified vanadium-bearing mineral in the unoxidized ores of the Sandy mine area, and as calcite is abundant in these ores, goldmanite probably is a product of a complex reaction involving vanadium clay and calcite. Other metamorphic minerals may have acquired vanadium and possibly uranium during metamorphism, but they have not been investigated.

THE NAME GOLDMANITE

The name goldmanite has been approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association.

The mineral is named for Marcus I. Goldman, for 37 years a sedimentary petrologist of the U. S. Geological Survey, and a perfectionist in all of his researches. The name is particularly appropriate because Dr. Goldman (with A. C. Spencer) studied the Entrada Sandstone, the host rock for goldmanite in the Laguna area, and associated units in southwestern Colorado (Goldman and Spencer, 1941).

Although the name goldmanite is intended to apply only to the mineral described here, it is suggested that the name be used for all calcium garnets in which the number of 6-coordinated vanadium atoms is greater than the sum of all other 6-coordinated atoms.

ACKNOWLEDGEMENTS

This study was greatly assisted by several people of the U. S. Geological Survey, none of whom, of course, is responsible for any misinterpretations or misstatements of fact that may be embodied in this report. Moench is particularly indebted to Mary E. Mrose for her friendly interest and material assistance in the early stages of the work, and to A. J. Gude, III, E. J. Young and Theodore Botinelly for the considerable assistance they gave in making the various mineralogic determinations. B. F. Leonard, G. L. Snyder, and D. E. Lee, all of the Survey, critically read the manuscript and made many helpful suggestions.

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Manuscript received, August 30, 1963; accepted for publication, February 29, 1964.