

MANGANOAN ILMENITE FROM A SIERRAN ADAMELLITE

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ABSTRACT

Manganoan ilmenite occurs as a late minor accessory constituent of an adamellite in the northwest part of the Bass Lake quadrangle, Mariposa County, California. The mineral is not zoned, but does show appreciable grain-to-grain variation in manganese and iron. Electron microprobe analysis of a grain containing highest manganese gives MnO 11.1, FeO 28.8, TiO₂ 52.0 Fe₂O₃ 4.5, Mn₂O₃ 3.3, Al₂O₃ 0.3, V₂O₅ 0.06 weight percent, summation 100.06 percent, corresponding to the structural formula [Fe²⁺_{1.19}Mn²⁺_{0.47}] [Ti_{1.94}Fe³⁺_{0.17}Mn³⁺_{0.12}Al_{0.02}V_{0.002}]O₆. Valence states of manganese and iron were estimated with the electron microprobe by comparing the L_{α1,2}/L_{β1} line intensity ratios of these elements with an analyzed ilmenite and a synthetic oxide.

INTRODUCTION

During an earlier study (Snetsinger, 1965) of the character and frequency of occurrence of heavy accessory mineral constituents in granitic rocks exposed south of the Yosemite Valley, California, an ilmenite was found, the enlarged cell dimensions of which suggested the presence of appreciable manganese. Detailed chemical investigation was not then feasible, but subsequent electron microprobe analysis has shown that the ilmenite is indeed a manganoan variety. Results of chemical study of this mineral are given below, together with some suggestions regarding its paragenesis.

OCCURRENCE; PETROGRAPHY

The manganoan ilmenite occurs in a quartz-rich adamellite exposed three miles southwest of the southernmost park boundary of Yosemite National Park, in the northwest part of the U.S. Geological Survey's 15' Bass Lake quadrangle. This rock unit is believed equivalent to the Taft adamellite of Yosemite Valley (Snetsinger, 1965). Modal analysis of the rock in which the ilmenite occurs gives: quartz, 43 percent; K-feldspar, 23 percent; plagioclase, 30 percent; ferromagnesian minerals (mainly biotite containing 1.1% MnO), 4 percent. The ilmenite is preferentially associated with biotite, is never larger than 50 μm in grain size, and, as determined by a quantitative separatory procedure, makes up 0.02 weight percent of the rock.

ANALYTICAL PROCEDURES

By a combination of heavy liquid and electromagnetic procedures, a pure separate of the ilmenite was obtained, and embedded and polished in a plastic mount for analysis with an ARL-EMX electron microprobe.

Titanium and iron were determined by reference to a wet-chemically analyzed ilmenite. Manganese was measured using the pure element, and for analysis of vanadium and

aluminum, other standard ilmenites containing these elements were used. All instrumental and appropriate matrix-effect corrections were made, but the latter were small for most elements owing to the similarity of sample and standards. An atomic number correction was, however, necessary in the determination of manganese, and was estimated by measuring iron in a well-analyzed chromite, using pure iron as a standard. After all other corrections were made, the factor necessary to obtain the proper iron value for the chromite was assumed due to atomic number difference, and this factor was applied to the manganese value proportionally according to the atomic number difference between the ilmenite and pure manganese. Had this correction not been made, the manganese value would have been too low by 9 percent of the amount present.

In estimating oxidation states of iron and manganese, use was made of the change in relative intensity of the $L_{\alpha_{1,2}}$ line to the L_{β_1} line with change in valence of these elements; as the trivalent increases over the divalent state, intensity of $L_{\alpha_{1,2}}$ decreases relative to L_{β_1} . This relation has been noted by Fischer (1964; 1965) and Andersen (1967). Taking iron as an example it is suggested that the intensity change may arise for the following reasons. In going from the neutral to the divalent state iron has lost its two N-shell electrons and is left with six electrons in the outermost (d) subshell of the M shell. Removal of an electron from this shell results in the trivalent state; the number of electrons in the outermost M subshell is now reduced to five. The L_{α_1} line is the most intense component of the $L_{\alpha_{1,2}}$ doublet, and occurs when an electron in the outermost M subshell makes a transition to a vacancy in the L shell. Because there are more electrons in the outer M subshell available to make this transition if the iron is divalent than there are if it is trivalent, the intensity of $L_{\alpha_{1,2}}$ is greater for Fe^{2+} than for Fe^{3+} ; the intensity of $L_{\alpha_{1,2}}$ measured relative to L_{β_1} therefore decreases with increasing oxidation state. This discussion applies analogously to manganese, and the same intensity change is observed. A small wavelength shift of the $L_{\alpha_{1,2}}$ line is also involved: in the trivalent state the M shell is pulled farther away from the L shell as a result of bonding, so the $L_{\alpha_{1,2}}$ line has a higher energy and a shorter wavelength than it does in the divalent state. But with the analytical setup used here the effect was negligible and no analytical use was made of it. Wavelength shift has, however, been successfully used to determine the valence states and coordination of iron and vanadium in nolomite (Taylor and Radtke, 1967).

For the manganous-manganic determination in the ilmenite, manganous ilmenite from the *Moorsfort* chondrite was used as a reference for Mn^{2+} , it being assumed that all the manganese was manganous in view of the reduced state of the meteorite (metallic nickel-iron is present). Synthetic Mn_3O_4 (obtained from Alfa Inorganics, Inc.) served to standardize the $MnL_{\alpha_{1,2}}/MnL_{\beta_1}$ intensity ratio for the Mn^{3+} state. Conceivably the different structural situation of manganese in Mn_3O_4 as compared to the ilmenites may have affected the $MnL_{\alpha_{1,2}}/MnL_{\beta_1}$ intensity ratio in Mn_3O_4 . But the influence of this on the Mn_2O_3 result is slight, because standard and sample ilmenites are close in composition and structure, Mn_3O_4 merely being used to define an upper limit for the Mn^{3+} state. The difference in intensity ratio in the ilmenite as compared to the standards is arbitrarily assumed due to Mn^{3+} , but it is possible that higher valence states are responsible. These could not be differentiated by the method employed.

A standard ilmenite containing known amounts of FeO and Fe_2O_3 was used to obtain the $FeL_{\alpha_{1,2}}/FeL_{\beta_1}$ ratio for comparison to the manganous ilmenite. An ilmenite was chosen that contained nearly the same amount of TiO_2 (51.76%) as the manganous one (52.0%), in order to eliminate interference of 7th-order TiK_{β_1} with $FeL_{\alpha_{1,2}}$ ($TiK_{\beta_1}^7 = 17.598 \text{ \AA}$; $FeL_{\alpha_{1,2}} = 17.602 \text{ \AA}$).

High sample currents were used in order to increase counting rates on the weak L lines; measurements were carried out at 15 kV. Because a ratio between the two lines was involved

and the two are close together no absorption corrections for the L lines were made. A problem with absorption would have arisen if an L absorption edge had been located between the $L_{\alpha_{1,2}}$ and L_{β_1} lines; such was not the case in the present analysis.

It is emphasized that this method does not give independent values for divalent and trivalent oxides, but rather gives a ratio for the amount of divalent is compared to trivalent oxide. This ratio is then used to apportion the two, given the amount of the element present, as determined in the usual way using the K_{α} line. Owing to possible errors in amounts of divalent and trivalent oxides in the standards, and low counting rates on the L lines, the amounts of Mn_2O_3 and Fe_2O_3 given in Table 1 are probably not better than ± 25 percent of the actual amounts. These may be considered semi-quantitative results. But it is of interest to know that ferric iron is present, that manganese in a higher than 2+ valence state is present, and to have an estimate of the amounts of both. Because of the small amount of material available, the data could not have been obtained in my other way.

TABLE 1. ANALYSES AND STRUCTURAL FORMULAE OF MANGANOAN ILMENITES

	Chemical analyses			
	(1)	(2)	(3)	(4)
SiO ₂	nil	0.80	—	—
Al ₂ O ₃	0.3	—	—	—
Fe ₂ O ₃	4.5	12.12	11.51	3.92
Mn ₂ O ₃	3.3	—	—	—
V ₂ O ₃	0.06	—	—	—
TiO ₂	52.0	51.79	46.98	50.68
FeO	28.8	21.27	27.39	30.25
MnO	11.1	14.40	14.02	15.15
Total	100.06	100.38	100.00	100.00
Numbers of metals on basis of 6 oxygens				
Si	—	0.04	—	—
Al	0.02	—	—	—
Fe ³⁺	0.17	0.44	0.44	0.15
Mn ³⁺	0.12	—	—	—
V	0.002	—	—	—
Ti	1.94	1.90	1.79	1.93
Fe ²⁺	1.19	0.87	1.16	1.28
Mn ²⁺	0.47	0.59	0.60	0.65
	1.66	1.46	1.76	1.93

(1) Manganoan ilmenite, present report.

(2) "Manganilmenite," Simpson (1929). Analyst, E. S. Simpson.

(3) "Manganoilmenite," Omori and Hasegawa (1955). Recalculated to 100.00% after deducting 0.64% H₂O and 0.32% SiO₂. Also includes 0.10% MgO. Original summation 99.67%. Analyst, S. Hasegawa.

(4) Manganoan ilmenite, Klement (1887). Recalculated (by the analyst) to 100.00%, to eliminate silicate and rutile impurities. Analyst, C. Klement.

CHEMICAL AND PHYSICAL PROPERTIES

The manganoan ilmenite contains no inclusions and is chemically unzoned. Grain-to-grain manganese content ranges, however, from roughly 8 to 14 weight percent total manganese as MnO (higher MnO values are the more common), with concomitant variation in total iron as FeO from about 41 to 33 weight percent. Vanadium and aluminum are minor, and magnesium, silicon, chromium and calcium are all below detection (<200 ppm). As manganese increases, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, as determined with the electron probe, decreases as a result of Mn^{2+} proxying Fe^{2+} over the compositional range of the grains encountered. Unfortunately the valence state of manganese could not be determined at lower manganese levels owing to diminished intensity of the L spectrum.

Analysis of a grain containing highest manganese is given in Table 1, together with structural formula on the basis of 6 oxygens. The total number of cations (3.91) is close to the ideal 4.00. The number of divalent metals is, however, appreciably deficient as compared with the theoretical 2.00, and the summation of titanium and the trivalent cations is in excess of the ideal 2.00. This suggests that some of the trivalent cations may be substituting for divalent ones; the ferric iron reported may, however, not be in the structure, but represent hematite in solid solution.

This is the first instance where manganese in a valence state higher than 2+ has been reported in an ilmenite. As there is no evidence of secondary alteration of the mineral or the rock in which it occurs, presence of a higher state is not considered due to deuteritic alteration or weathering; rather it suggests somewhat oxidative conditions in the environment in which the ilmenite initially formed.

Ilmenites with MnO higher than 5 percent are rare, but three others occur in the literature, and are listed in Table 1 with structural formulae. Including the present one, these appear to be the only ilmenite analyses existing in the range from about 5 percent MnO to the 46.92 percent MnO present in the type pyrophanite (MnTiO_3 ; Palache, Berman and Frondel, 1951, p. 537). Ilmenite in the *Moore'sfort* chondrite, however, contains 9.8 percent MnO.

Cell dimensions for the manganoan ilmenite are listed below for comparison with ilmenite and pyrophanite (data for the latter two from Deer *et al.*, 1962, p. 21).

	<i>Ilmenite</i>	<i>Manganoan ilmenite</i>	<i>Pyrophanite</i>
<i>a</i>	5.09 Å	5.12±0.02	5.14
<i>b</i>	14.16 Å	14.23±0.02	14.36

The values are intermediate between ilmenite and pyrophanite. It should

be noted that cell dimensions were obtained from a pure ilmenite concentrate, the grains of which range in composition; thus the values are not precisely those for the analysis reported in Table 1, but correspond to an ilmenite somewhat lower in MnO content. Comparable to pyrophanite, the manganoean ilmenite has a good cleavage; this is in contrast to ordinary ilmenite, which has none.

Magnetite associated with the manganoean ilmenite contains 0.92 percent MnO, but presents no other features of interest.

PARAGENESIS

Ilmenite cutting K-feldspar was noted in a sample of the adamellite; this is taken as an indication that the manganoean ilmenite may in part be of late origin. Regarding the source of the manganese, it is suggested that the element may have been concentrated during the natural course of magmatic evolution of the rock. Larger size (0.80 Å) of the Mn^{2+} ion as compared with the Fe^{2+} and Mg^{2+} ion (0.74 and 0.66 Å, respectively, data after Ahrens, 1952), would promote a tendency for its concentration relative to these elements in later, more silicic liquids as compared to the early, original magma (Goldschmidt, 1944, p. 630). Such a late enrichment in manganese has for example been noted in minerals of the Skaergaard intrusion (Wager and Brown, 1967, p. 197). Certainly, the adamellite in which the ilmenite occurs is acidic, and may well represent a late differentiate of some granitic sequence, the earlier members of which are not, however, exposed in the area.

Electron microprobe analysis shows that ilmenite, magnetite and biotite from other samples of the adamellite contain appreciable manganese, although the enrichment is not so great as in the minerals described above. Probably the element is abundant in accessory minerals of late members of other granitic series, but this possibility remains to be investigated.

ACKNOWLEDGMENTS

The writer is grateful to Drs. A. T. Anderson and Myron G. Best for analyzed standard ilmenites, and to Dr. Charles M. Taylor for critical review of the manuscript. Support during this study was provided by a NASA-National Research Council Postdoctoral Resident Research Associateship.

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Manuscript received, August 5, 1968; accepted for publication, December 3, 1968.