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Manganoan ilmenite from the Leinster Granite, Ireland

AN electron-microprobe study of the ferromagnesian silicate and oxide minerals of the Leinster Granite (Brindley, 1969), south of Dublin, has revealed accessory ilmenite that is unusually rich in MnO (Table I).

Analysis 1 is of a single grain from a quartz–biotite–diorite (specimen no. 43); in this rock other ilmenite crystals are somewhat poorer in MnO, but the mean MnO-content of three analyses is 8·61 wt. %. Analysis 2 is the mean of two grains from an adamellite (specimen no. 7411), in which a third ilmenite contained 9·17 wt. % MnO.

The data were obtained using a Japan Electron Optics Laboratory JXA–3A electronprobe microanalyser with a 1 μm beam at 25 kV. Metal standards were used for Fe, Mn, Ti, V, Cr, Co, and Ni; orthoclase was used for Al, wollastonite for Si, and enstatite for Mg. Total iron was calculated as FeO; no V, Cr, or Mg were detected, although these elements are present in ilmenites from other rocks of the intrusion. SiO_2 is uniformly high in all the grains analysed; it is considered unlikely to be due to inclusions since coexisting magnetite is generally low in SiO_2 (unpublished data) and, secondly, high-magnification absorbed-electron images of the grains show them to be homogeneous.

Calculated unit-cell contents are presented in Table I, where ferric iron has been calculated on the basis of stoichiometric hematite–ilmenite–pyrophanite solid solutions. The ilmenite from the quartz-biotite-diorite contains 6 mol. % hematite while that from the adamellite is a binary ilmenite–pyrophanite solid solution. In each case there is 28 mol. % pyrophanite. No attempt has been made to determine directly the valence states of Fe and Mn using the intensity ratios of the $L\alpha$ and $L\beta$ lines (Snetsinger, 1969); some workers consider that the ratios depend also on coordination (Czamanske and Mihalik, 1972).

Various analyses of manganoan ilmenite have been published, notably from the Finnmarka Complex, Norway, where ilmenites contain up to 63 mol. % pyrophanite in solid solution (Czamanske and Mihalik, 1972). Several other workers have presented analyses containing up to 15·15 wt. % MnO (Snetsinger, 1969; Klement, 1887; Simpson, 1929; Omori and Hasegawa, 1955).

Two hypotheses, not mutually exclusive, have been proposed to account for the concentration of manganese in ilmenite; firstly, that residual magmas, from which ilmenite sometimes crystallizes, may be enriched in Mn relative to Fe because of relative ionic radii (Czamanske and Mihalik, 1972); secondly, that the phenomenon is a result of oxidizing conditions during crystallization or post-crystallization history or both (Snetsinger, 1969).

TABLE I. *Chemical analyses of manganoan ilmenites*

	1	2		1	2
FeO	36·44	33·05	Fe^{3+}	0·1107	—
MnO	12·75	12·77	Fe^{2+}	0·6609	0·6954
TiO$_2$	49·12	52·02	Mn^{2+}	0·2735	0·2722
CoO	0·027	0·019	Ti^{4+}	0·9353	0·9843
NiO	0·018	0·011	Co^{2+}	0·0005	0·0004
V$_2$O$_5$	n.d.	n.d.	Ni^{2+}	0·0004	0·0002
Cr$_2$O$_3$	n.d.	n.d.	Si^{4+}	0·0319	0·0237
SiO$_2$	1·26	0·94	Al^{3+}	0·0131	0·0107
Al$_2$O$_3$	0·44	0·36			
MgO	n.d.	n.d.	Fe$_2$O$_3$	6 mol. %	—
			FeTiO$_3$	66	72
Total	100·06	99·17	MnTiO$_3$	28	28
			n.d.—not detected		

Neither hypothesis accounts in a satisfactory manner for the Leinster manganoan ilmenites. The first is invalidated by two observations: firstly, petrographic examination of thin sections shows that the ilmenite crystallized relatively early since it forms inclusions in all the major silicate phases, and secondly, the quartz-biotite-diorite was an early-crystallizing member of the intrusion (Brindley and Gupta, 1974). The second hypothesis is not satisfactory either, although more data may reveal that some modification of it might explain the ilmenite chemistry. The difficulty is that the biotites equilibrated mainly at 750 °C on the quartz–fayalite–magnetite buffer curve, although a few (not those containing the most manganoan ilmenites) equilibrated at 550 °C, at oxygen fugacities a little below the magnetite–hematite buffer (unpublished data).

A quantitative electron-microprobe study of coexisting magnetite, ilmenite, biotite (and amphibole, in a few rocks) is in progress, in an attempt to elucidate processes involved in formation of the ilmenites, and to test further the hypotheses outlined above. Chemical analyses of ilmenites from other intrusions could also possibly shed light on the problem.

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Aluminian xanthophyllite and paragonite from Japan

XANTHOPHYLLITE[1] from the 900-m level of the Dōshinkubo ore deposit, Chichibu mine, Saitama Prefecture, Japan, was described by Harada, Kodama, and Sudo (1965). Very similar material occurs in the 800-m level of the same mine as a constituent of pre-ore skarn, closely associated with diopside, wollastonite, idocrase, ellestadite, calcite, and thaumasite (Harada, Nagashima, Nakao, and Kato, 1971). The atomic ratios show that it has more dioctahedral character and is richer in aluminium than any xanthophyllite hitherto described. Chemical, optical, and X-ray data are included in Table I, with those of a margarite from the Shinkiura mine, Ōita Prefecture (Aoki and Shimada, 1965) for comparison. The optical absorption spectrum of this xanthophyllite is shown in fig. 1. In analogy with the assignments of Faye (1968) for the spectra of biotite, phlogopite, and chlorite, the 25300 cm^{-1} and 22300 cm^{-1} bands of the xanthophyllite may be spin-forbidden d-d bands of octahedrally coordinated Fe^{2+}, the 11800 cm^{-1} and 9800 cm^{-1} bands may be spin-allowed d-d transitions of Fe^{2+}, and the 14500 cm^{-1} band charge-transfer between Fe^{2+} and Fe^{3+}. The weakness of this last
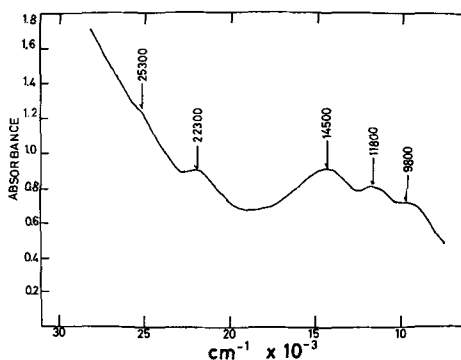

FIG. 1. Absorption spectrum of xanthophyllite; crystal flake 0·31 mm thick.

[1] This name is used here in its original sense, as a variety of clintonite low in Si, rather than the optical definition given by Deer, Howie, and Zussman (1962); there is no evidence that xanthophyllite from the type locality differs from clintonite in its optical orientation.

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