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ILMENITE IN ORDINARY CHONDRITES

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ABSTRACT

Chondritic ilmenite has the compositional range TiO_2 51.0–54.4, FeO 35.4–44.6, MgO 1.5–6.6, MnO 0.6–9.8, Cr_2O_3 0.03–1.40 wt. %. Neglecting ilmenite of unusual composition (high MgO, MnO or Cr_2O_3), the average structural formula is $(Fe_{1.75}Mg_{0.23}Mn_{0.08})(Ti_{1.96})O_6$.

Ilmenite composition shows a relation to chondrite classification: for "equilibrated" chondrites, iron content of ilmenite tends to increase as one passes from *H*- to *L*- to *LL*-group chondrites, whereas magnesium and manganese have the reverse tendency. Because the iron and magnesium variation is the same as observed in pyroxene, olivine and chromite of "equilibrated" chondrites, it is suggested that ilmenite is in equilibrium with these minerals. Owing to the rarity of ilmenite in ordinary chondrites insufficient data are available to detect trends within petrographic (*i.e.*, metamorphic) subgroups; therefore, a primary igneous or a metamorphic mode of equilibration cannot be distinguished.

INTRODUCTION

With the intention of aiding interpretation of the origin of ordinary[1] chondrites, a continuing electron microprobe study of mineralogical variation in this meteorite group has been undertaken. The work began when Keil and Fredriksson (1964) analyzed orthopyroxene and olivine in chondrites. They found that iron and magnesium in the ferromagnesian silicates varied according to the two chemical chondrite groups (*H* and *L*) established by Urey and Craig (1953), and were able to distinguish a third (*LL*) group. The distinction of *H*-, *L*-, and *LL*-group chondrites was made on the basis of changes in ferrous, metallic, and total iron contents as well as in Fe/Ni ratios in metal; ferrous iron increases from the *H* to *L* to *LL* groups, while metallic iron, total iron and Fe/Ni ratios in metal decrease (Urey and Craig, 1953; Keil, 1962a, b; Keil and Fredriksson, 1964). In addition (Keil and Fredriksson, 1964), it was found that mole percent FeO/(FeO+MgO) ratios in olivine and pyroxene of "equilibrated"[2] chondrites increase from *H* to *L* to *LL* groups.

[1] By "ordinary" chondrites we mean all chondrite types except carbonaceous and enstatite chondrites.

[2] The nickel-iron of even the most highly-"equilibrated" chondrites exhibits strong grain-boundary compositional gradients; this indicates disequilibrium. Hence the quotes around "equilibrated". As used here "equilibrated" means homogeneity (lack of zoning or grain-to-grain variation) of olivine and pyroxene; this is the sense initially given the term

Then Snetsinger *et al.* (1967) analyzed chromite from "equilibrated" chondrites and noted that composition of this mineral also shows a relation to chondrite classification: FeO and TiO_2 increase, while Cr_2O_3, MgO and MnO decrease from *H* to *L* to *LL* groups. When Van Schmus and Wood (1967) proposed a subclassification of chondrites according to degree of recrystallization, Bunch *et al.* (1967), working again with chromite, attempted to determine if this mineral exhibited any chemical relations to subgroup classification. They found some weak and often inconsistent indications of this, but were able to verify, with a larger number of analyses, the dependence of composition of chromite from "equilibrated" chondrites on chondrite classification. In the present paper data on the composition of ilmenite from chondrites are presented. Because ilmenite is very rare in the unequilibrated chondrites, data are statistically insufficient to allow conclusions to be drawn regarding trends which may exist within chondrite subgroups. It is shown, however, that composition of ilmenite from "equilibrated" chondrites is related to classification into *H*, *L* and *LL* groups and, therefore, the mineral is probably in equilibrium with coexisting phases such as olivine, orthopyroxene, and chromite.

Experimental Methods

Sample selection and description. Falls and fresh finds classified by Van Schmus and Wood (1967) were chosen from our laboratory collections. Of 70 polished sections examined, only 30 contained ilmenite, and in 10 of these the mineral was too fine grained for analysis. Ramdohr (1963) found ilmenite in over 50 percent of the stone meteorites he examined; the slight discrepancy may be due to the small sample areas available for examination in the current work. Undoubtedly ilmenite is present in many if not all ordinary chondrites, but is so very rare that likelihood of it being exposed on a small polished surface is slight. Accordingly, the analyses reported here had to be performed, in 18 out of 20 cases, on one grain of ilmenite per meteorite section. Therefore no comments can be made on grain-to-grain variation in a meteorite, nor was it possible to be selective about the textural situation of analytical grains: ilmenite in chondrules or matrix was analyzed. No exsolution lamellae were found, although the somewhat high TiO_2 content of *Prairie Dog Creek* ilmenite (Table 1) may be the result of interference from rutile underlying the analytical grain. Grains as small as 10 microns in size were successfully analyzed, but the average of grains studied was about 25 microns, the largest being about 100 microns in diameter.

Analytical procedures. Analyses were done with an ARL-EMX electron microprobe, using an accelerating voltage of 20 keV and approximately 0.02 μA sample current. A well-analyzed ilmenite was used to determine iron, magnesium, and titanium. Owing to similarity of standard and samples, no matrix-effect corrections were made for these elements. Manganese and chromium were measured by reference to pure metals; mass absorption and fluorescence corrections were made here. No atomic number correction was made for chromium, but for manganese an empirical correction was applied (see Snetsinger, 1969).

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by Dodd and Van Schmus (1965). Unequilibrated chondrites are those that contain inhomogeneous ferromagnesian silicates.

Chemical Properties

Analyses of the ilmenites, and structural formulae on the basis of 6 oxygens per unit cell, are given in Table 1, listed according to Van Schmus and Wood's (1967) subgroup classification. Total cations are almost always slightly in excess of the theoretical 4.00; this may possibly be due to presence of small amounts of ferric iron. Vanadium was carefully analyzed for in each ilmenite (using the method suggested by Snetsinger *et al.*, 1968) but was always below detection limit (<100 ppm). Absence of vanadium in ilmenite is in contrast to coexisting chromite, which contains an average of about 0.71 percent V_2O_3 (Bunch *et al.*, 1967). In several ilmenites aluminum was analyzed for but not found; it was not determined in the others. No zoning occurs in the largest grains and grain-edge effects made it impossible to detect zoning in smaller crystals.

Most of the analyses are not greatly different from any given terrestrial type, but some chondrites, listed separately in Table 2, were found to contain ilmenite with unusually high magnesium, manganese, and/or chromium contents. In all of these except *Dhurmsala* and *Mooresfort*, the ilmenite was preferentially associated with chromite. Unusual chromite compositions have been noted (Bunch *et al.*, 1967) when the latter mineral is associated with ilmenite; the same compositional anomalies appear to have affected these ilmenites, and they were not used in averaging the date given in Table 3, nor were they plotted in Figure 1. *Mooresfort* and *Dhurmsala* were eliminated from Tables 1 and 3 because their manganese contents are much higher than normal for their meteorite groups. Both *St. Michel* and *Mooresfort* ilmenites are of mineralogical interest because of their manganese contents: ilmenites with MnO greater than 5 percent are rare. The few terrestrial examples are listed in Snetsinger (1969).

Discussion

It is apparent from Table 3 that average composition of ilmenite from "equilibrated" ordinary chondrites is related to chondrite classification: FeO increases and MgO and MnO decrease from *H* to *L* to *LL* groups.[1] This trend is analogous to what was previously observed by Keil and Fredriksson (1964) for olivine and orthopyroxene, and by Snetsinger *et al.*

[1] Titanium does not show any variation simply because, manganese and iron having similar atomic weights, substitution of considerable amounts of manganese does not change the amount of titanium required. Proxying of appreciable magnesium for iron would increase the amount of titanium required, but this substitution has not taken place extensively enough for such an effect to be important. Chromium increases as one passes from the "equilibrated" *H* to *L* groups (Table 3) but does not change from the *L* to *LL* group.

TABLE 1. COMPOSITION OF ILMENITE FROM ORDINARY CHONDRITES

Group	Meteorite	Weight Percents						Cations on the Basis of Six Oxygens							
		FeO	MgO	MnO	TiO_2	Cr_2O_3	Total	Fe^{2+}	Mg	Mn	Σ^a	Ti	Cr	Σ^b	Total Cations
*(H)*3	*Brownfield*[c]	43.0	4.2	1.7	52.7	0.05	101.65	1.75	0.31	0.07	2.13	1.93	0.00	1.93	4.07
*H*3	*Prairie Dog Creek*	41.1	1.5	2.3	54.4	.06	99.36	1.71	.11	.10	1.92	2.04	.00	2.04	3.96
*H*4	*Bath*	40.4	4.7	2.6	53.1	.07	100.87	1.65	.34	.11	2.10	1.95	.00	1.95	4.05
*H*5	*Collescipoli*	41.7	4.3	2.8	51.4	.11	100.31	1.73	.32	.12	2.16	1.92	.00	1.92	4.08
*H*5	*Forest City*	41.6	4.0	3.1	51.0	.09	99.79	1.74	.30	.13	2.17	1.91	.00	1.91	4.08
*H*5	*Pantar*	40.3	3.9	3.3	52.8	.12	100.44	1.66	.29	.14	2.08	1.95	.00	1.95	4.04
*H*6	*Oakley*	39.8	4.3	3.7	51.7	.04	99.54	1.66	.32	.16	2.13	1.93	.00	1.93	4.07
Average		41.1	3.8	2.8	52.4	.08	100.90	1.70	.28	.12	2.10	1.95	.00	1.95	4.05
*(L)*3	*Mezo-Madaras*	43.4	2.3	1.0	51.8	.11	98.61	1.84	.17	.04	2.05	1.97	.00	1.97	4.03
*L*4	*Barratta*	41.9	3.0	1.4	52.6	.08	98.98	1.75	.22	.06	2.04	1.98	.00	1.98	4.02
*L*4	*Goodland*	42.1	2.8	1.4	53.4	.03	99.73	1.75	.21	.06	2.01	1.99	.00	1.99	4.01
*L*5	*Knyahinya*	41.8	3.4	1.4	52.8	.09	99.49	1.74	.25	.06	2.05	1.97	.00	1.97	4.02
*L*6	*Coon Butte*	41.9	3.1	1.5	52.6	.53	99.63	1.74	.23	.06	2.04	1.97	.02	1.97	4.02
Average		42.2	2.9	1.3	52.6	.17	99.17	1.76	.22	.06	2.04	1.98	.01	1.98	4.02
*LL*4	*Soko Banja*	43.3	2.3	1.1	53.1	.03	99.93	1.81	.17	.05	2.02	1.99	.00	1.99	4.01
*LL*6	*Jelica*	43.7	1.6	1.1	51.3	.56	98.26	1.86	.12	.05	2.03	1.97	.02	1.97	4.02
*LL*6	*Manbhoom*	44.6	2.0	1.1	52.1	.06	99.86	1.82	.15	.05	2.07	1.96	.00	1.96	4.03
Average		43.9	2.0	1.1	52.2	.22	99.42	1.83	.15	.05	2.04	1.97	.01	1.97	4.00
Average of all in Table 1		42.0	3.2	2.0	52.5	.14	99.84	1.75	.23	.08	2.07	1.96	.00	1.96	4.02

[a] Cation sum of Fe, Mg and Mn.
[b] Cation sum of Ti and Cr.
[c] Parentheses around group symbols indicate question as to classification in chemical group.

TABLE 2. COMPOSITION OF ILMENITE FROM ORDINARY CHONDRITES: UNUSUAL TYPES

Group	Meteorite	Weight Percents						Cations on the Basis of Six Oxygens							
		Feo	MgO	MnO	TiO_2	Cr_2O_3	Total	Fe^{+2}	Mg	Mn	Σ^1	Ti	Cr	Σ^2	Total Cations
H5	*Mooresfort*	35.4	2.8	9.8	51.8	.12	99.92	1.48	0.21	0.41	2.10	1.95	0.00	1.95	4.05
L5	*Paragould*	38.3	6.6	0.6	52.9	1.04	99.44	1.56	.48	.02	2.06	1.94	.04	1.94	4.04
L6	*St. Michel*	38.7	3.0	5.7	52.5	.04	99.94	1.61	.22	.24	2.07	1.96	.00	1.96	4.04
L6	*Walters*	41.0	3.4	1.0	52.3	1.40	99.10	1.71	.25	.04	2.00	1.96	.06	1.96	4.01
LL6	*Dhurmsala*	41.7	2.5	3.8	52.8	.08	100.88	1.72	.18	.16	2.07	1.96	.00	1.96	4.03

[1] Cation sum of Fe, Mg and Mn.
[2] Cation sum of Ti and Cr.

TABLE 3. ILMENITE FROM ORDINARY CHONDRITES: AVERAGES OF EQUILIBRATED GROUPS

Equilibrated Groups	Weight Percents						Cations on the Basis of Six Oxygens							
	FeO	MgO	MnO	TiO_2	Cr_2O_3	Total	Fe^{2+}	Mg	Mn	Σ^1	Ti	Cr	Σ^2	Total Cations
Average *H*5, 6:	40.9	4.1	3.2	51.7	.09	99.99	1.70	0.31	0.14	2.14	1.93	0.00	1.93	4.08
Average *L*5, 6:	41.9	3.3	1.5	52.7	.31	99.71	1.74	.24	.06	2.05	1.97	.01	1.97	4.01
Average *LL*6:	44.2	1.8	1.1	51.7	.31	99.11	1.87	.14	.05	2.06	1.97	.01	1.98	4.04

[1] Cation sum of Fe, Mg and Mn.
[2] Cation sum of Ti and Cr.

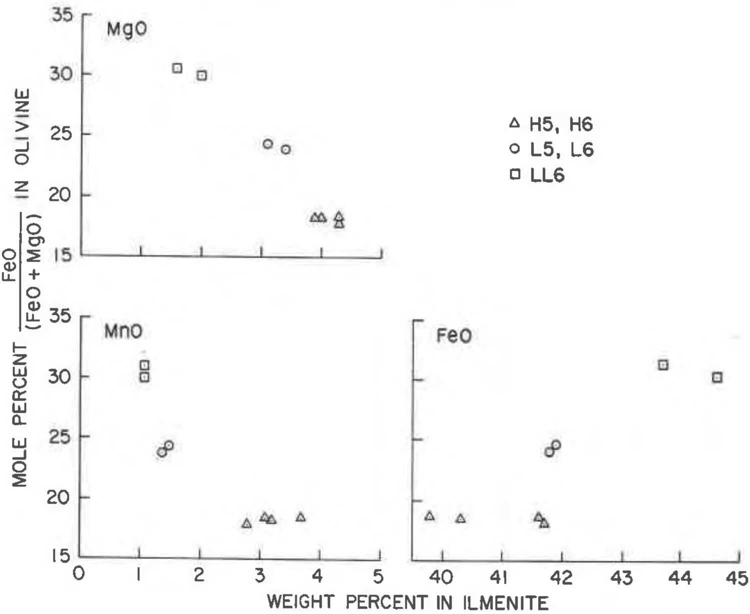

FIG. 1. Mole percent FeO/(FeO+MgO) in olivine *vs.* weight percent of MgO, MnO and FeO in ilmenite of "equilibrated" chondrites.

(1967) and Bunch *et al.* (1967) for chromite from "equilibrated" ordinary chondrites: in olivine and orthopyroxene FeO increases and MgO decreases, and in chromite FeO and TiO_2 increase and Cr_2O_3, MgO, and MnO decrease when passing from *H* to *L* to *LL* groups. In Fig. 1, FeO, MgO, and MnO of individual ilmenites are plotted against FeO/(FeO+MgO) ratios in coexisting olivines, illustrating the compositional relationships discussed. Although statistics are poor, compositional trends can be recognized. Similar graphs result when plotting orthopyroxene *vs.* ilmenite and chromite *vs.* ilmenite, although for the latter plots statistics are even poorer because chromite of about half of the ilmenite-bearing chondrites studied has not yet been analyzed. The close compositional relationship of ilmenite to olivine, orthopyroxene, and chromite in "equilibrated" ordinary chondrites suggests that it is in equilibrium with these phases. In Table 1 analyses of all but the unusual ilmenite types studied are listed. On the basis of the insufficient number of ilmenite analyses available, no comments can be made as to compositional trends within major chrondrite groups such as, for example, from *H*3 to *H*6; hence, the question of primary igneous *vs* secondary metamorphic equilibration cannot be discussed.

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