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METEORITIC RUTILE

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ABSTRACT

Rutile has not been widely recognized as a meteoritic constituent. Recent microscopic and electron microprobe studies show, however, that TiO_2 is a reasonably widespread phase, albeit in minor amounts. X-ray diffraction studies confirm the TiO_2 to be rutile. It was observed in the following meteorites—Allegan, Bondoc, Estherville, Farmington, and Vaca Muerta. The rutile is associated primarily with ilmenite and chromite, in some cases as exsolution lamellae.

Rutile, as a meteoritic phase, is not widely known. In their summary of meteorite mineralogy neither Mason (1962) nor Ramdohr (1963a) report rutile as a mineral occurring in meteorites, although Ramdohr did describe a similar phase from the Farmington meteorite in his list of "unidentified minerals." He suggested (correctly) that his "mineral D" might be rutile. He later identified it in the Mt. Browne chondrite (Ramdohr, 1963b) and in several mesosiderites (Ramdohr, 1964). The mineral was recently mentioned to occur in Vaca Muerta (Marvin and Klein, 1964) and in Odessa (El Goresy, 1965). We have found rutile in the meteorites Allegan, Bondoc, Estherville, Farmington, and Vaca Muerta; although nowhere an abundant phase, it appears to be rather widespread.

Of the several meteorites in which it was observed, rutile is the most abundant in the Farmington L-group chondrite. There it occurs in fine lamellae in ilmenite. The ilmenite is only sparsely distributed within the meteorite, although, wherever it does occur, it is in moderately large clusters—up to 0.5 mm in diameter—and it then is usually associated with chromite as well as rutile (Buseck *et al.*, 1965).

Optically, the rutile has a faintly bluish tinge when viewed in reflected, plane-polarized light with immersion objectives. It is probably strongly anisotropic, although this is difficult to determine positively as it occurs within a matrix—ilmenite—that is itself so strongly anisotropic. Because of its small size, internal reflections could only be noted in rare instances. The reflectivity is low and the hardness approximately that of the ilmenite.

The initial identification of the rutile was performed by electron beam scans across the area of interest (Fig. 1). In order to confirm the qualita-

TABLE 1. COMPOSITION OF MANGANESE-CHROMIUM-BEARING MAGNESIAN ILMENITE FROM THE FARMINGTON CHONDRITE AS OBTAINED BY ELECTRON MICROPROBE TECHNIQUES

Average of 53 analyses on 5 grains (in weight per cent)

Measured	Calculated		Ideal
Fe=25.8	FeO	33.19	47.34
Ti=34.4	TiO_2	57.38	52.66
Mg= 4.11	MgO	6.82	
Mn= 0.59	MnO	0.76	
Cr= 0.51	Cr_2O_3	0.75	
65.31		98.90	100.00

TABLE 2. COMPOSITION OF TITANIUM-MANGANESE-BEARING MAGNESIAN CHROMITE FROM THE FARMINGTON CHONDRITE AS OBTAINED BY ELECTRON MICROPROBE TECHNIQUES

Average of 50 analyses on 5 grains (in weight per cent)

Measured	Calculated		Ideal
Fe=22.4	FeO	28.8	32.09
Cr=38.4	Cr_2O_3	56.1	67.91
Mg= 3.19	MgO	5.29	
Ti= 1.72	TiO_2	2.87	
Mn= 0.63	MnO	0.81	
Al= 2.96	Al_2O_3	5.59	
69.30		99.46	100.00

TABLE 3. COMPOSITION OF RUTILE FROM THE FARMINGTON CHONDRITE AS OBTAINED BY ELECTRON MICROPROBE TECHNIQUES (IN WEIGHT PER CENT)

Measured	Calculated		Ideal
Ti=57.3	TiO_2	95.58[1]	100.00

[1] The difference to 100 per cent is iron. The iron is probably not a constituent of the rutile but originates from the electron beam overlapping ilmenite.

tive identification, quantitative electron microprobe analyses were run (Tables 1–3). The intensity readings were corrected for deadtime, background, mass absorption, fluorescence, and atomic number using methods previously described (*e.g.*, Keil and Andersen, 1965). The Ti content of the rutile was measured using a synthetic, spectrographically pure rutile standard.

The composition of the rutile was determined by moving the sample in 1-micron steps under a fixed electron beam. As the lamellae are very fine (on the order of a few microns in width), the electron beam is bound to overlap the host mineral ilmenite. Hence, the measured Ti content is slightly lower than expected (the ideal Ti content would be 59.9 per cent). The measured value of 57.3 per cent represents the highest value in a

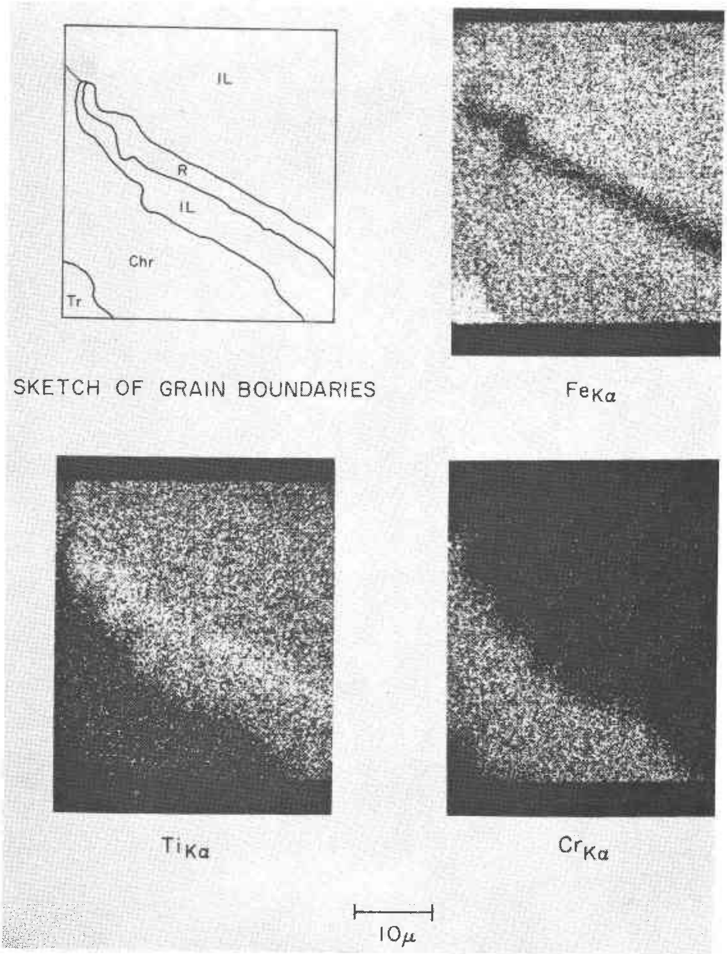

FIG. 1. Electron beam scanning pictures of a rutile lamella (R) in ilmenite (Il), associated with chromite (Chr) and troilite (Tr) from the Farmington chondrite. The pictures were obtained by scanning the electron beam over the microscopically selected area in the sample and recording the signals from the counter on the cathode ray tube of an oscilloscope, the cathode ray beam scanning the tube in synchronism with the electron beam scanning the sample.

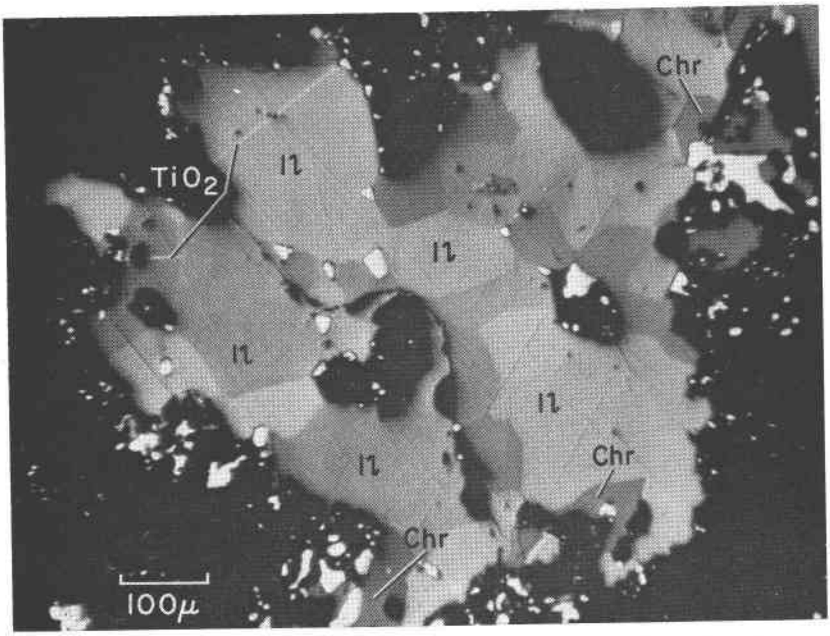

FIG. 2. Farmington chondrite. Polycrystalline ilmenite (Il) showing various shades of gray due to bi-reflectance, with rutile lamellae (TiO_2), associated with chromite (Chr), nickel-iron and troilite (white). Black is silicate matrix.

series of several hundred points. The small amount of iron which is detected when measuring the rutile lamellae is probably also a result of the overlapping. In view of this ambiguity it cannot be positively asserted that the rutile is either pure or stoichiometric. The ilmenite is fairly rich in Mg and should be called manganese-chromium-bearing mangnesian ilmenite following the terminology suggested by Palache *et al.* (1944). The chromite contains Ti as well as Mg and thus may be called titanium-manganese-bearing magnesian chromite. Terrestrial ilmenites and chromites commonly also contain Mg, there being solid solution series of geikielite ($MgTiO_3$) and magnesiochromite ($MgCr_2O_4$), respectively. The ilmenite and chromite were qualitatively scanned for all the elements with atomic numbers greater than that of Na; only those elements shown in Tables 1 and 2 were present in amounts greater than 0.05 weight per cent.

The electron microprobe analysis clearly shows the mineral in question to be a titanium dioxide; this technique, however, cannot distinguish between the several polymorphs. Presumably because rutile is more stable under most geologic conditions than either anatase or brookite other investigators have assumed that meteoritic titanium dioxides consisted of rutile. No x-ray measurements have been reported. Unfortunately the small size of the TiO_2 lamellae and scarcity of the Farmington material preclude separation of the phase and thus x-ray diffraction measurements.

The presumptive rutile was also identified with the microprobe in the Bondoc meteorite. In an attempt to concentrate the titanium dioxide, severely weathered outer crust of Bondoc was taken and treated first with HCl and then with $HNO_3 + HF$ and then again with HCl in order to dissolve all but the most resistant minerals. Further concentration of the very small amount of insoluble residue proved necessary to get a good x-ray pattern. Therefore, first magnetic splits and then specific gravity splits were made. The resulting material is pure rutile whose x-ray powder diffraction data are essentially identical with those of the ASTM rutile.

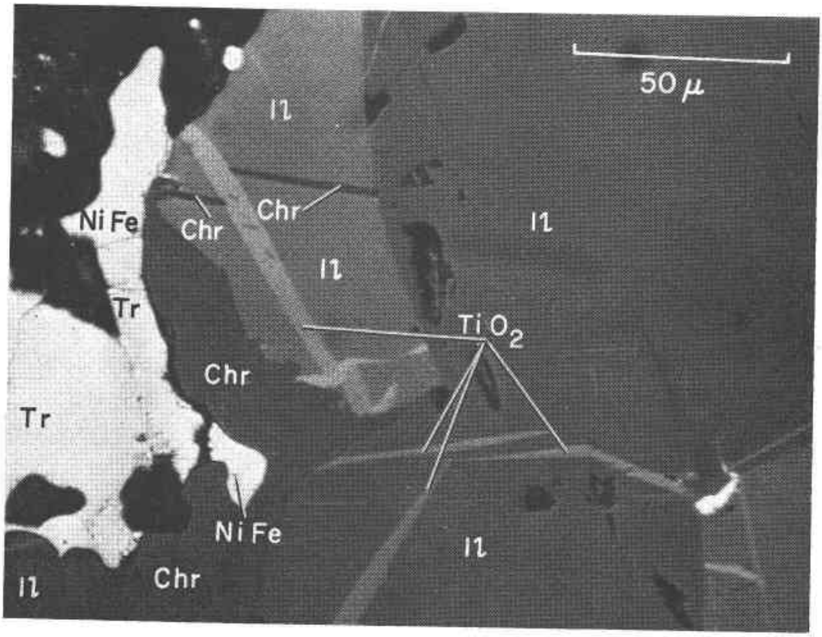

FIG. 3. Farmington chondrite. Lamellae of rutile (TiO_2) within ilmenite (Il), associated with chromite (Chr), troilite (Tr), and nickel-iron (NiFe). Black is silicate matrix. Chromite also occurs as lamellae in ilmenite. Note the peculiar relationship between the rutile and chromite lamellae occurring together in the ilmenite grain shown in the center of the figure.

The occurrence of rutile in the Farmington meteorite is interesting for not only are there rutile lamellae within the ilmenite, but chromite lamellae occur in the same area. Some of the chromite grains look like exsolution lamellae but others are continuous with adjacent and larger, granular chromite grains (Figs. 2, 3). Rutile and chromite lamellae locally occur together in one and the same ilmenite grain as is shown in the center of Fig. 3. This grain exhibits a rather peculiar relationship between the rutile and chromite lamellae. The rutile seems to crosscut the chromite and also seems to offset it in places. However, the edges of the host ilmenite grain do not show any marked physical displacements. Note also that the left chromite lamella seems to penetrate somewhat into the rutile lamella.

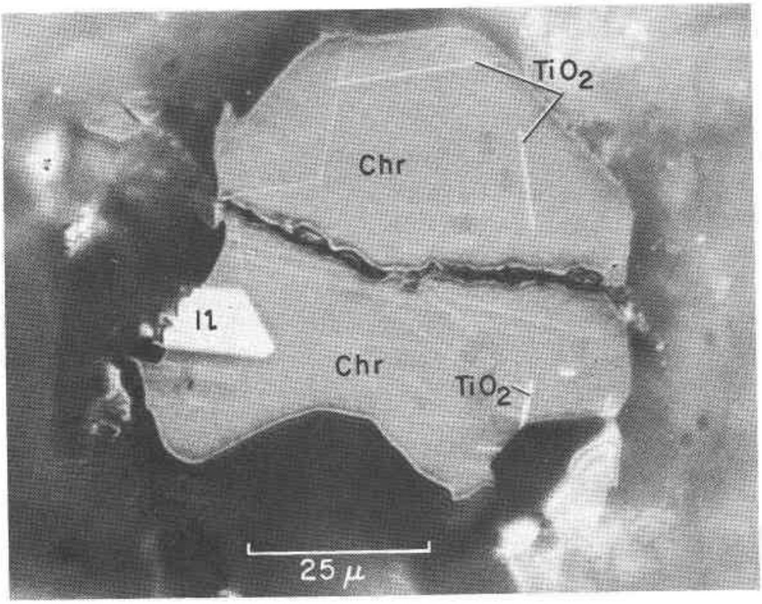

FIG. 4. Estherville mesosiderite. Chromite crystal (Chr) with rutile lamellae (TiO_2), associated with ilmenite (Il), in a silicate matrix. Oil immersion.

In most of the other meteorites, rutile is associated with chromite. In Estherville, a mesosiderite fall, chromite is widespread within the silicate areas. Ilmenite commonly occurs with the chromite, either in euhedral crystals or thin lamellae. The rutile is less abundant and it is restricted to long, thin lamellae within the chromite. These lamellae appear to be crystallographically oriented and presumably resulted by exsolution from chromite (Fig. 4). Its grayish-blue color and higher reflectivity than chromite or ilmenite serve to identify it, even though it is commonly at the limit of resolution at maximum magnification (1265X). It is reasonably widespread.

Rutile has recently been mentioned as occurring in Vaca Muerta (Marvin and Klein, 1964) as well as in other mesosiderites (Ramdohr, 1964). In Vaca Muerta—a mesosiderite find—the rutile occurs together with chromite, both in lamellae in the chromite as well as in individual grains. It is interesting to note that the rutile does not only occur in lamellae in the chromite, but also that chromite lamellae occur within large rutile grains (Fig. 5).

The chromite in Allegan—an H-group chondrite fall—contains 1.20 weight per cent TiO_2 (Merrill and Stokes, 1900). Being moderately Ti-rich it was thought that it might also contain rutile. In fact, Allegan does contain rutile as a very minor accessory mineral, but it is disseminated as discrete grains within the silicate matrix, rather than as lamellae in chromite.

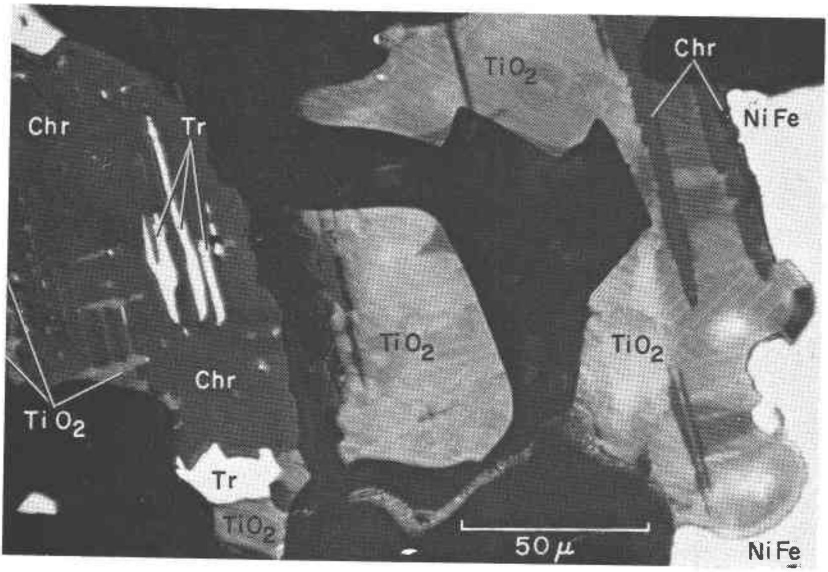

FIG. 5. Vaca Muerta mesosiderite. Chromite (Chr) with lamellae of troilite (Tr) and of rutile (TiO_2), and rutile with lamellae of chromite, in contact with metallic nickel-iron (NiFe). Dark matrix is constituted of silicates. Oil immersion.

Bondoc is an extremely unusual meteorite (Nininger, 1963). It consists of fist-size, rounded pods of metal within a predominantly silicate matrix. The metal, consisting largely of kamacite, is in sizeable grains between which there are inclusions of nonmetallic minerals, mainly silicates and some apatite. The rutile occurs within these nonmetallic segregations either together with chromite or as discrete small, angular grains not far away from it.

The mineralogical association in the vicinity of the rutile in meteorites is rather interesting as it includes kamacite, troilite, chromite, and in places ilmenite. Rutile has been seen in contact with ilmenite, chromite, and kamacite. Unfortunately, the regions of interest in the Fe-Ti-Cr-O system have not been adequately described; otherwise this complex assemblage would very likely provide enough information to determine the pressure-temperature conditions at the time of formation.

In Farmington the rutile appears to have been derived from the ilmenite. This is commonly the case in terrestrial materials, although the reactions are slightly different. In the terrestrial case ilmenite breaks down when oxidized, first by oxidation of the ferrous to ferric iron, with concurrent addition of water and then decomposes further to yield goethite plus amorphous TiO_2 (Kukovskii and Kononov, 1959). The latter readily recrystallizes. In meteorites, having a relatively low f_{O_2}, this reaction is unlikely—reduction appears much more probable. The reaction

$$2FeTiO_3 \rightarrow 2TiO_2 + 2Fe + O_2 \tag{1}$$

has been suggested for ilmenite breakdown (Ramdohr, 1964).

Experimental measurements indicate that ilmenite and rutile cannot coexist stably at very high temperatures as they react to form $FeTi_2O_5$, a mineral in the pseudobrookite solid solution series. On cooling, however, the $FeTi_2O_5$ decomposes to rutile plus ilmenite at $1140 \pm 10°$ C. (Lindsley, 1965),

$$FeTi_2O_5 \rightarrow FeTiO_3 + TiO_2 \tag{2}$$

clearly indicating that the assemblage observed in the Farmington meteorite formed below that temperature.

A limited amount of thermochemical data is available. In order to use the existing data it must be assumed that minor constituents in the minerals do not appreciably affect the thermodynamic properties and that the phases are stoichiometric (if they are not, the calculations must be revised—in the case of rutile see, *e.g.*, Moser *et al.*, 1965; Taylor and Schmalzried (1964) point out that stoichiometric ilmenite cannot coexist stably with Fe at 1300° C.—it is inferred, however, that it is stoichiometric at lower temperatures). Thus, applying free energy values given by Taylor and Schmalzried (1964) to the reduction reaction (eq. 1), it can be shown that rutile will be the stable phase only for oxygen fugacities less than $10^{-21.1}$ atm and less than $10^{-14.6}$ atm at 800° and 1100° C., respectively, these being the temperature limits of the applicable thermodynamic data. These results are in agreement with calculations made from the virial coefficients given by Kubaschewski and Evans (1958). They are presumably not unreasonable for conditions within a meterorite body, although it must be emphasized that they apply with certainty to only very small areas within the meteorite. There is presumably insufficient amounts of these minerals to buffer the entire meteorite mass.

Bulk chemical compositions, including TiO_2 determination, are available for several of the meteorites in which rutile was found. The stony fraction of Allegan contains 0.10 weight per cent TiO_2 (Merrill and Stokes, 1900), the Bondoc pyroxene contains 0.22 weight per cent TiO_2 (Wiik, pers. comm., 1965), and the Farmington meteorite contains 0.17 weight per cent TiO_2 (Buseck *et al.*, 1965). These values may be compared to the average values of superior analyses of 53 stony meteorites, which is 0.11 weight per cent TiO_2 (Urey and Craig, 1953). This agrees with the average value of 0.11 weight per cent TiO_2 for 13 chondrites analyzed by Wiik and Wahl (Moore and Brown, 1961, Table 2) and for 86 chondrites analyzed spectrographically by Moore and Brown (1961). It is slightly lower than the mean of 0.15% given by Mason (1965). Thus, on the basis of limited compositional data, the rutile-bearing meteorites do not appear to be exceptionally Ti-rich. Presumably it is likely that more careful optical examination will show that rutile is present in many meteorites.

Although texturally much of the rutile appears to be the result of exsolution from ilmenite, it has been reported (*e.g.*, Edwards, 1960), that based on experimental evidence, "ilmenite and rutile do not form solid solution to any marked degree." This is confirmed by recent unpublished measurements of Taylor (written comm. to P. R. Buseck, 1965). The fact that rutile lamellae seem to crosscut chromite lamellae within ilmenite of Farmington supports this contention, as do the small rutile grains in Bondoc, which occur isolated from either chromite or ilmenite. It appears likely that the rutile has several origins—a) reduction from ilmenite (Farmington), b) exsolution from chromite (Estherville), and c) primary (?) crystallization as a minor accessory mineral (Allegan, Bondoc). Origin of rutile by decomposition of $FeTi_2O_5$ is possible but appears unlikely as the ilmenite to rutile ratio is not in accordance with equation (2).

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REFERENCES

BUSECK, P. R., B. MASON AND H. B. WIIK (1966) The Farmington meteorite—mineralogy and chemistry. *Geochim. Cosmochim. Acta* **30**, 1–8.

EDWARDS, A. B. (1960) *Textures of the Ore Minerals and Their Significance.* Aust. Inst. Min. and Met., Melbourne.

EL GORESY, A. (1965) Mineralbestand und Strukturen der Graphit—und Sulfideinschlüsse in Eisenmeteoriten. *Geochim. Cosmochim. Acta* **29,** 1131–1151.

KEIL, K. AND C. A. ANDERSEN (1965) Electron microprobe study of the Jajh deh Kot Lalu enstatite chondrite. *Geochim. Cosmochim. Acta* **29,** 621–632.

KUBASCHEWSKI, O. AND E. LL. EVANS (1958) *Metallurgical Thermochemistry.* Pergamon Press, London.

KUKOVSKII, E. G. AND YU. V. KONONOV, (1959) *X*-ray diffraction study of the products of rutilization of ilmenite. *Rentgenogr. Mineral'n. Syr'ya, Gl. Upr. Geol. i Okhrany Nedr pri Sov. Min. Ukr. SSR, Tr. Pervogo Vses. Soveshch., Kiev* **1,** 120–127 (*CA*, **59,** 11105d).

LINDSLEY, D. H. (1965) Lower thermal stability of $FeTi_2O_5$-Fe_2TiO_5 (pseudobrookite) solid solution series (abs.) *Geol. Soc. Am. Spec. Paper* (in press).

MARVIN, U. B. AND C. KLEIN (1964) Meteoritic zircon. *Science* **146,** 919–920.

MASON, B. (1962) *Meteorites.* John Wiley and Sons.

———(1965) The chemical composition of olivine-bronzite and olivine-hypersthene chondrites. *Am. Mus. Novitates,* **2223.**

MERRILL, G. P. AND H. N. STOKES (1900) A new stony meteorite from Allegan, Michigan. *Proc. Washington Acad. Sciences* **2,** 41–51.

MOORE, C. B. AND H. BROWN (1962) The distribution of manganese and titanium in stony meteorites. *Geochim. Cosmochim. Acta* **26,** 495–502.

MOSER, J. B., R. N. BLUMENTHAL AND D. H. WHITMORE (1965) Thermodynamic study of nonstoichiometric rutile (TiO_{2-x}). *Jour. Am. Cer. Soc.* **48,** 384.

NININGER, H. H. (1963) Meteorite with unique features. *Science,* **139,** 345–347.

PALACHE, C., H. BERMAN AND C. FRONDEL (1944) *Dana's System of Mineralogy,* **1,** John Wiley & Sons, Inc.

RAMDOHR, P. (1963a) The opaque minerals in stony meteorites. *Jour. Geophys. Res.* **68,** 2011–2036.

——— (1963b) Beobachtungen am Opakerzbestand einiger Meteoriten besonders von New South Wales. *Chem. Erde* **23,** 119–145.

——— (1964) Opaque minerals in stony meteorites. *Carnegie Inst. Ann. Rept. Director Geophys. Lab.* 217–218.

TAYLOR, R. W. AND H. SCHMALZRIED, (1964) The free energy of formation of some titanates, silicates and magnesium aluminate from measurements made with galvanic cells involving solid electrolytes. *Jour. Phys. Chem.* **68,** 2444–2449.

UREY, H. C. AND H. CRAIG (1953) The composition of the stone meteorites and the origin of the meteorites. *Geochim. Cosmochim. Acta* **4,** 36–82.

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Noted added in proof: In a paper which only recently came to our attention, Ramdohr (*Monatsber. deutschen Akad. Wiss., Berlin,* 7, 923–938, 1965) describes rutile from several mesosiderites.