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SIGNIFICANCE OF IRON-RICH SILICATES IN THE MEZÖ-MADARAS CHONDRITE

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ABSTRACT

Several chondrules in the Mezö-Madaras chondrite contain the disequilibrium mineral assemblage: ferrous olivine—magnesian pyroxene—merrihueite [approximately $(K \geq Na)_2(Fe \geq Mg)_5Si_{12}O_{30}$] ± metallic nickel-iron. The ferrous silicates in this assemblage were probably formed by introduction of FeO into an earlier igneous assemblage which consisted of enstatite or clinoenstatite, a magnesian analogue of merrihueite, and silica. Textural and chemical evidence indicate that this alteration of the chondrules took place before they were incorporated in the chondrite.

INTRODUCTION

Several recent studies of the compositions of olivines and pyroxenes in chondrites have shown that a minority of these meteorites contain olivines and pyroxenes of variable composition (Mason, 1963a; Keil and Fredriksson, 1964). Dodd and Van Schmus (1965) showed that such heterogeneous silicates occur only in chondrites which, on the basis of petrographic evidence (little or no chondrule-matrix intergrowth; presence of clear, mafic glass in chondrules), are either unrecrystallized or but slightly recrystallized. They suggested that variable olivines and pyroxenes may have been characteristic of the parent materials of chondrites, and that the homogeneous silicates observed in most chondrites are due to metamorphism. It remains to be proved that the variations are truly primary and do not represent, as Wood (1962) suggests, an intermediate stage of metamorphism between Renazzo-like parent material (highly reduced chondrules; highly oxidized matrix) and ordinary, equilibrated chondrites.

Fredriksson and Keil (1963) have noted that the presence of exceptionally iron-rich olivines in chondrites (*e.g.*, individual grains with compositions of $Fa_{36.1}$ and $Fa_{91.2}$ in Chainpur and Murray respectively) suggests that variable silicates are primary, for Wood's model leads one to

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expect the chondrules in slightly metamorphosed chondrites to contain silicates which are less ferrous than those in equilibrated chondrites, not more ferrous. This argument is not conclusive, however, because locally high oxygen fugacities during metamorphism might also produce irregularly distributed iron-rich silicates. Certainty about the significance of ferrous silicates in the chondrites requires knowledge of the mineral associations in which they occur.

The purposes of this paper are

1) to describe an unusual association of iron-rich and iron-poor silicates in the Mezö-Madaras chondrite, 2) to present evidence that this assemblage developed before the chondrite agglomerated, and 3) to suggest a possible paragenesis for the assemblage.

THE MEZÖ-MADARAS CHONDRITE

The Mezö-Madaras chondrite fell in Transylvania in September, 1852. Of many stones which made up the fall, about 22.7 kg were recovered. Major amounts of the meteorite now reside in Vienna (Natural History Museum), Berlin (Berlin University), Tübingen (Tübingen University) and Budapest (Hungarian National Museum) (Prior, 1953). The material used for the work reported here is part of a small sample from the Nininger Meteorite Collection of Arizona State University.

Mezö-Madaras is an unequilibrated ordinary chondrite,[1] which shows evidence of slight metamorphism (Dodd and Van Schmus, 1965). Its texture is shown in Fig. 1. The stone is a low-iron chondrite on the basis of a bulk chemical analysis by Rammelsberg (Urey and Craig, 1953), a modal analysis by Keil (1962), and a mean olivine composition of Fa_{26} (Mason, 1963a). Wahl (1952) calls Mezö-Madaras a polymict accumulation breccia, an appropriate description in view of the heterogeneity of the particles which compose it.

MICROPROBE ANALYSES

The electron microprobe analyses reported here were made under our supervision by the Advanced Metals Research Corporation of Burlington, Massachusetts. The microprobe used was built by A.M.R. and is closely similar to the Philips AMR-3 instrument.

Iron and silicon were determined with the microprobe, the latter solely to check optical identifications of minerals. Both elements were measured against a standard olivine from the Springwater pallasite (Fa_{18}; analysis in Mason, 1963b). The iron concentrations in olivine and pyroxene were read from an empirical curve, prepared for this study, which relates the

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[1] *i.e.*, a chondrite whose bulk and mineral compositions are appropriate to one of the classes of ordinary chondrites, but whose olivines and pyroxenes are of variable composition.

iron concentrations in analyzed olivines and orthopyroxenes to their Fe *x*-ray intensities relative to that of the standard ($I_{unknown}/I_{Springwater}$). As a check, we prepared a similar theoretical calibration curve, taking account of the effects of absorption, atomic number, and takeoff angle. Use of this curve would give iron concentrations which are slightly greater (at most 4% of the amount present) than those given by the empirical curve and reported here.

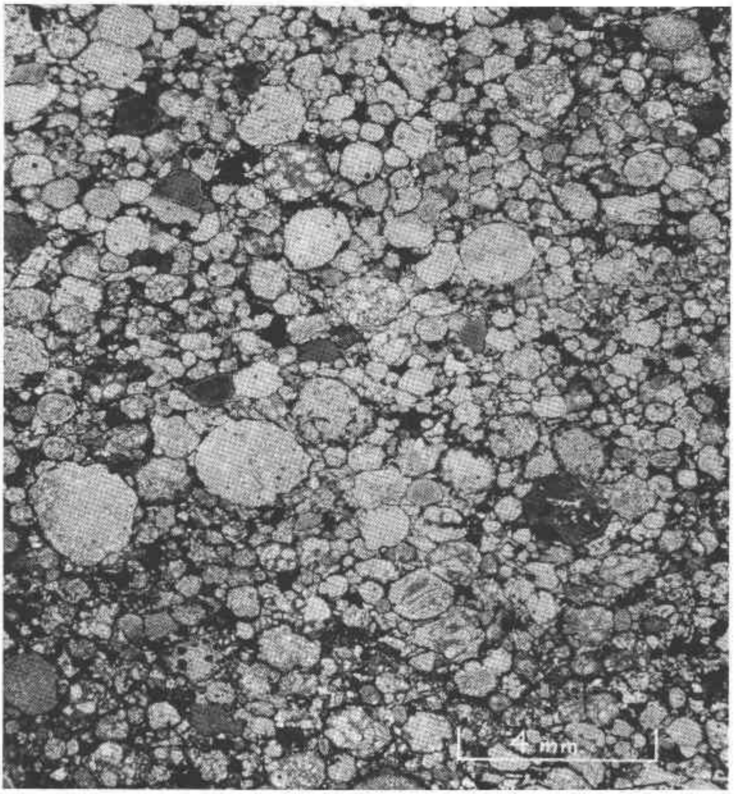

FIG. 1. Photomicrograph of the Mezö-Madaras chondrite.

The iron content of merriheuite was also determined relative to that of Springwater olivine. Because no empirical calibration curve could be prepared for merrihueite, a theoretical curve was used to secure the data given in Table 1. In general, the effect of other constituents on iron calibration curves is small for silicate minerals; hence the curve for merrihueite, like the theoretical curve for olivine and pyroxene, probably gives slightly high concentrations of iron.

TABLE 1. IRON CONTENTS (WEIGHT %) OF MINERALS IN MERRIHUEITE-BEARING AND ADJACENT MERRIHUEITE-FREE CHONDRULES IN MEZÖ-MADARAS. ALSO PRESENTED ARE MEAN IRON CONTENTS AND MEAN FAYALITE (Fa) AND FERROSILITE (Fs) CONTENTS IN OLIVINE AND PYROXENES. SUMMARY DATA FOR THE CHONDRITE AS A WHOLE ARE GIVEN FOR COMPARISON.

Area	*Merrihueite-bearing chondrule*	*Merrihueite-free chondrules*
Fig. 2	*Olivine:* 11 measurements %Fe = 20.8–48.2 (mean 41.4 = Fa_{68}) *Pyroxene:* 31 measurements %Fe = 1.0–6.5 (mean 4.1 = Fs_{74}) *Merrihueite:* 19 measurements %Fe = 10.8–24.8 (mean 18.2)	*Olivine:* 11 measurements %Fe = 7.9–19.4 (mean 12.1 = Fa_{16}) *Pyroxene:* 12 measurements %Fe = 7.8–12.9 (mean 9.7 = Fs_{18}) —
Fig. 3	*Olivine:* 9 measurements %Fe = 40.2–46.4 (mean 44.2 = Fa_7) *Pyroxene:* 16 measurements %Fe = 4.6–10.3 (mean 6.1 = Fs_{11}) *Merrihueite:* 10 measurements %Fe = 10.5–20.5 (mean 15.1)	*Olivine:* 11 measurements %Fe = 5.2–44.2 (mean 26.3 = Fa_{39}) *Pyroxene:* 22 measurements %Fe = 2.8–13.7 (mean 6.8 = Fs_{12}) —
Fig. 4	*Olivine:* 11 measurements %Fe = 41.5–49.8 (mean 45.1 = Fa_{76}) *Pyroxene:* 12 measurements %Fe = 2.8–7.2 (mean 4.4 = Fs_8) *Merrihueite:* 4 measurements %Fe = 14.2–21.9 (mean 17.3)	*Olivine:* 14 measurements %Fe = 3.1–27.2 (mean 12.2 = Fa_{17}) *Pyroxene:* 13 measurements %Fe = 1.1–7.1 (mean 3.7 = Fs_6) —
Entire stone (Fig. 5)	*Olivine:* 96 measurements %Fe = 3.4–24.4 (mean 17.4 = Fa_{24}) *Pyroxene:* 70 measurements %Fe = 1.8–17.9 (mean 8.7 = Fs_{16})	

The accuracy of individual analyses reported in Table 1 is estimated to be ±5% of the amount of iron present.

PETROGRAPHY AND MINERALOGY

In addition to the familiar chondrule types, Mezö-Madaras contains several examples of a very unusual mineral assemblage with consists of iron-rich olivine, iron- and calcium-poor clino-pyroxene (clinoenstatite-

FIG. 2. Photomicrograph, in plane light, of a chondrule in Mezö-Madaras which consists of clinoenstatite (white), olivine (light gray) and merrihueite (gray to black areas within chondrule). The border of the chondrule is indicated by a dotted line. Numbers are olivine compositions in mol % Fa. See also Fig. 6.

clinobronzite), merrihueite,[1] and, in some instances, metallic nickel-iron. Figures 2 through 4 and 6 show three chondrules in which this assemblage occurs.

Pyroxene is the predominant mineral in most of the chondrules. It consists of coarse plates which are commonly radially disposed in a texture suggestive of excentroradial chondrules.[2] In some cases, the pyroxene in a chondrule consists of a single, large (up to 1.2 mm across), poly-

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[1] Approximate composition $(K \geq Na)_2(Fe \geq Mg)_5Si_{12}O_{30}$. (Dodd *et al.*, 1965)

[2] Krinov (1960). The term applies to chondrules which consist of radiating fibers or plates of pyroxene. As the pyroxene does not radiate from the center, "excentroradial" is preferable to "radial."

synthetically twinned grain. The iron content of pyroxene in this assemblage (Table 1) varies somewhat both within individual chondrules and among chondrules, but it is typically in the range of clinoenstatite (Fs_{0-10}).

The merrihueite in this assemblage has been described elsewhere (Dodd *et al.*, 1965). It occurs in pyroxene as green inclusions, each of which is an aggregate of minute crystals. Merrihueite is always associated with ferrous olivine, which typically forms selvages between merrihueite and the adjacent pyroxene. Olivine also occurs alone along the rims of the chondrules. In both occurrences, it consists of an aggregate of minute, yellow grains, the largest of which is about 0.1 mm across.

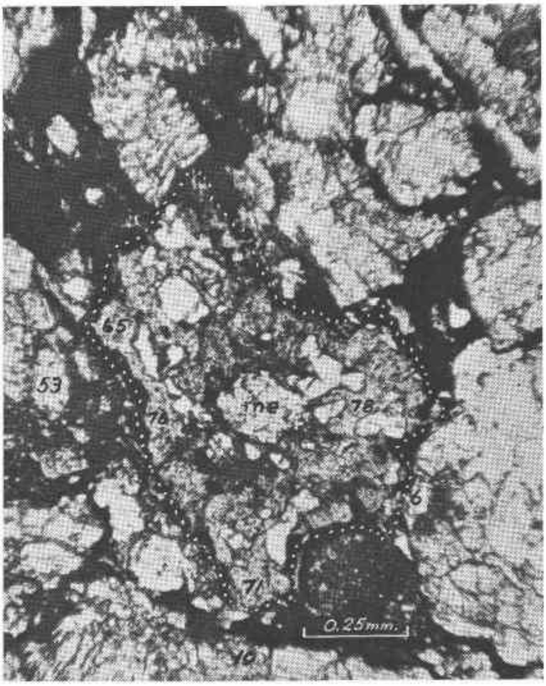

FIG. 3. Photomicrograph, in plane light, of a chondrule fragment in Mezö-Madaras. The principal minerals are olivine (light gray), clinoenstatite (white), and merrihueite (me). The chondrule is outlined with a dotted line. Numbers are olivine compositions in mol % Fa.

The iron contents of olivine and merrihueite in this assemblage are given in Table 1. Both minerals are of variable composition but are generally iron-rich. The olivine is chiefly hortonolite-ferrohortonolite

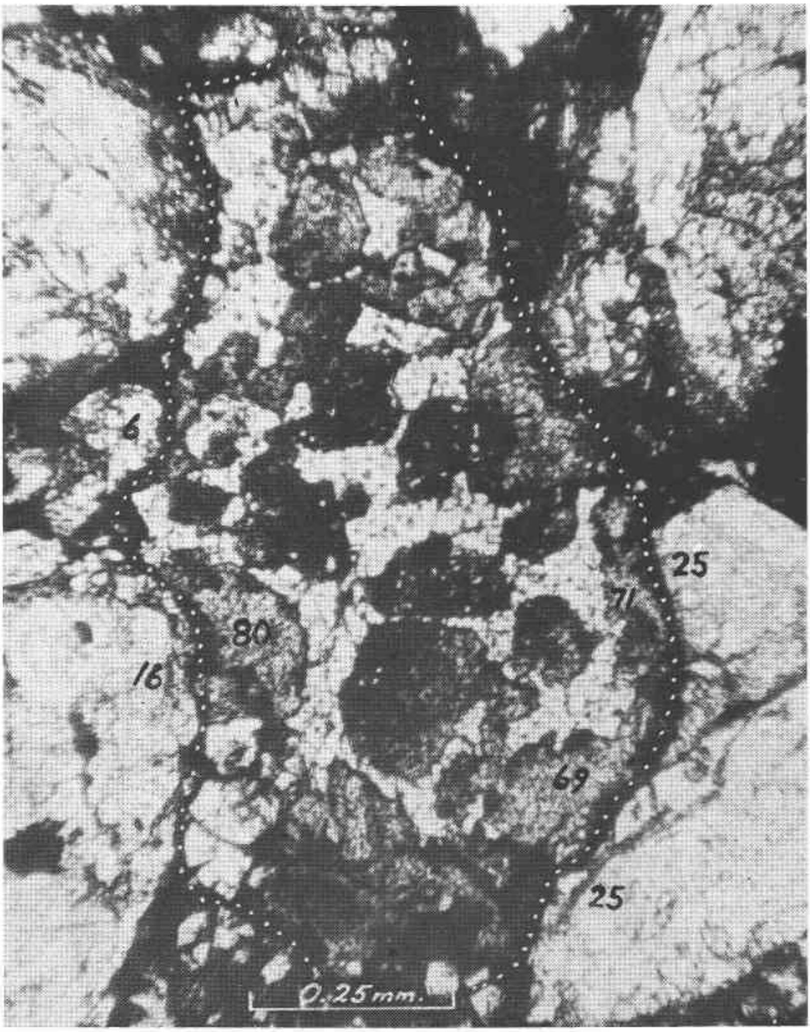

FIG. 4. Photomicrograph, in plane light, of a chondrule fragment in Mezö-Madaras, consisting of olivine (gray), clinoenstatite (white), and merrihueite (black areas). The chondrule is outlined with a dotted line. Olivine compositions (numbers) are given in mol % Fa.

(fa_{50-90}). Merrihueite has a range of Fe/(Fe+Mg) ratios (atomic) of approximately 0.4 to 1.0.[1]

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[1] Because there are at least three possible substitutions in merrihueite—Mg for Fe, Mn for Fe, and Na for K—the iron concentrations alone do not define (Fe/(Fe+Mg) ratios. The ratios given above are based on the assumptions that K$\approx$Na (atomic) and that Mn is

Metallic nickel-iron occurs in some of the chondrules as minute (≤ 20 micron) grains which occur in the olivine, typically at or near olivine-pyroxene boundaries. The mineral is of trivial abundance and is not characteristic of the assemblage.

DISCUSSION

Pre-agglomeration origin of iron-rich olivine. A major question raised in the introduction to this paper is whether the ferrous olivines in Mezö-Madaras formed before or after the chondrite agglomerated. The microprobe data in Table 1 and Fig. 2 to 4 bear on this question.

The data in Table 1 show that olivine within the merrihueite-bearing chondrules is more ferrous than that in nearby merrihueite-free chondrules. The latter has a range of composition which is consistent with that observed in a random survey of olivines in the entire chondrite (Fig. 5a). In contrast to the olivine data, those for pyroxene show that this mineral has similar ranges of composition in merrihueite-bearing and merrihueite-free chondrules and in the meteorite as a whole (Fig. 5b).

Analyses of pairs of olivine grains just inside and just outside of the merrihueite-bearing chondrules are particularly instructive (Figs. 2 to 4), for they show that iron-rich and iron-poor olivines occur as little as 0.2 mm apart. It is hard to picture a metamorphic process, even one involving local variations in oxygen fugacity, which could produce such large variations in iron content over such small distances. We therefore conclude that the ferrous olivines in the merrihueite-bearing chondrules formed when these chondrules were independent bodies, *i.e.*, before they entered the meteorite, and not during post-agglomeration metamorphism.

Physical history of merrihueite-bearing chondrules. Having referred the formation of ferrous olivines in these chondrules to the pre-agglomeration history of the chondrite, we shall now attempt to interpret that history. The physical development of the particles can be inferred, roughly, through a consideration of their textures. The relevant observations and inferences can be summarized as follows:

1. The radial habit of the coarse pyroxene plates in several of these chondrules suggests that they are recrystallized excentroradial chondrules. Such chondrules are generally interpreted as products of quenching of molten droplets, on the basis of their smoothly spherical or ovoid shapes, their internal texture, and their content of glassy or cryptocrystalline material. In Mezö-Madaras and other chondrites, chondrules of

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trivial. Both assumptions are approximately true for the one chondrule (Figs 2, 6) which has been analyzed in detail (Dodd *et al.*, 1965).

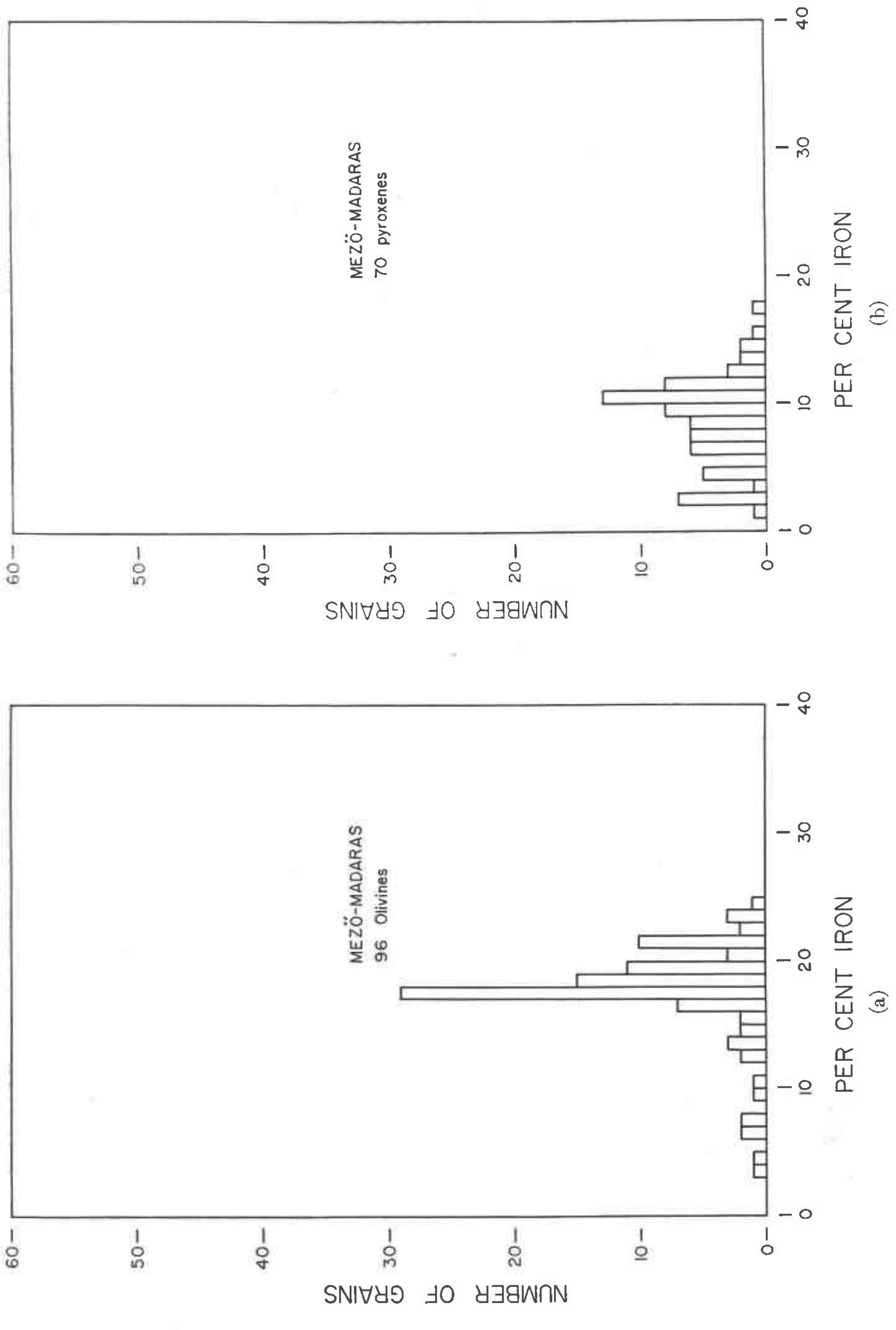

FIG. 5. Iron contents of (a) 96 olivines and (b) 70 pyroxenes (orthopyroxenes and low-Ca clinopyroxenes) in the Mezö-Madaras chondrite.

this type show a textural gradation from finely fibrous to coarsely crystalline; this gradation is presumably due to either differences in the rate of cooling from the melt or to different degrees of recrystallization. From these considerations, we infer that the merrihueite-bearing chondrules began as molten droplets, which were quenched and then either cooled slowly to form coarse pyroxenes or were recrystallized.

2. Although one of the merrihueite-bearing chondrules (and another which contains no merrihueite but has a rim of ferrous olivine) has an oval outline in thin section and possesses a complete excentroradial pattern, the rest have irregular shapes and show incomplete excentroradial patterns. It appears that the irregular particles are chondrule fragments rather than entire chondrules.

3. Ferrous olivine is irregularly distributed in the merrihueite-bearing chondrules, but it generally follows the present fragment boundaries. From this fact, we conclude that the rimming olivine developed after the original chondrules were dismembered.

It is clear from this discussion that these particles had already experienced complex histories when they were incorporated in the Mezö-Madaras chondrite. The simplest conceivable sequence consists of 1) formation and quenching of molten droplets; 2) slower cooling or reheating to develop coarse pyroxene; 3) fragmentation of some of the chondrules; and 4) development of ferrous olivine.

Paragenesis of the assemblage olivine—pyroxene—merrihueite. It is more difficult to establish the chemical and mineralogical history of these chondrules. There are no other known occurrences of merrihueite with which to compare this one, and the pertinent chemical systems are only partly known.[1]

The assemblage ferrous olivine—clinoenstatite—merrihueite certainly does not represent equilibrium conditions of formation, as all of the minerals have variable compositions and the iron-rich olivine and iron-poor pyroxene are clearly incompatible. Of the three minerals, only the

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[1] The systems K_2O-MgO-SiO_2 (Roedder, 1951) and Na_2O-MgO-SiO_2 (Botvinkin, *et al.* 1937; Schairer *et al.*, 1953, 1954) are known in detail at one atmosphere pressure. Merrihueite-like compounds—$K_2Mg_5Si_{12}O_{30}$ and $Na_2Mg_5Si_{12}O_{30}$—are stable at the liquidus in these systems. Fewer data are available for analogous systems involving FeO. Roedder (1952) did not find $K_2Fe_5Si_{12}O_{30}$ in his reconnaissance of the liquidus of the system K_2O-FeO-SiO_2, nor was $Na_2Fe_5Si_{12}O_{30}$ established in studies of the system Na_2O-FeO-SiO_2 by Carter and Ibrahim (1952) and Schairer *et al.*, Yoder and Keene (1953, 1954). However, the phase diagram of Schairer (1954, p. 126) includes an area labelled "several fields." One of these as yet unidentified fields may be that of $Na_2Fe_5Si_{12}O_{30}$, but the data now available do not indicate whether the K-Fe and Na-Fe compounds—the synthetic quivalents of merrihueite—are stable at the liquidus or only below it.

FIG. 6. Enlargement of part of Fig. 2, showing the textural relations of olivine (yellow), clinoenstatite (white) and merrihueite (bluish green). Plane light.

pyroxene is of orthodox composition (Table 1) and has a relict igneous texture. The rimming ferrous olivine can be plausibly interpreted as a product of recrystallization of the pyroxene with introduction of FeO, the iron to be provided by iron oxides or, with oxidation, metallic iron in the environment. Merrihueite may also be secondary after a magnesian silicate, possibly $K_2Mg_5Si_{12}O_{30}$. If both olivine and merrihueite are assumed to be secondary, then our problem is to reconstruct an original magnesian assemblage which can account for the textural and chemical relations of the present assemblage.

If our basic assumption is correct, then the molten chondrules must have had compositions near that of enstatite but with a small amount of K_2O and Na_2O present. Roedder's phase diagram (1951, p. 127) for the system K_2O-MgO-SiO_2 suggests two possible crystallization paths for such melts:

1. If the melt composition lay in the field of primary clinoenstatite, this mineral would crystallize first and would crystallize alone until most of the melt was solid. It would be joined at a late stage by tridymite and, finally, $K_2Mg_5Si_{12}O_{30}$.
2. A melt in the forsterite field would precipitate forsterite first and then forsterite plus enstatite. The subsequent course of crystallization would depend on the initial composition but the product in all cases would be clinoenstatite with a small amount of forsterite and $K_2Mg_5Si_{12}O_{30}$.

The first model best fits the mineralogical and textural data for these chondrules. Quenching of a melt in the clinoenstatite field would produce a sheaf of fibrous pyroxene and interstitial glass enriched in silica and K_2O. During subsequent growth of the pyroxene crystals, caused by either slow cooling or reheating of the chondrules, quartz and $K_2Mg_5Si_{12}O_{30}$ could crystallize between the pyroxene plates. Finally, introduction of FeO could convert the quartz and some of the pyroxene to ferrous olivine and the K-Mg phase to merrihueite. This model adequately accounts for the present location of merrihueite and its association with ferrous olivine.

The second model has nothing to recommend it. There is no evidence in the chondrules for primary crystallization of olivine. Furthermore conversion of a primary assemblage of olivine, clinoenstatite and $K_2Mg_5Si_{12}O_{30}$ to the present assemblage of ferrous olivine, clinoenstatite and merrihueite raises a problem of chemical balance: Addition of FeO to an iron-poor pyroxene can produce olivine with 50–60% of the fayalite molecule (the limit depending on the iron content of the pyroxene), but it cannot produce the extreme fayalite contents encountered in these chondrules without a compensating loss of MgO from the chondrules. This problem is more severe if the original assemblage includes olivine. It does not arise in the first model, where the presence of free silica permits the formation of olivine of any fayalite content without loss of MgO.

We therefore propose that the original assemblage in the merrihueite-bearing chondrules formed by quenching and recrystallization of melts in the clinoenstatite field of the (simplified) system K_2O-MgO-SiO_2. This interpretation might be checked by examining the areas between pyroxene plates in excentroradial chondrules which lack ferrous silicates. If our model is correct, these areas should contain quartz and $K_2Mg_5Si_{12}O_{30}$. Both of these minerals, if fine-grained, could easily be misidentified as plagioclase.

Summary of Conclusions

The disequilibrium mineral assemblage ferrous olivine-clinoenstate-merrihueite occurs in several chondrules in the Mezö-Madaras chondrite. It is thought to have formed through introduction of FeO into a primary assemblage of clinoenstatite, quartz, and $K_2Mg_5Si_{12}O_{30}$. This alteration took place after some of the chondrules had been fragmented, but before the chondrules were agglomerated to form the chondrite.

Acknowledgments

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