PHOSPHATE-BEARING MICROSPHERULES IN CHONDRULES OF UNEQUILIBRATED ORDINARY CHONDRITES

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Abstract: Microspherules, up to *ca.* 200 μm in size, composed mainly of metal cores and various amounts of phosphates usually at the rim are described in chondrules and igneous-textured clasts from ordinary chondrites of petrologic types 3 and 4 and one type 5 chondrite. Phosphates found in microspherules in petrologic types 3 and 4 are mostly whitlockite and those in type 5 include apatite as well. Their chemical composition is almost identical to those in equilibrated ordinary chondrites. One of those spherules in Chainpur shows quite complex texture with native copper and lawrencite-like phase. Though many points on the formation history of phosphate-bearing bodies are left as future problems, their xenolithic origin was indicated by the features of some of those spherules. They were probably formed from molten droplets of metal and schreibersite (in the same event as the chondrule formation?) followed by oxidation reaction in advance of their being captured by coarser silicate chondrule melt.

1. Introduction

Whitlockite and chlorapatite are the common accessary minerals in equilibrated ordinary chondrites and they usually occur interstitially among ferromagnesian silicates in matrices. These phosphates have been considered to be one of the phases crystallized at the latest stage in chondrites on the basis of their occurrence similar to plagioclase. Recently, however, phosphates have been identified in the matrices of highly unequilibrated chondrites, Chainpur (LL3) and Krymka (L3), associated with metal and sulphide phases, *i.e.* inside the metal-sulphide nodules, inside the coarse polycrystalline metal and in large troilite-rich areas including metal and traces of silicates (Rambaldi and Rajan, 1982). It exhibited an evidence for the primitive phosphates in ordinary chondrites. Their microprobe analyses show that the phosphate is whitlockite with 2–3 wt% of Na_2O and their MgO/FeO ratios are much lower than those from equilibrated ordinary chondrites and other meteorite groups (Table 1). Their high iron and nickel contents compared with whitlockite in equilibrated chondrites are possibly due to the presence of Fe-oxide in intimate association with the phosphate (Rambaldi and Rajan, 1982) or may be the influence of adjacent metal because of their fine grain size.

During the textural and compositional survey of many ordinary chondrites of various petrologic types, we have encountered a number of phosphate-bearing microspherules in chondrules and in some igneous-textured clasts (lithic fragments with igneous texture) from types 3, 4, and rarely in type 5 chondrites. The finding of those

microspherules is apparently more frequent in unequilibrated chondrites than in higher petrologic types, *i.e.* most of type 3, many of type 4 and only one of type 5 chondrites among 5, 6 and 7 meteorites studied, respectively. Electron microprobe analyses were made on the polished sections of four chondrites, in which many microspherules with phosphates coarse enough for quantitative analysis were found: namely, Chainpur (LL3), Mezö Madaras (L3), Saratov (L4) and Arapahoe (L5). Phosphate-bearing microspherules are quite unique in the feature and occurrence as well as chemistry. Though the origin of these bodies has not been thoroughly deciphered yet, at least some of those microspherules show evidences of their xenolithic origin. This report gives the description and some preliminary discussions on the origin of these phosphate-bearing microspherules in chondrules.

2. Occurrence and Chemistry of Phosphate-bearing Microspherules

The shape of the phosphate-bearing bodies are mostly spherical and often droplet-like, and rarely lense- or dumbell-like. Spherules in type 5 chondrite, Arapahoe, are deformed compared with those in unequilibrated chondrites. The size ranges from submicron up to about 200 micrometers. In a polished section of usual size (approx. 2–8 cm^2), one to a few chondrules with phosphate-bearing microspherules are discovered. Phosphate-bearing microspherules were only found, so far, in the groundmass (glassy material often with microcrystalline crystals) of porphyritic chondrules or being tightly surrounded by olivine or pyroxene crystals in granular chondrules. Figure 1 shows the typical occurrence of phosphate-bearing bodies in a chondrules of Saratov (L4). Though only in some chondrules and clasts, the number of phosphate-bearing bodies appears to be roughly in inverse proportion to their size. Mineral assemblage of these microspherules is fairly simple in most cases. They are composed of dominant cores of kamacite and taenite, and varied amount of phosphate which occurs usually at the rim. Phosphates are also present very frequently as small blebs enclosed in metal spherules. Those phosphates are mostly whitlockite but apatite was also found in a chondrite of petrologic type 5, Arapahoe. Troilite frequently occurs in cores associated with metal phases. Schreibersite was also found in the cores of some microspherules in an igneous clast from Chainpur. It is very rich in nickel (up to 54.7 wt%) and the average formula is approximately $(Fe_{0.40}Ni_{0.62})_3P$. The outer rim of the microspherules is not always smooth but often rugged to varied extent and rarely even curled (Fig. 2). Phosphate at the rim often shows an apparent idiomorphic outline against metal cores (Fig. 2). Very fine to dust-sized grains of chromite or chromite-like phase are frequently included in phosphates arranged along the margin of them (Figs. 3 and 6). Though the amount of this oxide phase is usually small, microspherules are rarely surrounded almost entirely by thin film of chromite-like phase. In several spherules, phosphates thickly cover the metal core with an irregular outline (Fig. 3). Phosphate rims occupy up to nearly 70 vol% in those spherules, according to the planimetric estimation on the cross section.

The following two types of microspherules are chemically distinct from this dominant type of spherules. One of the microspherules in a chondrule from Saratov

Fig. 1. Typical occurrence of phosphate-bearing microspherules in chondrules. Each spherule is composed of metal, sometimes troilite and various amount of whitlockite at the rim or as small blebs. Saratov (L4). Reflected light.
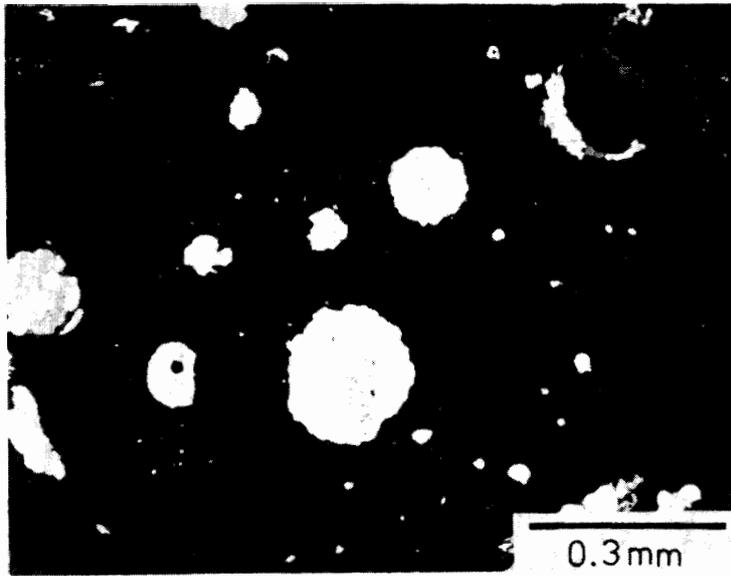
Fig. 2. The commonest type of phosphate-bearing microspherules in chondrules and igneous-textured clasts. They consist of whitlockite (Wh) at the rim and a core of metallic iron (kamacite, Kam and taenite, Tae). Whitlockite is idiomorphic toward metal core but rounded toward oustide. Rugged surface probably exhibits some reaction with host materials. Chainpur (LL3). Backscattered electron image (BEI).
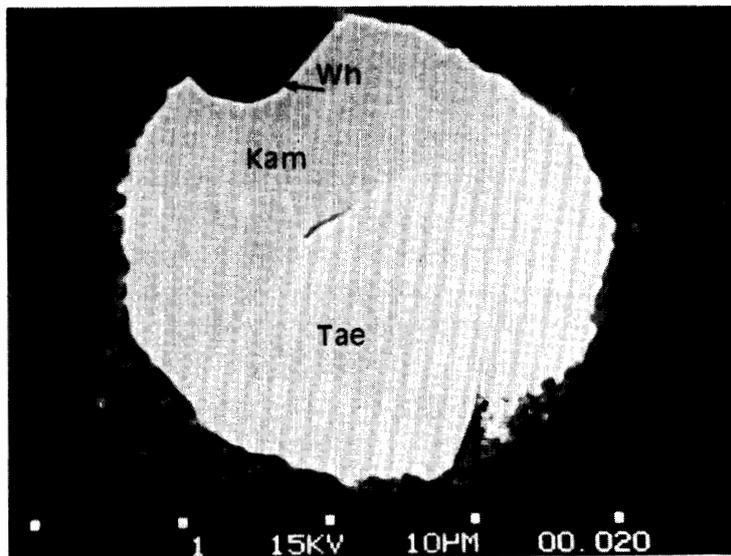
Fig. 3. A microspherule thickly rimmed by whitlockite. Dust-sized chromite (Chr) is aggregating along the outer rim of whitlockite. The outline is slightly bent by phenocrysts of zoned spinel (Sp) and olivine (Ol). Olivine phenocrysts (Ol) in this chondrule include many rounded relict crystals of hypersthene (Hy). Saratov (L4). BEI.
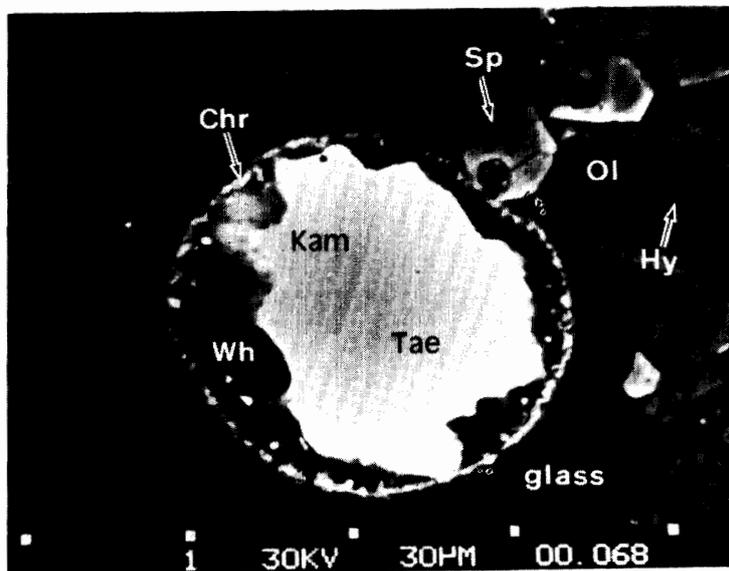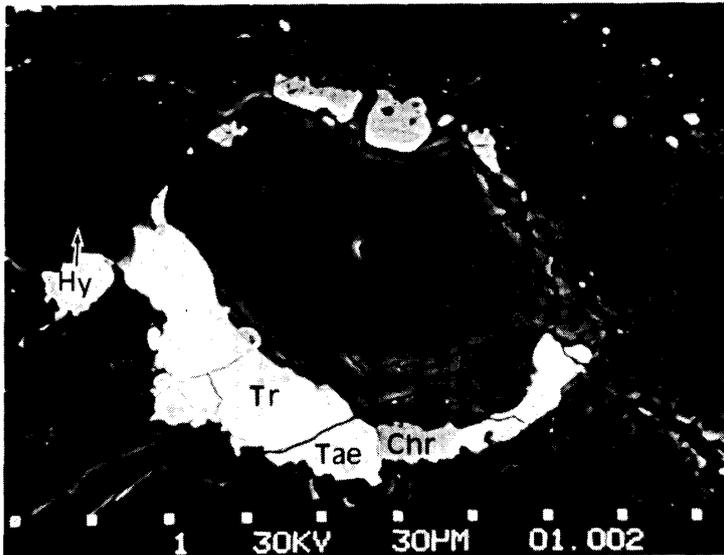
Fig. 4. A microspherule with a coarse whitlockite core and rim of troilite (Tr), taenite, and chromite (Chr). Whitlockite includes many globular diopside (Di), which is thought to be relict crystals. A rounded apatite grain (Ap) is also seen near the rim of whitlockite. Saratov (L4). BEI.

(L4) consists mainly of spherical whitlockite at the center and the rim composed of metal, troilite and chromite (Fig. 4). The whitlockite encloses many rounded fine grains of diopside ($Wo_{45.6}En_{48.7}$ on the average), which appear to be relict crystals. A rounded apatite grain of about 50 micrometers across is also seen near the rim.

One of the igneous-textured clasts in Chainpur (LL3) includes numerous microspherules consisting of metal cores and phosphates at the rim. Among them one spherule with a conspicuous feature is recognized. It is a complex assemblage of irregular-shaped grains of kamacite, taenite, native copper, whitlockite and a compound of iron, chlorine and nickel, which seems to be (or originated as) lawrencite (Fig. 5). Quantitative analysis by electron probe of the last phase was unsuccessful because of the volatilization at the electron bombardment. This phase is deliquescent and rapidly decomposes in the air. Adjacent metallic iron was partly oxidized already in the freshly cut surface probably by the influence of hydrochloric acid due to the decomposition of this lawrencite-like phase (Mason, 1962).
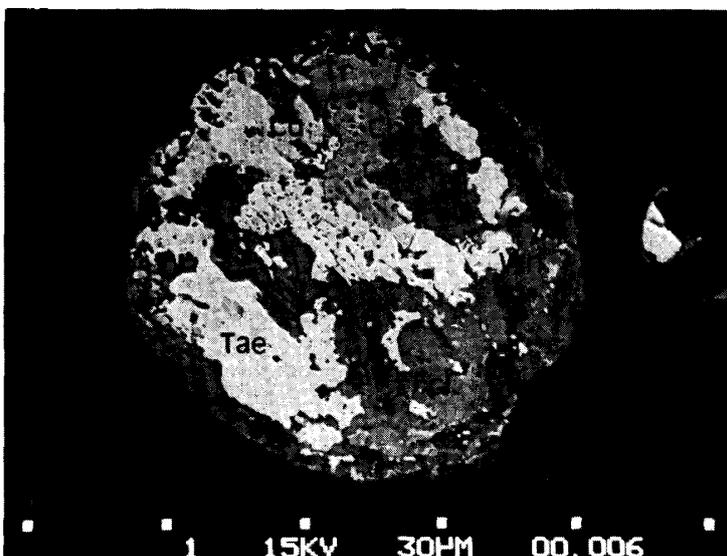
Fig. 5. A chemically complex microspherule in an igneous-textured clast from Chainpur (LL3). It consists of irregular-shaped grains of metal, troilite, chromite, native copper (Cu), whitlockite, iron oxide (FO) and a compound of Fe, Cl and Ni (Fcl). The last phase is highly deliquescent and considered to be lawrencite. BEI.

Table 1. *Microprobe analyses of phosphates in microspherules in chondrules and igneous-textured clasts.*

Meteorites	No. anal.	P_2O_5	CaO	FeO	NiO	MgO	Na_2O	F	Cl	Total
Chainpur	14	46.37	44.05	1.82	—	3.51	2.73	0.03	0.01	98.69*
Mezö Madaras	12	46.04	44.72	2.72	—	3.30	2.69	0.00	0.02	99.52*
Saratov	22	46.07	44.82	1.06	—	3.50	2.72	0.01	0.02	98.36*
Saratov (ap)**	8	41.53	52.37	0.29	—	0.02	0.37	0.58	5.36	100.57*
Chainpur***	24	44.5	46.5	3.4	0.14	3.2	1.97	—	—	99.71
Krymka***	9	43.5	43.2	7.2	0.70	2.5	1.88	—	—	98.98

* These totals include trace of Al_2O_3, Cr_2O_3, and MnO.
** (ap) indicates apatite. Others are whitlockite.
*** After RAMBALDI and RAJAN (1982).

Table 1 lists the average compositions of phosphate minerals from several chondrites. These phases are fairly homogeneous in each meteorite. The calculated formulae of whitlockite from Chainpur, Mezö Madaras, and Saratov are approximately

$$Na_{0.27}(Ca_{0.81}Mg_{0.09}Fe_{0.03})_3(P_{1.01}O_4)_2 ,$$

$$Na_{0.27}(Ca_{0.82}Mg_{0.08}Fe_{0.04})_3(P_{1.00}O_4)_2$$

and

$$Na_{0.27}(Ca_{0.83}Mg_{0.08}Fe_{0.02})_3(P_{1.01}O_4)_2 ,$$
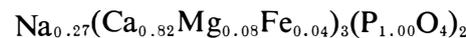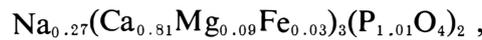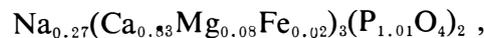
respectively. These formulae are almost identical with each other and are also in good agreement with the spectroscopic analyses reported from three ordinary chondrites, Allegan (H5), Waconda (L6) and Holbrook (L6) (FUCKS, 1962). The compositions of metal phases in microspherules are essentially identical to those in the other parts of host meteorites. The Ni content of kamacite and taenite in phosphate-bearing microspherules in Chainpur, Mezö Madaras and Saratov was 4.07, 46.07%; 4.20, 47.91%; and 4.64, 44.69%, respectively.

In addition to those microspherules in chondrules or in clasts, coarser metal grains in matrix especially from chondrites of lower petrologic types also frequently enclose fine globular grains of phosphates, usually whitlockite. This type of phosphates is probably of the similar kind to those reported by RAMBALDI and RAJAN (1982).

3. Discussion on the Origin of Microspherules

Phosphate minerals are always associated with metal phase in microspherules in chondrules and igneous-textured clasts. This mode of occurrence strongly implies that phosphorus in them was originally present in solid solution in metal and probably also in schreibersite. It means that phosphate was formed from metal or schreibersite by some dephosphorization reaction either within or out of chondrules. OLSEN and FUCHS (1967) proposed the following reaction for the interpretation of coexistence of phosphates and phosphides in iron meteorites:

$$3CaMg(SiO_3)_2 + 4O_2 + 3Fe + 2(P)^{Fe} = Ca_3(PO_4)_2 + 3MgFe(SiO_3)_2 , \tag{1}$$

where $(P)^{Fe}$ indicates phosphorus in metallic iron. Though the relict-like crystals of diopside found in a Saratov microspherule (Fig. 4) seem to support this reaction, co-existence of whitlockite and hypersthene was not discovered in any microspherules studied. Alternatively, the following oxidation reaction is considered to be most straightforward and likely in this case:

$$4(P)^{Fe} + 6CaO + 5O_2 = 2Ca_3(PO_3)_2 . \tag{2}$$

This is also applicable for schreibersite by adding the dephosphorized nickel-iron in the right term. It seems to be worthy of note that this reaction brings a significant volume increase in a microspherule especially in the case of schreibersite. The volume of whitlockite formed from schreibersite by this reaction amounts to roughly three times of phosphide. The ample amount of whitlockite in some microspherules (e.g. Fig. 3) is probably due to the oxidation of schreibersite.

Metal is known to be often present in chondrules as droplets or globular blebs of different sizes, and they have been considered to be due to the metal-silicate fractionation which formed immiscible liquid of metal in silicate melt (Wood, 1967; Kurat, 1984). Could whitlockite be formed inside those metal spherules by reacting with a chondrule material? The following several occurrences of phosphate-bearing microspherules seem to indicate their xenolithic origin, i.e. they were formed in different environments and incorporated in chondrules.

(a) In chondrules the outline of phenocrysts rarely underwent deformation by adjacent phenocrysts in chondrules. Contrarily it is often the case that the arrangement of adjacent phenocrysts is obviously affected by the presence of microspherules. This clearly indicates that the groundmass material of chondrules still had fluidity and the crystallization of phenocrysts was not ended when the solidification of phosphate-bearing microspherules started. Then, assuming that the crystallization of whitlockite in microspherules took place inside the chondrule groundmass, it would be expected that whitlockite crystals should be also idiomorphic toward outside of microspherules. As mentioned previously, phosphates in microspherules are actually idiomorphic to metal core but rounded toward outside. Such an occurrence seems to be understood only when the spherules solidified in the free space, where the surface tension of whitlockite works more effectively to maintain its spherical outer surface than in silicate melt.

(b) Chromite or chromite-like mineral often occurs along the outer rim of phosphate as seen in Figs. 3 and 6. In Saratov those microspherules with chromite rim are coexisting with Mg-Al-rich spinels which show distinct chemical zoning (Fig. 3). The compositions of these spinels range Mg 4.9–16.1%, Al 21.1–61.1%, Fe 17.3–28.3% and Cr 2.7–42.7%. In contrast, chromite at the rim of microspherules is almost depleted in Mg and Al according to the qualitative analysis. It is also indicative of their different origins, because such different kinds of spinel group minerals usually never occur in a single chondrule according to the study of Yabuki et al. (1983).

(c) In addition, the features of some microsperules support their xenolithic origin. One of the microspherules in Mezö Madaras bears appearance to have been partly broken by collision (Fig. 6). Though such a microspherule is quite rare, it

Fig. 6. A partly broken (upper part) microspherule from Mezö Madaras (L3). It is a clear-cut evidence that those microspherules had encountered some collision in space before they were captured by coarser silicate melt. Unbroken part of the spherule is thinly rimmed by chromite (or chromite-like phase). BEI.
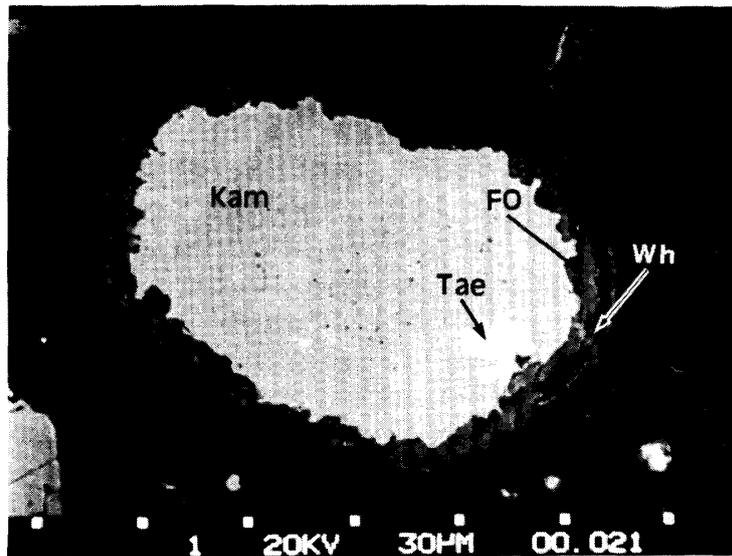
Fig. 7. Elongated microspherules arranged in a preferred orientation. It is indicative of a relative motion between this group of spherules and the host chondrule melt. Mezö Madaras. BEI.
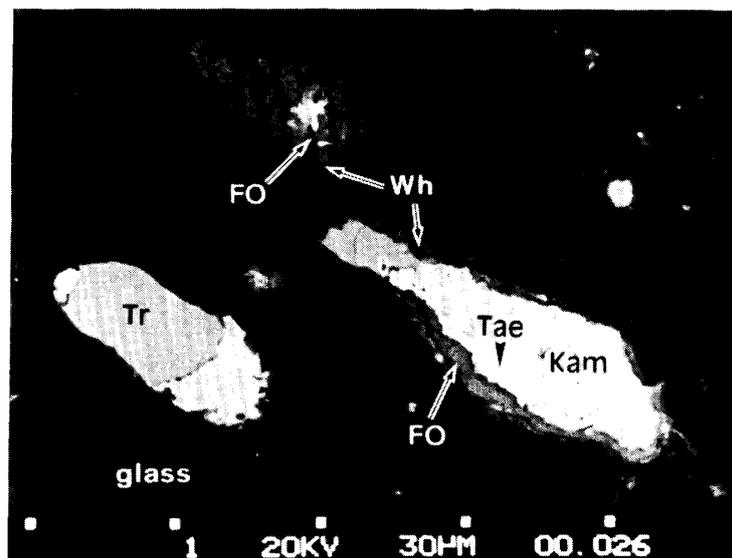
definitely shows the evidence that at least some of the phosphate-bearing microspherules in chondrules had experienced collision in the free space before they were captured into silicate melt.

(d) Many microspherules contain various amounts of oxidized iron usually along the rim of metal core (e.g. Fig. 6) even in chondrules with forsteritic olivine in fairly fresh meteorite surface. The oxidization of iron is considered to be unlikely to be formed in situ under the reduced condition in those chondrules. This occurrence of iron oxide appears to be the traces of oxidation reaction which formed phosphate at the margin of spherules.

(e) The arrangement in a preferred orientation exhibited by some groups of spherules as seen in Fig. 7 suggests some kinetic force acted on those groups of bodies. It may have a relationship to the direction of movement of those spherules before being captured by silicate chondrule melt.

It seems rather natural to consider that metal and schreibersite also formed molten

droplets during the event of chondrule formation, *i.e.* impact, lightening or some other phenomena. The source of the metal and phosphide grains might be the nebular condensate themselves or fragments of some precursor materials or fragments of a pre-existing iron meteorite material. By oxidation of molten droplets of these materials chromite could be the first phase to crystallize, in case their chromium content was relatively high. Thus fine-grained chromite arranged along the outer surface of microspherules could be understood. Assuming the xenolithic origin of those microspherules is true, they must have once come across the environment with enough CaO and O_2 as gas phase so as to proceed the reaction (2). Unfortunately, the observation of microspherules does not give us any information about where the oxidation of these bodies took place. It is also left as future problem if apatite found in spheroidal bodies in chondrules in Arapahoe is common in chondrites of higher petrologic types, *i.e.* if apatite occurs only in higher petrologic types or not. Anyhow, it seems plausible that those phosphate-bearing microspherules which were formed in free space had a chance to be captured by much coarser silicate melt after their solidification.

Acknowledgments

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