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Native metal in diogenite meteorites[1]

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Abstract

Metal particles in eight of the nine known diogenites have been analyzed for Fe, Co, and Ni by electron microprobe. Those in Shalka, Tatahouine, Garland, and the majority in Ellemeet contain less than 1.5 weight percent Ni. The metal in Johnstown ranges from 2.5 to 5.4 weight percent Ni. Some metal grains in Ibbenbüren, Peckelsheim, and Roda contain more than 50 weight percent Ni; other grains in these meteorites contain between 2 and 5 weight percent Ni. Except for Ellemeet, the Co content of diogenite metal is generally higher than in the metal in chondrites. Some metal grains in Roda have the highest Co content ever reported for meteoritic metal (up to 27.3 weight percent). The differences in metal compositions and abundances among the diogenites imply that relationships among the members of the group are more distant than implied by the results of previous studies by other workers.

Introduction

The diogenites are achondritic meteorites consisting almost entirely of orthopyroxene (Fs_{23-28}, Gooley, 1972) with accessory amounts of plagioclase, olivine, troilite, chromite, native metal, and tridymite. The diogenites are also commonly called hypersthene achondrites.[2]

Native metal is quantitatively insignificant in the diogenites, ranging from a reported high of 0.33 percent (probably weight percent) in the Johnstown meteorite (Hovey, 1925) to a trace in Ibbenbüren. Despite its low abundance, the native metal is an important phase, because its presence reflects a low oxygen fugacity during the formation and/or metamorphic history of these meteorites, and its composition may provide unique evidence pertaining to genetic relationships among the members of this small group of meteorites.

Considerable variation is evident in the abundance, particle size, morphology, texture, chemistry, and mode of occurrence of the metal particles among the individual members of the diogenite group. Therefore, some general features will be discussed first, then each diogenite will be reviewed in greater detail. Due to the common association of troilite and chromite with the metal, these phases are included in the discussion.

Electron microprobe analyses for Fe, Co, and Ni have been conducted on the metallic particles in 8 of the 9 recorded diogenites. Phosphorus and sulfur are generally below the detection limit. Sulfur is detectable in some metal with coexisting troilite, and Cr is detectable in some metal with coexisting chromite. Secondary fluorescence may account for both. No schreibersite was found in the diogenites. The diogenite Manegaon was unavailable for this study, but Peckelsheim, recently identified as a diogenite (Gooley, 1972) is included.

Description and data

Opaque microscopy and electron microprobe analyses were conducted on 1 thin section each for Ellemeet and Garland, 1 polished section of Peckelsheim,

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[2] The compositional limits used by meteoriticists for defining hypersthene are different from those usually used by mineralogists; hypersthene in meteoritic terms contains more than 20 percent of the ferrosilite end member.

2 polished sections each of Johnstown and Tatahouine, and 3 polished sections each of Ibbenbüren, Roda, and Shalka. Hand specimens of Johnstown, Shalka, and Tatahouine were available for representative comparison.

All of the diogenites except Tatahouine are breccias, and are made up of clasts of orthopyroxene in a fine-grained matrix of the same material. Metal particles occur both within the large pyroxene clasts and as discrete particles in the fine-grained pyroxene matrix of the meteorites. The metal particles which occur in the large pyroxene clasts generally have smooth and well-rounded shapes, while those in the fine-grained matrix generally are deeply scalloped, and very irregular in shape. The matrix metal particles are generally larger than those in the large pyroxene clasts. In some diogenites the metal particles in the fine-grained matrix have higher Ni and Co contents than those in the larger pyroxene clasts from the same meteorite. Both troilite and chromite commonly occur with the metal particles, both in the fine matrix and in the large pyroxene grains. Coexisting kamacite and taenite were found only in one metal particle in Peckelsheim.

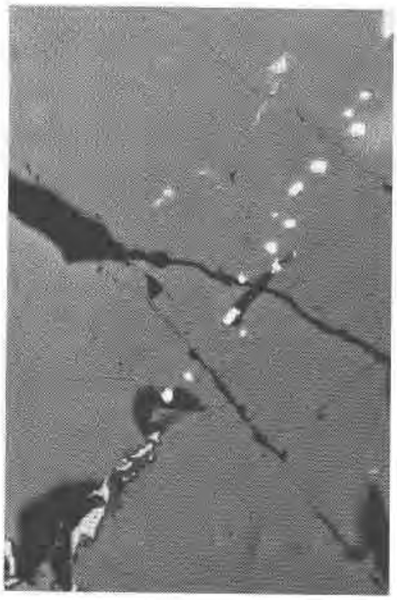

FIG. 1. Plane of metal and chromite particles in a pyroxene crystal in Johnstown. The bright particles are metal; each particle is associated with small chromite grain. The larger gray irregular-shaped grain at lower right is chromite. The dark gray material associated with the chromite and with some metal grains is tridymite. Photo length—1 mm.

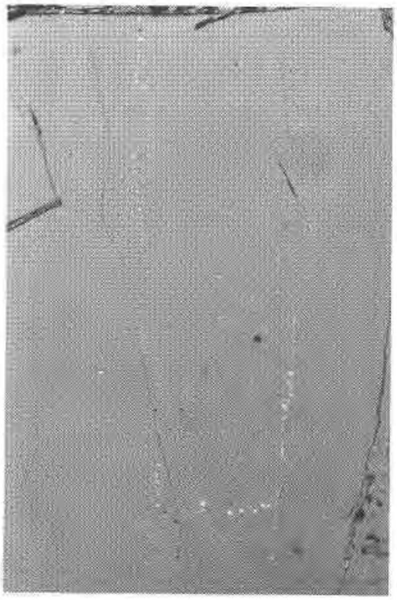

FIG. 2. Planes of opaque mineral particles in a pyroxene crystal in Peckelsheim, arranged such that they appear to outline a former crystal or series of fractures. Photo length—500 μm.

A common mode of occurrence for all 3 of the opaque mineral phases chromite, troilite, and metal is in the form of numerous small rounded particles arranged in noncrystallographic planar arrays within pyroxene clasts. In a polished section the planes appear as rows of opaque mineral grains traversing the surfaces of the pyroxene crystals (Figs. 1 and 2). A plane of particles may contain one, two, or all three opaque phases in any combination or association. In some pyroxene clasts several intersecting planes are present, arranged such that they appear to define the boundaries of previously existing anhedral pyroxene grains or series of fractures (Fig. 1). Generally, the planes do not stop at a fracture in the pyroxene clasts, but traverse and thus predate the fractures.

In some diogenites, it is common to find small (<5 μm) silica inclusions associated with the metal and chromite particles in the pyroxene crystals. Some were identified optically as tridymite, but most are too small for identification and can be detected only by fluorescence under the electron beam. The presence of a minor amount of Al in some of the larger inclusions (not analyzed quantitatively) was revealed by the energy dispersive detector.

Ellemeet

Table 1 lists the compositions of the metal particles in Ellemeet and 5 other diogenites. The larger particles in the fine-grained pyroxene matrix have higher Ni and Co contents than the particles which occur within the pyroxene clasts. Native metal is rare in our one thin section of Ellemeet.

Garland

Based on the observations of one thin section of Garland, this meteorite is comparable in native metal content to Johnstown. All the metal particles are highly irregular in shape, and occur in the fine-grained matrix material. They are generally larger than most metal particles found in diogenites; the largest particle observed is about 250 × 500 μm in size. The metal in Garland has a very low Ni content (Table 1). Some of the metal particles in Garland are associated with troilite in a complex intergrowth characteristic of Fe–FeS eutectic crystallization. The Garland meteorite is the only diogenite in which the evidence of the Fe–FeS eutectic crystallization was found even though metal and troilite coexist in juxtaposition in others.

Ibbenbüren

Native metal is rare in Ibbenbüren; troilite and chromite are more abundant, but the total abundance of opaque minerals is estimated to be less than 0.1 percent. Eight metal particles were found in a 200 μm sized cluster, arranged so that the particles were separated by no more than about 40 μm of silicate material. Considering the scarcity of metal in Ibbenbüren, it would seem unusual to find such a cluster of particles unless there was some genetic or three-dimensional association among them. It is probable that these particles are remnants of a larger metal particle which was cut during the sample preparation. The analytical results are given in Table 2. Four of the particles are very Ni-rich, and three of them have abnormally high Co contents. Despite the suspected association among the metal particles in Ibbenbüren, the compositions do not appear to form an equilibrated assemblage.

TABLE 1. Compositional ranges of the metal particles in 5 diogenites

Diogenite	Pyroxene Matrix	Ni wt. % Range	Median	Co wt. % Range	Median	Median Ni/Co
Ellemeet	Clast Fine	0.69-1.09 7.20-8.29	1.02 7.74	0.07-0.41 0.12-	0.11 0.12	9.3 64.5
Garland	Fine	0.04-0.68	0.09	0.19-0.61	0.44	0.2
Johnstown	Clast Fine	2.50-3.20 3.13-5.40	3.10 4.44	0.65-0.78 0.68-1.81	0.71 1.01	4.4 4.4
Shalka	Fine	0.03-0.20	0.07	1.16-2.54	1.66	0.04
Tatahouine	Clast*	0.42-1.92	0.76	0.53-0.92	0.75	1.0

*Tatahouine is not a breccia.

TABLE 2. Compositions of metal particles in Ibbenbüren and Peckelsheim. Dashes between values indicate compositional ranges over a number of particles; commas between values indicate compositions of each phase in 2-phase particles.

Metal	Fe	Co	Ni
Ibbenburen			
Kamacite	88.8-90.6	5.58-7.60	3.03-3.65
Taenite	47.7-50.7 69.6	1.13-2.66 1.92	45.5-51.9 27.1
Peckelsheim			
Kamacite	92.5	2.31	3.77
Taenite	78.5-83.4	1.43-1.22	18.3-15.4
2-phase	95.1,93.2 90.3,46.1	0.94,0.93 3.73,0.47	3.01,5.07 5.07,52.2

Johnstown

Metal particles in the Johnstown meteorite range in size from less than a micron up to about 1.3 mm across, and occur both within the larger pyroxene clasts and as discrete inclusions in the fine-grained matrix. The metal particles in the fine-grained matrix appear to be larger and more irregular in shape than those in the larger pyroxene clasts.

Planes of metal particles are common in Johnstown (Fig. 1). The particles that are found in the planes are generally on the order of about 2 μm in size, but some planes contain particles between 10 and 20 μm. These larger particles commonly are associated with small chromite grains.

Many of the metal and chromite particles in the large pyroxene clasts are associated with grains of tridymite. The compositional ranges of the metal particles in Johnstown are given in Table 1. The metal which occurs in the fine-grained matrix tends to have higher Ni and Co contents (with some overlap) than the metal in the large pyroxene clasts. Mason and Jarosewich (1971) reported Ni contents of 3.1 ± 0.3 weight percent and Co contents of 0.50 to 0.65 weight percent ave. 0.59 weight percent for the metal in Johnstown. The range of Ni and Co abundances obtained by them is therefore less than that of the present study.

Peckelsheim

Numerous planes of micron-sized troilite grains are present in some of the pyroxene clasts in Peckelsheim. Some of these troilite grains are associated with metal grains. Microprobe analysis of these metal particles was not possible due to their small size.

Five metal particles large enough for analysis were found in the section (Table 2). One unusual 2-phase particle consists of two portions which are slightly different from each other in color and reflectivity, and are separated by a sharp boundary. The Ni content of one phase is about 3.0 weight percent and of the other about 5.1 weight percent. Cobalt contents up to 3.7 weight percent were found in the kamacite in Peckelsheim; Ramdohr and El Goresy (1969) reported 4.16 weight percent. Peckelsheim contains the only 2-phase kamacite–taenite particle found in this study.

Roda

Based on observations of 3 polished sections, the metal content of Roda is estimated at less than 0.1 percent. The majority of metal occurs as irregular-shaped particles in the fine-grained matrix. One plane of small ($<5\ \mu m$) metal particles and one larger ($\sim 25\ \mu m$) individual metal particle were found in a pyroxene clast. The particles in the plane are associated with chromite grains, and are too small for microprobe analysis. The metal particles in the fine-grained matrix are generally larger (up to about $50 \times 75\ \mu m$) than those in the larger pyroxene clasts. Metal particles in Roda are commonly associated with sulfides, generally troilite. Table 3 gives the compositional ranges of the metal particles in Roda.

Six metal particles that have the highest Co contents ever reported in meteoritic metal were found in Roda. Due to their small size and proximity to sulfides, two of the six were not analyzed quantitatively. Qualitative analyses show that these two particles are compositionally similar to the other four. The Co-rich metal particles are very inhomogeneous, with Ni and Co varying inversely, and no regular pattern to the compositional variations was detected. The largest of these metal particles is about 25 μm across.

Five of the six Co-rich particles were associated with sulfides; it is quite possible that the sixth, which was one of the larger particles, may have had associated sulfides which were removed during sample preparation. The three larger metal particles associated with sulfides have small sulfide inclusions within the interior of the metal. Most of the sulfide is troilite. Pentlandite was identified by semiquantitative analysis; mackinawite was identified by its optical properties (Schot *et al.*, 1972) and semiquantitative analysis.

TABLE 3. Compositions of metal particles in Roda

Metal Type	Ni wt. % Range	Ni wt. % Median	Co wt. % Range	Co wt. % Median
Kamacite	2.15-4.27	3.1	0.52-1.79	0.8
Taenite	51.7-53.3	53.0	1.27-1.82	1.4
Co-rich Particles	1.75-2.18	2.0	20.7-27.3	23.6
Homog.*	0.83-2.67		16.8-30.7	

*Homog. refers to compositional variance within a single Co-rich particle.

Shalka

Metal occurs in Shalka as fairly large (up to about 0.5 mm) irregularly shaped inclusions in the fine-grained matrix material. The compositional ranges are listed in Table 1. The metal in Shalka and Garland has the lowest Ni content of any of the diogenites, but the metal particles in Shalka tend to have higher Co contents than those in Garland.

Tatahouine

Tatahouine is generally composed of green, unbrecciated orthopyroxene with dark, almost black bands, up to about 2 mm wide, running through the material. The dark color of the bands appears to be the result of a high concentration of opaque particles (chromite, troilite, and metal). An estimated 90 percent of the opaque particles are troilite. Most of the particles are too small for analysis. Metal and troilite are associated in some particles, but generally metal is found alone. The metal composition in Tatahouine follows the trend of low Ni contents found in the other diogenites Ellemeet, Garland, and Shalka (Table 1).

Discussion

Considering the similarities between the members of the diogenite group (Mason, 1963; Taylor *et al.*, 1965; Gooley, 1972), the marked differences in the nature of the metal are interesting and significant. The metal particles in Shalka and Garland have Ni contents generally about 0.1 weight percent. Those in Tatahouine and most in Ellemeet contain about 1 weight percent Ni, and some in Ellemeet contain about 6–7 weight percent Ni. Johnstown metal ranges in Ni content from 2.5 to 5.4 weight percent. Ibbenbüren, Peckelsheim, and Roda have some metal containing greater than 50 percent Ni. Striking differences can also be seen in Co contents. Ellemeet metal generally has a low Co content, about 0.1 weight percent. Median values for Garland, Johnstown, Shalka, and Tatahouine range from 0.4 to 1.7, with subtle distinctions evident in these 4 members (Table 1). Peckelsheim metal contains up to about 4 weight percent Co, Ibbenbüren up to about 7.6 weight percent, and Roda contains metal with up to 27.3 weight percent Co.

Previous investigations of the diogenites have implied close genetic relationships between these meteorites and other groups of achondrites (Taylor *et al.*, 1965). References to the "parent body" or to "the event" in a singular sense have been made in discussing their origins and histories (Lovering, 1962; Moore, 1962; Mason, 1963; Duke and Silver, 1967; Jérome, 1970). Differences among the diogenites in the abundance of metal and especially its composition appear to imply that the relationships among the members of the diogenite group may not be as close as previously suggested.

The mode of occurrence of the metal, troilite, and chromite particles arranged in planar arrays within the larger pyroxene clasts indicates that the diogenites have undergone one or more metamorphic episodes in their histories. The following multistage mechanism for the formation of the planar arrays of metal grains is proposed: (a) a reduction of the siderophile elements in the pyroxene, predominantly along fractures or grain boundaries, and diffusion of the metal to the fractures; (b) annealing and/or recrystallization of the pyroxene, leaving the planar arrays of particles to mark the positions of previous fractures; (c) new fractures then formed, probably both during cooling and with subsequent brecciation. Chromite and troilite grains are found in planar arrays similar to those of metal particles, indicating a similar mechanism of particle growth along preexisting fractures or grain boundaries, subsequent recrystallization, etc. The formation of excess silica will result from reduction of Fe from the pyroxene; SiO_2 is commonly associated with the metal particles, especially in the Johnstown meteorite. Reduction origins have been previously discussed for achondritic metal (Duke, 1965; Lovering, 1964) and for lunar metal (Reid *et al.*, 1970; Brett *et al.*, 1971; and others).

Williams (1971a) studied the system FeO–MgO–SiO_2–O_2 and applied the results to the equilibrated chondrites (Williams, 1971b). He reports a value for log fO_2 of -17.5 ± 1.2 at 880°C for this group of meteorites; the ± 1.2 uncertainty is due mainly to sizeable compositional variations of the chondrites. Application of Williams' method to the Johnstown meteorite gives log $fO_2 = -18.5$ at the same temperature; a similar value is valid for any of the diogenites in which native metal and silica coexist, as the compositions of pyroxene (and most metal) of the diogenites are similar. The 880°C temperature for the diogenites was chosen to compare them to the chondrites as closely as possible, and is not assumed to be the formation temperature for these meteorites. The comparison shows, however, that the diogenites were affected by fO_2 conditions on the reducing end of the range for equilibrated chondrites.

In Ellemeet, the large compositional and size differences between the metal particles which occur within the pyroxene clasts and those which occur in the fine-grained matrix imply different origins for the two types. The small metal particles within the clasts probably are products of reduction from the silicate. The larger, more Ni-rich metal grains which occur in the fine-grained matrix may or may not be indigenous material. An assumption that they are indigenous suggests a paragenetic sequence of metal formation such as proposed by Brett *et al.*, (1971) for lunar metal. Their mechanism requires that metal occurring in early-formed minerals is more enriched in Ni and Co than that in later formed minerals. A suggestion that the Ni-rich grains are not indigenous diogenite material requires a foreign source, such as a "meteorite" impacting on the parent body of the diogenites. The two types of metal represent the only nonequilibrated assemblage that we have observed in Ellemeet. A foreign source for the Ni-rich metal is consistent with this observation.

In Johnstown, small differences in the Ni and Co contents between the small metal grains which occur within orthopyroxene clasts and the larger ones in the fine-grained matrix are apparent, but the Ni/Co ratios are the same (Table 1). A reasonable explanation is as follows: Native Fe produced by reduction from the silicate during some metamorphic event would be incorporated into previously existing metal particles, altering their composition by dilution. The smaller metal grains would be more affected compositionally than the larger ones, but the Ni/Co ratio of all the metal grains would remain unchanged.

The compositions of the metal particles in Ibbenbüren and Peckelsheim (Table 2) reflect an unequilibrated assemblage. Each meteorite contains metal particles with Ni contents of about 50 weight percent, others with 14–25 weight percent Ni, and still others with 3–5 weight percent Ni. The Co contents of some of the metal particles in both meteorites are also high, and must be included in equilibrium considerations. The unequilibrated metal assemblage is enigmatic considering the other minerals that make up the bulk of the diogenites, which appear to form equilibrated assemblages (Gooley, 1972). The Fe–Ni–Co phase diagram is not well defined, but is presently being determined (J. I. Golstein, personal communication). Perhaps this seemingly unequilibrated metal is actually an equilibrated assemblage, explainable when the above study is complete.

We are unable to satisfactorily explain the origin of the Co-rich metal in Roda. The meteorite contains metal particles with ~25 weight percent Co and ~2 weight percent Ni, some with ~1.4 weight percent Co and ~53 weight percent Ni, and some with ~1 weight percent Co and 3 weight percent Ni. As with Ibbenbüren, the question of whether these phases represent an equilibrated assemblage is unresolved due to the uncertainties in Fe–Ni–Co system. Present phase diagrams for this system indicate an unequilibrated assemblage. The fact that most of the Co-rich metal particles are associated with sulfides may be a clue to their origin, but alternatively, may simply reflect a more chalcophile nature for Co.

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