Geochimica et Cosmochimica Acta Vol. 44, pp. 211 to 216
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0016-7037/80/0201-0211$02.00/0

Electron microprobe study of a 'mysterite'-bearing inclusion from the Krymka LL-chondrite

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(*Received* 3 *July* 1979; *accepted in revised form* 2 *October* 1979)

Abstract—The black inclusion from the Krymka LL3 chondrite previously found to contain 'mysterite' by LEWIS *et al.* (1979) belongs to a hitherto unknown class of carbonaceous chondrites. Its olivine and pyroxene compositions, Fo 97–99 and En 96, respectively, are characteristic of carbonaceous chondrites and its plagioclase composition, An 100, is characteristic of C3's. It contains a peculiar group of Co-, Cr-rich metal grains whose compositions are similar, but not identical, to those in C2 chondrites and which also bear some similarities to those in Renazzo. Its weight ratios of total Fe/SiO_2 and SiO_2/MgO are 0.74 and 1.43, respectively, and its atomic ratio of Si/Al is 10.7, exactly the same as in carbonaceous chondrites. Its bulk chemical composition is very close to that of the Murchison C2 chondrite. The association of mysterite with a special type of carbonaceous chondrite material suggests that mysterite formed by low-temperature condensation in a different region of the nebula from other carbonaceous chondrites.

INTRODUCTION

IN A STUDY of volatile elements in chondrites, LAUL *et al.* (1973) noted that, among others, Supuhee, an H6 chondrite, and Krymka, an LL3, have anomalously high Bi and Tl contents. To account for this, they postulated that these meteorites contain a volatile-rich late nebular condensate, which they termed 'mysterite'. In a later trace element study of dark clasts from Supuhee, HIGUCHI *et al.* (1977) discovered extraordinary enrichments of Bi and Tl, leading them to the conclusion that the late condensate materials occur as distinct petrographic components. A petrographic and electron microprobe study of several Supuhee clasts led to the discovery of one which has mineralogical and chemical similarities to C1 and C2 chondrites, but which is not identical to either of these two meteorite types (LEITCH and GROSSMAN, 1977). In that work, it was suggested that this new type of carbonaceous chondrite could very well be the carrier of mysterite in Supuhee since such material must have formed under different conditions of low-temperature condensation than C1 or C2 chondrites and could have different volatile element contents from these. This was not directly testable, however, since trace element data were not available for that particular clast.

LEWIS *et al.* (1979) presented noble gas and trace element data for a black inclusion from Krymka and found that it possesses the high Bi and Tl contents characteristic of mysterite. This paper gives the results of a petrographic and electron microprobe study of the same inclusion aimed at seeing whether it possesses any other attributes of low-temperature condensates and, if so, whether it has any relationship to the previously-studied Supuhee clast.

DESCRIPTION

A polished thin section was made from a piece of the inclusion studied by LEWIS *et al.* (1979). The section is 1.8 mm in its longest dimension and contains a 0.5 mm Krymka chondrule at one end. The clast (Fig. 1) contains sparse, elongated, sub-rounded orthopyroxenes from 5 to 80 μm in longest dimension, as well as sparse, rounded olivines up to 10 μm in size. Ni-Fe with rims of troilite is found in composite grains down to the submicron size range and in aggregates up to 20–30 μm in size. These grains are all embedded in an extremely fine-grained matrix in which individual particles could not be resolved with an SEM at 16,000 ×. There is a slight suggestion of an overall lineation in the clast caused by the parallel alignment of the long axes of the coarser particles. Although there may be flattening in the plane of the lineation, there is no evidence for restriction of the coarser particles to discrete planes. The chondrule adjacent to the clast consists of olivine, orthopyroxene and clinopyroxene, mantled by a finer-grained rim of troilite, orthopyroxene and traces of metal and olivine.

ANALYTICAL TECHNIQUES

Unless otherwise indicated, all electron microprobe analyses reported here, both focused beam and broad beam, were obtained by energy-dispersive techniques with the same system and under the same operating conditions as those in ALLEN *et al.* (1978). Wavelength-dispersive analyses were also obtained in the same way as in ALLEN *et al.* (1978), with a beam current of 0.33 μA.

RESULTS AND DISCUSSION

Because the sizes of the mineral grains in the clast are usually smaller than the diameter of the electron beam, attempts to analyse pure phases were usually unsuccessful because of the presence of adjacent, unwanted minerals within the analytical volume.

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Table 1. Microprobe analyses of olivines and pyroxenes (wt%)

	Olivines		Pyroxenes	
	1	2	1	2
SiO_2	42.32	42.64	59.22	60.02
Cr_2O_3	0.18	0.33	0.32	0.21
FeO	2.53	0.67	2.44	2.40
MnO		0.24		
MgO	53.83	55.37	37.46	37.56
CaO	0.21	0.11		
Total	99.07	99.36	99.44	100.19
	Cations/4 oxygens		Cations/6 oxygens	
Si	1.01	1.01	2.01	2.02
Cr	0.00	0.01	0.01	0.01
Fe	0.05	0.01	0.07	0.07
Mn		0.01		
Mg	1.92	1.95	1.90	1.88
Ca	0.01	0.00		
Mg/Mg+Fe	0.97	0.99	0.96	0.96

Thus, we report here spot analyses of only the largest grains.

Two grains of olivine were identified in this way. The analyses in Table 1 show that their compositions are Fo 99 and Fo 97. In addition, two pyroxenes were identified whose compsitions, also shown in Table 1, are En 96. These exceedingly iron-poor compositions are rare in ordinary chondrites, but are common in all classes of carbonaceous chondrites and in enstatite chondrites, although olivine is only an accessory phase in the latter group.

Table 2 shows analyses of two grains, identified as plagioclase on the basis of these results. They are both An 100, a composition whose only other meteoritic occurrence is in high-temperature condensate inclusions in C3 chondrites.

Analyses of four grains of metallic nickel-iron and one of troilite are given in Table 3. Particularly noteworthy are the unusually high Co and Cr contents in all of the metal grains and the high P content in sample 3. The latter sample also has a Ni/Fe ratio higher than the solar value, while the remaining metal grains have ratios lower than the solar ratio. GROSSMAN and OLSEN (1974) found that metal grains in C2 chondrites contain 4–8 mol% Ni, 0.2–0.7% Co, 0.2–1.0% Cr and 0.3–6% P and that their Ni/Fe ratios are usually higher, but sometimes lower, than the solar value. They also noted that the metal in Renazzo has similar Ni and Co contents to these, but lower P (0–0.09 mol%) and Cr (0.17–0.24 mol%), although Cr is still much higher than in most meteoritic metal. Examination of Table 3 shows that metal in this inclusion is generally similar in composition to C2 metal grains, but its Co content is even higher, and Ni usually even lower, than in these. Its low P content, except for sample 3, and low Cr, except for sample 1, cause it to resemble Renazzo metal more than that of C2's.

Thus, on the basis of mineral chemistry, the Krymka inclusion appears to belong to a hitherto unknown class of carbonaceous chondrites which has plagioclase compositions otherwise restricted to C3 chondrites and metal phase compositions similar to those found only in C2 chondrites, but with affinities to those in Renazzo.

In Table 4, the bulk chemical composition of the Krymka inclusion is compared to those of the Murchison C2 chondrite, Renazzo and a clast from Supuhee. In presenting these data, all analyses were recalculated to show all S as FeS, all the remaining Fe as FeO, and all Ni and Co as the metals. The data for Krymka represent the mean composition of nine different 70 μm dia regions within the inclusion, selected by avoiding large grains and analysed by broad beam microprobe techniques. The Murchison data are the mean of two wet chemical analyses (JAROSEWICH,

Table 2. Microprobe analyses of plagioclase (wt%)

	1	2
SiO_2	40.75	42.21
Al_2O_3	35.69	35.56
FeO^*	2.61	1.39
MgO^*	2.85	1.25
CaO	17.21	18.67
K_2O		0.13
S^*	0.26	0.22
Total	99.37	99.43
	Cations/8 oxygens	
Si	2.00	2.02
Al	2.06	2.00
Ca	0.91	0.96
K		0.01

* For these elements, most of the amount present is likely to be due to contamination from surrounding phases.

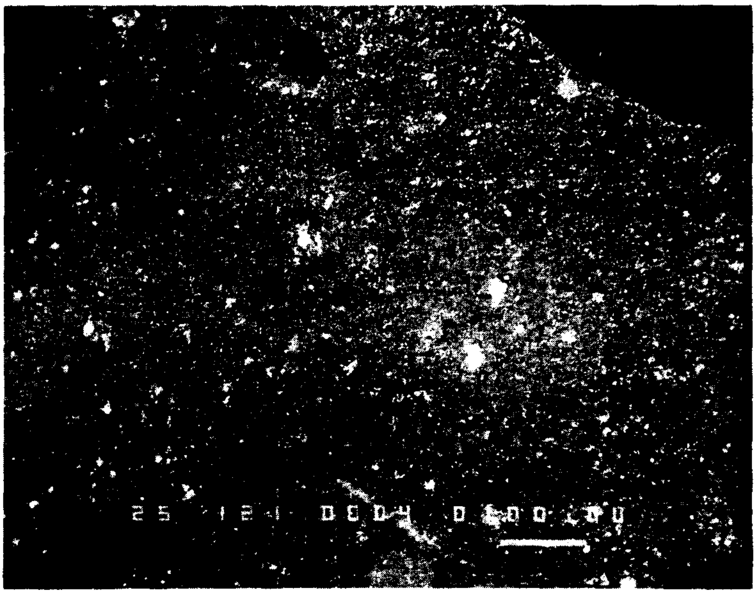

Fig. 1. SEM photomicrograph of Krymka inclusion. Enstatite and forsterite (dark) and troilite or composites of troilite and metal (white) are embedded in a very fine-grained matrix. Scale bar is 100 μm.

Table 3. Compositions of metal and troilite grains

	Metal[1]				Troilite[2]
	1	2	3	4	5
Fe	92.34	91.71	89.06	92.86	60.47
Ni	3.05	3.53	7.83	3.54	<0.5
Co	1.45	1.36	1.52	1.43	0.44
Cr	0.46	0.24	0.14	0.06	
Si	0.25	0.32	0.52	0.06	
P	0.17	0.22	0.85	<0.04	0.21
S[3]	0.16	0.14	0.26	0.20	33.72
Total	97.88	97.52	100.18	98.15	94.84[4]

[1] Analysed by wavelength-dispersive techniques. Values in mol%.
[2] Analysed by energy-dispersive techniques. Values in wt%.
[3] S contents of metal grains, samples 1–4, may be at least partly due to contamination by surrounding troilite.
[4] After subtraction of a total of 6.74% Na_2O, MgO, Al_2O_3, SiO_2 and K_2O due to contamination by surrounding silicates. After subtracting P as Fe_3P, the atomic (Fe + Co)/S ratio is 1.017. This ratio is well within analytical uncertainty of unity.

1971; FUCHS *et al.*, 1973) and those for Renazzo come from the work of MASON and WIIK (1962). The data for the Supuhee clast are the average of eleven broad beam analyses (LEITCH and GROSSMAN, 1977). The low sum in the Murchison analysis is due mainly to the presence of ~ 13% volatiles such as H_2O, C and CO_2 which could not be determined by the microprobe techniques used in the Krymka analysis and were therefore omitted from the Murchison composition in preparing this comparative table.

The bulk composition of the Krymka inclusion is seen to be remarkably similar to that of Murchison, apparently confirming our inference based on mineral chemistry that the Krymka inclusion is a carbonaceous chondrite. Na is the only element whose abundance is significantly different in the two objects, but this may simply be a sampling problem, since Na appears to be extremely heterogeneously distributed within individual C2's (FUCHS *et al.*, 1973). In Table 4, Renazzo's analytical sum is much higher than Murchison's. There are two reasons for this. First, Renazzo contains only ~7% volatiles. Second, Renazzo, unlike C2's, contains a large quantity of metallic Fe, 11%, and this has all been calculated as FeO here. These characteristics of its bulk composition, as well as its lower FeS, serve to distinguish it from the Krymka inclusion also.

The Krymka inclusion has a weight ratio of total Fe/SiO_2 of 0.74, within the range for each of the enstatite, carbonaceous and H-group ordinary chondrite classes (VAN SCHMUS and WOOD, 1967). The weight ratio of SiO_2/MgO is 1.43, almost identical to that for carbonaceous chondrites and quite different from that of ordinary and enstatite chondrites (VAN SCHMUS and WOOD, 1967). Furthermore, on the SiO_2 *vs* MgO graph of CLARKE *et al.* (1970), the Krymka

Table 4. The bulk composition of the Krymka inclusion, compared with Murchison, Renazzo and a clast from Supuhee (wt%)

	Krymka Inclusion	Murchison	Renazzo	Supuhee Clast
SiO_2	29.80±0.87[1]	28.15	33.83	29.2
Al_2O_3	2.37±0.19	2.10	2.36	2.71
Cr_2O_3	0.40±0.05	0.44	0.56	0.44
FeO	22.37±1.03	20.38	29.14	15.5
MnO	0.14±0.13	0.21	0.24	0.38
MgO	20.87±0.37	19.42	23.76	21.0
CaO	1.43±0.40	1.82	1.78	3.28
Na_2O	0.10±0.15	0.41	0.55	1.35
K_2O	0.05±0.07	0.04	0.04	0.57
FeS	7.37±1.27	8.56	3.59	14.3
Ni	1.10±0.18	1.37	1.35	1.12
Co	0.14±0.16	0.06	0.11	
Total	86.14	82.96	97.31	89.85

[1] Each uncertainty listed represents one standard deviation of an individual.

inclusion plots in the field of C2 chondrites, very close to Santa Cruz and Al Rais. Although its Si/Al atomic ratio of 10.7 is very close to the mean for all carbonaceous chondrites and different from that in ordinary and enstatite chondrites (AHRENS *et al.*, 1969), its Si/Ca atomic ratio of 19.4 falls in the range of the enstatite chondrites. This is not thought to be very meaningful, however, since the CaO content varies in the broad beam analyses by a factor of 2.8, from 0.83 to 2.31%.

In summary, the bulk chemical composition of the Krymka inclusion, like its mineral chemistry, indicates that it is a carbonaceous chondrite with strong affinities to the C2's. By analogy, its low analytical sum in Table 4 is probably due to the presence of large amounts of volatiles, chiefly H_2O, as in C2's. Consequently, we also infer that the matrix of this inclusion is composed principally of phyllosilicates. Since such phases in other carbonaceous chondrites are very fine-grained, this inference would explain the very fine grain size of the matrix of the inclusion.

As can also be seen from Table 4, there is a close similarity in bulk chemical compositon between the Krymka inclusion and the Supuhee clast, the only major difference being a considerably higher FeS/total Fe ratio in the latter than in the former. There are mineralogical differences between the two, such as the presence of Mn-rich carbonate and magnetite in the Supuhee clast. LEITCH and GROSSMAN (1977) showed that that clast is also a special kind of carbonaceous chondrite, exactly like no other, but bearing mineralogical and chemical similarities to both C1's and C2's. They suspected that it was a carrier of mysterite because other Supuhee clasts with unknown mineralogy contain enrichments in Bi and Tl (HIGUCHI *et al.*, 1977). The overall similarity in composition between that clast and the Krymka inclusion studied here strengthens that connection.

CONCLUSION

HIGUCHI *et al.* (1977) suggested that mysterite condensed in a particular nebular region from which a large fraction of the higher-temperature dust had been lost. We now know with certainty that mysterite resides in special variants of the observed carbonaceous chondrite groups. These must have had their own nebular formation locations, different from those of the normal carbonaceous chondrites. These unusual 'meteorite types' contain large fractions of low-temperature condensate minerals. It is thus probable that their Bi and Tl condensed from a low-temperature solar nebular gas in a different region from the Bi and Tl of other carbonaceous chondrites. Our findings thus support the idea of HIGUCHI *et al.* (1977) that mysterite condensed in a special nebular region, although none of our results bear directly on the question of whether large amounts of dust had been lost from this location.

Acknowledgements—We thank E. ANDERS and R. N. CLAYTON for helpful discussions. This work was supported by the National Aeronautics and Space Administration through grant NGR 14-001-249 and by the ALFRED P. SLOAN Foundation.

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