# Sulfide textures of a unique CO3-chondrite (Y-82094) and its petrogenesis

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Abstract: The unique CO3-chondrite Y-82094 contains abundant FeNi metals. FeNi metal grains are often surrounded by troilite. More than one hundred troilite rimmed FeNi metals have been found in three polished thin sections of Y-82094 (CO3). These structures are frequently found in all CO3s. The troilite rim was formed by the reaction of FeNi metal in the core with S-rich gas. However, there are some differences in the metal-sulfide association between Y-82094 and other CO3s. In Y-82094, rims include two features that have not been observed in other CO3s: fizzed troilite and deviation of a reaction rim. In addition, FeNi metal cores include abundant large phosphates ( $\sim 10 \,\mu$ m). In Y-82094, there is a large discrepancy of subtype classification between 3.0 obtained from variation in olivine composition, and 3.5 determined by thermoluminesc-These features could be explained by shock metamorphism ence (TL). accompanying shock melting and subsequent rapid cooling. The shock effects were particularly effective for opaque mineral assemblages but not effective for silicates.

Y-82094 has other unique features which cannot be explained by shock metamorphism; (1) mean chondrule size of Y-82094 being larger than those of CO3s irrespective of low petrologic subtype from olivine random analyses, and (2) unique bulk chemical composition. Thus Y-82094 is a unique CO3. This could mean that the formation and thermal history of Y-82094 is different from other CO3, implying that Y-82094 does not come from a different parent body from that of the other CO3s.

#### 1. Introduction

Sulfide rims surrounding FeNi metal are commonly found in CO3-chondrites (Imae and Kojima, 2000). It has been suggested that troilite rimmed FeNi metal was formed by reaction of FeNi metal with S-rich gas (Imae, 1994; Lauretta *et al.*, 1996a). If sulfide formation occurred in the solar nebula, we may be able to derive some constraints for the thermal history of the early solar system and the chemical composition of the nebula. For example, the thickness of the sulfide rim would reveal information on the role of sulfide formation (Imae and Kitamura, 1995; Lauretta *et al.*, 1996b).

The CO3 group has been subclassified according to the degree of the thermal metamorphism (McSween, 1977; Scott and Jones, 1990). Several studies related to the sub-classification of CO3s have been carried out (McSween, 1977; Scott and

Jones, 1990; Sears *et al.*, 1991a; Kojima *et al.*, 1995; Shibata, 1996). As for Japanese Antarctic CO3s, Kojima *et al.* (1995) studied refractory inclusion and clarified the relationship between subtype and alteration processes of refractory inclusions in Y-790992, Y-81020 and Y-82050. Shibata (1996) described cohenite in least metamorphosed CO3s (Y-74135, Y-81020, Y-81025 and ALH-77307).

In the present study, we describe unique opaque mineral assemblages in Y-82094 classified as CO3 by Yanai and Kojima (1995) and we address the question of the origin of the sulfide textures. Shibata and Matsueda (1994) have described FeNi metals and phosphates in Y-82094. The present paper will present additional new results focused on the origin of sulfide textures and describe Y-82094 as a unique CO3.

#### 2. Experiments

Three polished thin sections of 91-1 (Fig. 1), 96-1 and 96-2 of Y-82094 from National Institute of Polar Research (NIPR) with surface areas of 1.3, 0.51, and 0.42 cm<sup>2</sup>, respectively, were examined in the present study.

Random analyses to determine the subtype were carried out by an electron probe microanalyzer (EPMA; JEOL JXA-733). Additional analyses were carried out with JEOL JXA-8800 EPMA. The Bence and Albee correction method (Bence and Albee, 1968) for oxides and ZAF corrections for opaque minerals were used. The diameter and the rim thickness of rimmed FeNi metals were measured under



Fig. 1. A polished thin section of Y-82094, 91-1 under the optical microscope.

the reflected light of the optical microscope (OM).

#### 3. Sample descriptions

#### 3.1. Bulk chemical composition

Available bulk chemical compositions of CO3s by wet chemical analyses from the Japanese Antarctic meteorites collection were compared with that of Y-82094 (Table 1) (Yanai and Kojima, 1995). Bulk  $H_2O(+)$  and  $H_2O(-)$  of Y-82094 are lower than those of any CO3 analyzed (Table 1). It is also noted that Y-82094 has the highest MgO and the lowest FeO (Table 1). The content of FeNi metal in Y-82094 is highest among known CO3s.

#### 3.2. Chondrule size

The silicate chondrule size of  $420 \,\mu m$  on average (Fig. 2) is larger than that of other CO3s (120–170  $\mu m$ ) (Dodd, 1981; Rubin, 1989).

# 3.3. Degree of shock metamorphism

About 80% of olivine grains in chondrules and fragments showed undulatory extinction under crossed polars. According to the shock classification scheme for carbonaceous chondrites by Scott *et al.* (1992), the shock stage of Y-82094 is classified to be S2. This is consistent with the shock stage of Y-82094 reported by Scott *et al.* (1992). Since fourteen of fifteen CO3 chondrites except one CO3 classified S3 (Felix) have been classified to be S1 (Scott *et al.*, 1992), S2 is relatively

	ALH-77003	Y-790992	Y-791717	Y-81020	Y-82050	Y-82094	A-882094
SiO₂	34.09	31.24	33.28	31.82	32.91	34.21	31.9
TiO₂	0.13	0.18	0.2	0.16	0.08	0.2	0.14
Al <sub>2</sub> O <sub>3</sub>	2.81	4.05	2.74	4.15	2.73	5.67	3.08
Fe <sub>2</sub> O <sub>3</sub>	0	3.26	1.98	7.63	2.86	0	0.73
FeO	20.42	24.57	26.26	15.94	19.42	14.28	26.39
MnO	0.21	0.16	0.25	0.2	0.31	0.18	0.29
MgO	23.99	23.93	23.38	23.11	24.1	26.92	24.25
CaO	2.23	1.79	2.1	2.15	2.07	2.55	1.91
Na₂O	0.58	0.4	0.47	0.13	0.33	0.39	0.27
K₂O	0.06	0.04	0.06	0.02	0.05	0.03	0.04
H₂O(-)	0.35	1.42	0.75	1.75	0.87	0.3	0.79
H2O(+)	1.6	2.6	1.18	4.4	1.4	0.1	3.6
P₂O₅	0.26	0.22	0.28	0.19	0.28	0.36	0.05
Cr <sub>2</sub> O <sub>3</sub>	0.5	0.52	0.5	0.51	0.52	0.54	0.51
NiO%(ppm)		1.65					
FeS	4.79	4.12	5.08	3.99	7.82	4.04	4.24
Fe	6.6		0	2.54	2.57	9.05	
Ni% (ppm)	1.23		1.22	1.05	1.32	1.1	1.5
Co%(ppm)	0.057	0.048	0.045	0.045	0.05	0.069	0.033
Total	99.9	100.19	99.77	99.78	99.69	99.98	99.72
Total Fe	25.51	24	25.02	22.8	24.64	22.72	24.72

Table 1. Bulk compositions of representative CO3 chondrites in NIPR\*.

\* From Yanai and Kojima (1995)



Fig. 3. EPMA random analyses of olivine (a) and pyroxene (b).

high for a shock level in CO3 chondrites.

#### 3.4. Degree of weathering

Limonite veins of about 50  $\mu$ m suggest that Y-82094 has experienced minor weathering in Antarctica according to the definition by Kojima and Imae (1998).

#### 3.5. Random analyses of olivine and pyroxene to determine the subtype

The fayalite (Fa) and ferrosilite (Fs) contents of olivines and pyroxenes, respectively, obtained by random analyses are plotted in Fig. 3. Averages of Fa and Fs contents in olivine and pyroxene are 2.6 and 1.5 mol%, respectively, and coefficients of variation (C.V.) (Sears *et al.*, 1991b) are 83.1 and 100, respectively. Y-82094 is classified as 3.0 based on the mean Fa (Scott and Jones, 1990).

## 3.6. Textures of opaque minerals

Abundant FeNi metals (kamacite and taenite) and troilite are present (Fig. 4 and Fig. 5). The chemical compositions of FeNi metals and phosphate inclusions have been determined by Shibata and Matsueda (1994). FeNi metals and troilite occur in chondrules, chondrule rims and matrices. In matrix, troilite rimmed FeNi



Fig. 4. A typical troilite rimmed FeNi metal. The PTS number is 91-1. (a) A typical rimmed FeNi metal grain in matrix under the OM (transmitted light). (b) Under the OM (reflected light). Tr=troilite. (c) Core FeNi metals under the BEI. Kam=kamacite. Tae=taenite. (d) The boundary between FeNi metal and sulfide rim. The core metal includes phosphate inclusions. The troilite layer shows fizzed troilite. The troilite rim includes FeNi metal. The boundary between FeNi metal and sulfide is not smooth but complex. Phos=phosphate. Tr layer=troilite layer.

metal grains within the size range of  $100 \,\mu$ m to  $350 \,\mu$ m (Fig. 4) can be found. This type of occurrence of rimmed troilite FeNi metals is dominant in opaque mineral assemblages in Y-82094. Troilite rimmed FeNi metals in matrices often include Ni-rich taenite (Fig. 4c). The structure of the boundaries between FeNi metal and troilite (Fig. 4d) is generally complex, described as intergrowth by Shibata and Matsueda (1994). It is also a eutectic texture suggesting melting and rapid cooling in the Fe-Ni-S system. The morphology of rimmed FeNi metals in matrix of Y-82094 is not usually spherical but irregularly shaped and often deformed (Fig. 4). The radius of metal cores is in the range of  $20-100 \,\mu$ m with a rim-thickness of 10-



Fig. 5. The PTS number is 91-1. (a) Rimmed FeNi metals on a chondrule under the OM (reflected light). Small FeNi metals are shown as arrow. Kam=kamacite. Tr=troilite. Chond=chondrule. Mat=matrix. (b) Rimmed FeNi metals of (a) in transmitted light. (c) Sulfide veins connecting rimmed FeNi metals in a chondrule (reflected light). (d) The transmitted light of (d).

 $50\,\mu m$  as determined under the OM (Fig. 6). With increasing grain size, the thickness of troilite is larger (Fig. 6). The interpretation of this distribution is discussed by Ima and Kojima (2000). In the matrix of Y-82094 abundant small kamacite droplets less than  $10\,\mu\text{m}$  in diameter can be seen (Fig. 5a). FeNi metal grains of similar size are not observed in the other CO3 chondrites (17 Antarctic CO3 chondrites and 4 non-Antarctic CO3s from NIPR and 2 non-Antarctic CO3 in USNM). On the other hand, abundant small FeNi metals within matrix are observed in Leoville (CV3). This meteorite has experienced significant shock metamorphism (S3) observed by Scott et al. (1992). In Y-82094 inclusions of phosphates (whitlockite and brianite) with a few  $\mu$ m (Fig. 4d) are abundant in the periphery of metal grain or on the interface between metal and sulfide. This observation is consistent with that by Shibata and Matsueda (1994). The large number of inclusions in FeNi metals are characteristic of Y-82094. They are not found in other CO3 chondrites. There are no phosphate inclusions within the sulfide rims (Fig. 4d).

Small grain of FeNi metals are often found enclosed in sulfide rims (Fig. 4d).



Fig. 6. The size and thickness distribution of troilite rimmed FeNi metals. A linear relationship can be seen. Two interpretations are possible from the analyses: (1) a larger grain has a thicker rim, and (2) the thickness is constant irrespective of the grain size.



The sulfide rims are porous (Fig. 4d). Most troilite in Y-82094 can be referred as fizzed troilite or metal-troilite fizzes described by Scott (1982), Scott *et al.* (1992) and Bennett and McSween (1996) (Fig. 4d). They are uniformly distributed over the thin sections. It has been suggested that fizzed troilite is formed by rapid cooling after shock melting of metal and sulfide mixtures. Applying the shock classification using opaque minerals of FeNi metal and troilite for L chondrites by Bennett and McSween (1996), the degree of shock for Y-82094 is more than S4 inconsistent with the classification using olivine textures (S2). EPMA analyses of FeNi metals both in chondrules and matrices (Fig. 7) are consistent with those by Shibata and Matsueda (1994).

In the rims of chondrules, the size of metal grains in contact with the chondrule is less than  $100 \,\mu\text{m}$  (Fig. 5a and b). Metal is often elongated along the chondrule surface. These rimmed FeNi metals are larger than metal droplets within chondrules and smaller than rimmed FeNi metals in matrix in average. FeNi metal phase on the chondrule periphery is kamacite not taenite. The metals often have sulfide rims only of the side facing matrix but not of the side facing the interior of the chondrule, that is, the interface between the chondrule and the metal grain (Fig. 5a and b). This is a characteristic feature of commonly observed in rimmed FeNi metals of the chondrule periphery.

In chondrules, abundant kamacite droplets with the size of  $10 \,\mu$ m to  $50 \,\mu$ m can be observed (Fig. 5c and d). They are usually free of sulfide rims. However, in some cases, chondrules contain rimmed FeNi metals, which are often connected with each other to form a network of sulfide veins (Fig. 5c and d). The frequency of the occurrence of rimmed FeNi metals in chondrules is much lower than that in the matrix and in chondrule rims. In FeNi metals from chondrules, the frequency of inclusions such as phosphates is low, which is consistent with the observation of Shibata and Matsueda (1994).

### 4. Discussion

#### 4.1. Unique CO3 of Y-82094

The mean Fa content of olivine by random analyses is quite low compared with those of other CO3s, and suggests a metamorphic grade of 3.0 as described earlier according to the definition by Scott and Jones (1990). On the other hand, TL analysis classifies Y-82094 as 3.5 (Sears *et al.*, 1991a). In the case of subtypes from TL, there is a tendency for the metamorphic degree to increase with weathering and/or shock metamorphism (K. Ninagawa, personal communication). The discrepancy between the subtype from random analyses and that from TL may thus reflect alteration and/or a shock since Y-82094 has suffered weathering on Antarctica and has a higher shock stage than other CO3s.

As mentioned in Section 3.2, the mean chondrule size of Y-82094 is larger than that in other CO3s. Chondrule size tends to be related to subtypes, that is, there is a tendency that chondrule size is larger with increasing metamorphic grade (Rubin, 1989). In the case of Y-82094, the relationship between subtype based on the random analyses of olivine and chondrule size is inconsistent with the study by Rubin (1989). We cannot ascribe the discrepancy to shock event and/or weathering on Antarctica. As mentioned in Section 3.1, several unique bulk chemical features are present in Y-82094. Thus, Y-82094 is a unique CO3.

#### 4.2. The timing of shock metamorphism and sulfide formation

Fizzed troilite characteristic of rims surrounding FeNi metals occurs overall in thin sections. We cannot explain sulfide formation as a result from shock metamorphism, as sulfide textures are present in all CO3s but shock metamorphism has effected only some CO3s. We thus conclude that shock metamorphism occurred after sulfide formation.

Sulfide textures surrounding metal grains in contact with chondrules occur only at the side facing matrix in Y-82094 (Fig. 5a and b). They are absent in other CO3s except for a few occurrence in the Lancé (CO3) chondrite. The existence of fizzed troilite is also found in both meteorites, Y-82094 and Lancé. For the origin of the texture of the restricted rims surrounding FeNi metals, two models are considered. The first possibility is that initially, before sulfide formation a chondrule and a FeNi Sulfide textures of a unique CO3-chondrite and its petrogenesis

metal grain were in close contact with each other and FeNi metal has reacted with gaseous S only at the side facing matrix. The other possibility is that after a continuous sulfide rim with a uniform thickness had formed a rimmed FeNi metal, shock melting produced fizzed troilite which was forced toward matrix by compaction. The first model can not explain the absence of this texture in other CO3s. The second model is consistent with shock metamorphism. Thus the unique texture observed on some chondrule peripheries could have been produced by shock melting.

The abundance of P in rimmed FeNi metal cores in Y-82094 is lower in other CO3s (Shibata and Matsueda, 1994). There is, however, more oxidized P in Y-82094 as reflected in the high abundance phosphate inclusions in FeNi metals in this meteorite. The grain size of phosphate inclusions in Y-82094 is significantly larger compared with other CO3s. Phosphates formed by oxidation at low grade thermal metamorphism (3.0 to 3.1) (Zanda *et al.*, 1994). The larger size of phosphate grains could be the result of the coarsening by shock metamorphism. The shock metamorphism must then have occurred at the final metamorphic stage after the thermal metamorphism that established the subtype.

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#### References

- Bence, A. E. and Albee, A. L. (1968): Empirical correction factors for the electron microanalysis of silicates and oxides. J. Geol., 76, 382-403.
- Bennett, M. E., III and McSween, H. Y., Jr. (1996): Shock features in iron-nickel metal and troilite of L-group ordinary chondrites. Meteorit. Planet. Sci., 31, 255-264.
- Dodd, R. T. (1981): Meteorites. Cambridge, Cambridge Univ. Press, 368 p.
- Imae, N. (1994): Direct evidence of sulfidation of metallic grain in chondrites. Proc. Jpn. Acad., 70, Ser. B, 133-137.
- Imae, N. and Kitamura, M. (1995): Sulfidation of metallic iron in the primordial solar nebula. Proc. NIPR Symp. Antarct. Meteorites, 8, 139–151.
- Imae, N. and Kojima, H. (2000): On the relationship between troilite and/or magnetite rimmed FeNi metals and subtype in CO3 chondrites. Antarct. Meteorite Res., 13, 65-77.
- Kojima, H. and Imae, N. (1998): Meteorites News. 7 (1). National Institute of Polar Research.
- Kojima, T., Yada, S. and Tomeoka, K. (1995): Ca-Al-rich inclusions in three Antarctic CO3 chondrites, Yamato-81020 and Yamato-790992: Record of low-temperature alteration. Proc. NIPR Symp. Antarct. Meteorites, 8, 79–96.
- Lauretta, D. S., Kremser, D. T. and Fegley, B., Jr. (1996a): A comparative study of experimental and meteoritic metal-sulfide assemblages. Proc. NIPR Symp. Antarct. Meteorites, 9, 97-110.
- Lauretta, D. S., Kremser, D. T. and Fegley, B., Jr. (1996b): The rate of iron sulfide formation in the solar nebula. Icarus, 122, 288-315.
- McSween, H. Y., Jr. (1977): Carbonaceous chondrites of the Ornanas type: a metamorphic sequence.

Geochim. Cosmochim. Acta, 41, 477-491.

- Rubin, A. E. (1989): Size-frequency distribution of chondrules in CO3 chondrites. Meteoritics, 24, 179–189.
- Scott, E. R. D. (1982): Origin of rapidly solidified metal-troilite grains in chondrites and iron meteorites. Geochim. Cosmochim. Acta, 46, 813-823.
- Scott, E. R. D. and Jones, R. H. (1990): Disentangling nebular and asteroidal features of CO3 carbonaceous chondrite meteorites. Geochim. Cosmochim. Acta, 54, 2485-2502.
- Scott, E. R. D., Keil, K. and Stöffler, D. (1992): Shock metamorphism of carbonaceous chondrites. Geochim. Cosmochim. Acta, 56, 4281-4293.
- Sears, D. W. G., Batchelor, J. D., Lu, J. and Keck, B. D. (1991a): Metamorphism of CO and CO-like chondrites and comparisons with type 3 ordinary chondrites. Proc. NIPR Symp. Antarct. Meteorites, 4, 319-343.
- Sears, D. W. G., Hasan, F. A., Batchelor, J. D. and Lu, J. (1991b): Chemical and physical studies of type 3 chnodrites-XI: Metamorphism, pairing, and brecciation of ordinary chondrites. Proc. Lunar Planet. Sci., 21, 493-512.
- Shibata, Y. (1996): Opaque minerals in Antarctic CO3 carbonaceous chondrites, Yamato-74135, -790992, -81020, -81025, -82050 and Allan Hills-77307. Proc. NIPR Symp. Antarct. Meteorites, 9, 79-96.
- Shibata, Y. and Matsueda, H. (1994): Chemical composition of Fe-Ni metal and phosphate minerals in Yamato-82094 carbonaceous chondrite. Proc. NIPR Symp. Antarct. Meteorites, 7, 110-124.
- Yanai, K. and Kojima, H. (1995): Catalog of the Antarctic Meteorites. Tokyo, Natl Inst. Polar Res., 230 p.
- Zanda, B., Bourot-Denise, Perron C. and Hewins, R. H. (1994): Origin and metamorphic redistribution of silicon, chromium, phosphorus in the metal of chondrites. Science, 265, 1846-1849.

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