Thermal History of Dehydrated CY Chondrites Reconstructed from their Fe-sulfide Grains

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Introduction: Following low temperature (<200 °C) aqueous alteration, the CY carbonaceous chondrites experienced significant post-hydration heating (>500 °C) on their parent body, evidenced by dehydrated phyllosilicates, secondary recrystallized olivine, the destruction and modification of organics, low water contents, and melting of Fe-sulfides [e.g., 1-4]. However, the timing, duration and mechanism of this heating is currently poorly defined. Constraining the thermal history of the CY chondrites is an important step to understanding the evolution of the water-rich C-complex asteroids, and the distribution and transport of volatiles in the early solar system. Our studies also provide a framework for interpreting the samples returned from Ryugu, as the initial results of JAXA's Hayabusa2 mission suggest that materials on Ryugu record periods of both aqueous and thermal alteration [5].

Sulfides are widespread in the carbonaceous chondrites and are sensitive to both aqueous alteration and thermal metamorphism. The unheated CM and CR chondrites contain primary and secondary Fe-sulfides that can provide a detailed record of the conditions within the nebula prior to accretion, as well as aqueous alteration on the parent bodies [6-9]. The CY chondrites contain a third generation of sulfides, specifically pyrrhotite ([Fe,Ni]_{1-x}S) containing inclusions of pentlandite ([Fe,Ni]₉S₈), that formed from the cooling of a monosulfide solid solution (MSS, [Fe,Ni]_{1-x}S) during the metamorphic event [e.g., 6, 7]. Experimental work on synthesized MSS compositions has shown that the textural features and compositions of these sulfides are diagnostic of their cooling histories [10-12].

Here, we have systematically characterized the pyrrhotite-pentlandite grains within the matrices of CY chondrites of heating stages III (peak temperature 500-700 °C) and IV (peak temperature >750 °C) [13], to infer their thermal history.

Samples and Methods: We have characterized up to 20 coarse (>40 µm) sulfide grains within each of five CY chondrites: Yamato (Y-) 82162 and Y-86029 (both Stage III [2]), Y-86789 and Y-86720 (likely paired, Stage IV [2, 14]), and Belgica (B-) 7904 (Stage IV [2]). Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) has been carried out at 20 kV and 1.5 nA for one polished section of each sample using a ZEISS Evo 15LS SEM equipped with an Oxford Instruments Aztec EDS system at the Natural History Museum (NHM). To improve the spatial EDS resolution to the sub-micrometre scale, one grain in B-7904 was analysed at 6 kV using an FEI Quanta field emission SEM and Bruker annular EDS detector at the NHM.

Results: The sulfide grains can be separated into two assemblage types - pyrrhotite containing inclusions of pentlandite (PoPn), and pyrrhotite containing inclusions of both pentlandite and metal (PoPnM). Table 1 summarizes the number of grains belonging to each assemblage type, the average nickel content of the pyrrhotite and pentlandite, and the typical size of the pentlandite and metal inclusions. Within each sample, the pentlandite inclusions are commonly associated with cracks in the pyrrhotite, and occasionally occur as isolated blebs within the pyrrhotite grains. In Y-82162, the pentlandite inclusions are oriented laths, whereas in Y-86029, Y-86720, Y-86789 and B-7904 they are irregular in shape and randomly oriented. The PoPnM grains are only present in the Stage IV meteorites Y-86720, Y-86789 and B-7904 the metal inclusions are anhedral and typically <5 μ m in size, although the largest inclusion is ~20 μ m in size. In Y-86720 and Y-86789 the metal inclusions are irregular in shape and tend to form along the outer edge of the sulfide grains. Large area elemental EDS mapping of complete sections show that the paired meteorites Y-86789 and Y-86720 both contain a sulfide-poor lithology. All analysed grains within the sulfide-rich lithology are PoPnM type, while in the sulfide-poor lithology they are PoPn type.

Sample (section	Heating	No. of PoPn	No. of PoPnM	Avg. Po Ni	Avg. Pn Ni	Typical Pn	Typical M
number)	Stage	grains	grains	content (wt%)	content (wt%)	inclusion size	inclusion size
Y-82162 (45-1)	III	11		0.15 ± 0.10 [106]	14.9 ± 1.9 [74]	<5 µm	
Y-86029 (51-A)	III	10		0.15 ± 0.04 [57]	12.1 ± 2.3 [58]	<5 µm	
B-7904 (64-A)	IV		7	0.18 ± 0.08 [38]	14.7 ± 1.4 [17]	<15 µm	<5 µm
Y-86720 (59-A)	IV	9	11	0.13 ± 0.04 [52]	14.4 ± 2.4 [15]	$<12 \ \mu m$	<10 µm
Y-86789 (81-A)	IV	8	8	0.11 ± 0.07 [61]	15.0 ± 1.8 [46]	<10 µm	<10 µm

Table 1. Properties of the Fe-sulfide grains in Stage III and IV CY chondrites.

Po = pyrrhotite, Pn = pentlandite, M = metal, No. = number. Avg. = average. The number of data points for the average Ni contents are in parentheses.

Discussion: Annealing experiments on synthesized MSS compositions show a sequence of pentlandite exsolution textures that evolve with time, where the final morphology of the pentlandite is largely dependent on the cooling rate [10-12]. The quickest cooling rates (<10 K/hr) produce irregular and randomly oriented pentlandite inclusions, while slower cooling rates (>100 K/hr) result in oriented blades/lamellae of pentlandite [11]. The oriented laths of pentlandite within Y-82162 suggest that the sulfides within this sample experienced a slower cooling rate in comparison to those observed in Y-86029, B-7904, Y-86720 and Y-86789. If impacts were the source of heat, this possibly suggests that Y-82162 samples a deeper layer of insulating regolith than the other CY chondrites. Alternatively, Y-82162 might originate from the surface of a parent body that orbited sufficiently close to the sun for solar radiation to keep temperatures elevated for a longer period of time [15]. However, other factors such as the peak metamorphic temperature and the initial MSS composition (metal:S ratio and Fe:Ni ratio) also affect the final pentlandite abundance and morphology. While the experimental work of [10-12] is useful for estimating relative cooling rates between meteorite samples, the ranges of sulfide compositions and environmental conditions considered in these studies are not directly comparable to those on the parent body(ies) of the CY chondrites. For example, the experimental work did not produce any metal-bearing sulfide grains like those observed in Y-86720, Y-86789 and B-7904. It has been suggested that the Fe,Nimetal inclusions formed through the thermal decomposition of pentlandite and pyrrhotite at temperatures >610 °C under reducing conditions at an f_{S_2} near the iron-troilite buffer [7, 16], but the influence of the metal inclusions on the texture and morphology of pentlandite requires further experimental work.

Kimura et al. [6] and Harries and Langenhorst [7] also studied the sulfides within Y-86720 (section 71-3 and fragment 86, respectively) and B-7904 (section 94-1 and fragment 114, respectively). In both samples, they only identified metal-bearing sulfide grains that lacked pentlandite (i.e. PoM grains). In contrast, we observed only PoPnM grains within B-7904, and identified two different lithologies within Y-86720 and Y-86789 that contain either PoPnM or PoPn grains. This is consistent with these meteorites being breccias and suggests that the different lithologies each experienced different thermal histories. Based on the thermal decomposition of pentlandite into Fe,Ni-metal with higher temperatures [7, 16], we suggest a decreasing order of peak metamorphic temperature between the lithologies to be PoM > PoPnM > PoPn. Evidence for heterogeneous heating among the different lithologies could explain variable estimates for peak metamorphic temperatures within the literature. For example, estimates for Y-86720 range from 500 °C [17] up to 850 °C [18], while for B-7904 they vary between 400 °C [19] and 900 °C [18].

Heterogeneous heating within the CY chondrites could result from highly localized variations in the metamorphic conditions. Alternatively, the PoM lithology might have been heated metamorphic event, before impacts mixed different lithologies to for



Figure 1. EDS net intensity map of a PoPnM sulfide grain in B-7904. (6V, 890 pA, 319 kcps, 1680x1680 pixels, 50 nm pixel size, 129 min). Fe – green, Ni – red, S – blue.

conditions. Alternatively, the PoM lithology might have been heated to a greater extent than the PoPn lithology during the metamorphic event, before impacts mixed different lithologies to form a heterogeneous breccia. It is also possible that the primary and/or secondary sulfides within each lithology were compositionally very different prior to heating.

Summary: There are differences in the textural features of the sulfide grains and their associations with Fe,Ni-metal among each of the CY samples, and also among different lithologies within the samples. This suggests the CY chondrites experienced varied thermal histories. Deciphering the cause of these differences will allow us to further develop thermal models for hydrous asteroids.

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