Sulfide mineralogy of heated CM/CI-like chondrites as indicator of asteroidal processes

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Introduction. Thermal alteration of C-type asteroidal regoliths may induce mineralogical and spectral changes and is therefore of interest to ongoing missions such as Hayabusa2 or OSIRIS-REx. Heating effects superposed on earlier aqueous alteration of CM/CI-like chondrites have been described from multiple meteorites beginning in the late 1980s (e.g., [1], [2], [3]) and continue to be found and systematically classified into heating stages (HS I to IV with increasing temperatures [4]). Yet, it is not clear what kind of process is responsible for the thermal overprint and whether it specifically operated on CM/CI-like parent bodies or can be generally expected to affect asteroids and their regolith surfaces. Clearly, the hydrated mineralogy of CM/CI-like meteorites is highly susceptible to changes via thermal processes, and their effects, such as the amorphisation and recrystallization of phyllosilicates, can be readily observed. However, similar thermal events may go unnoticed in non-hydrated meteorite types due to a lack of suitable mineral indicators if heating persisted only for a relatively short time as indicated by CM/CI-like chondrites.

Sulfide minerals such as pyrrhotite ($Fe_{1-x}S$), troilite (FeS) and pentlandite [$(Fe,Ni)_9S_8$] are particularly sensitive to heating and, even before melting, may decompose by loss of sulfur and textural changes [5]. Therefore, they potentially may serve as an alternative indicator of thermal events not only for C-type asteroidal surfaces but also for S-type asteroids such as 25143 Itokawa visited by Hayabusa.

Samples and Methods. TEM studies of the sulfide mineralogies of Yamato (Y-)791198 (CM2, HS I), Y-793321 (CM2, HS II), Y-86720 (CM/CI-like, HS IV), Belgica (B-)7904 (CM-like, HS IV) have been described by [5] and will be summarized here. Additionally the meteorites Y-980115 (CI-like, HS II; [6]) and North West Africa (NWA) 11024 (CM-like, HS III/IV; [7]) have been investigated by SEM and TEM using FIB preparation. Study of the mildly heated CM2 chondrite Jbilet Winselwan (HS II;[8]) is ongoing.

Observations. Compared to the pristine Y-791198 the slightly heated regolith breccia Y-793321 [9] shows only subtle changes in sulfide mineralogy, mostly limited to increased grain sizes of exsolved pentlandite and troilite lamellae in pyrrhotite-bearing, former monosulfide solid solution (MSS) grains. Nanocrystalline phosphorus-bearing pentlandite, occasionally carrying chromium nitride in both meteorites [10] also shows an increase in grain size.

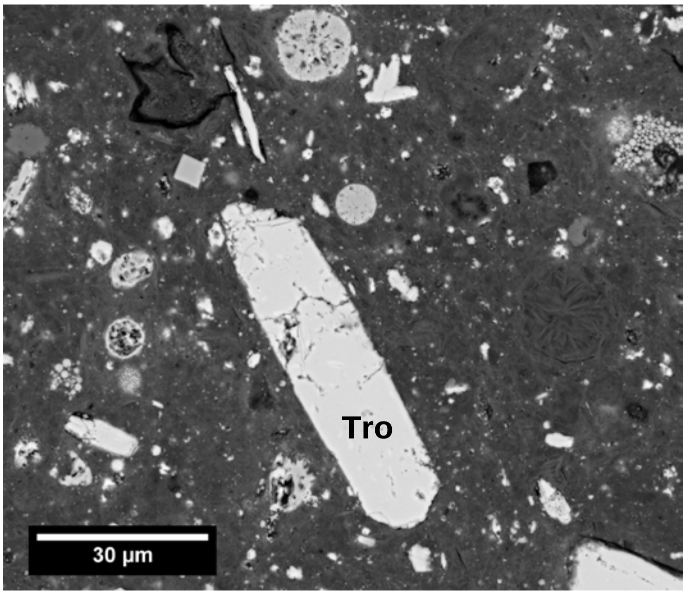

Figure 1. Euhedral sulfide crystals in Y-980115 are replacements of troilite (Tro) after hydrothermally formed pyrrhotite.

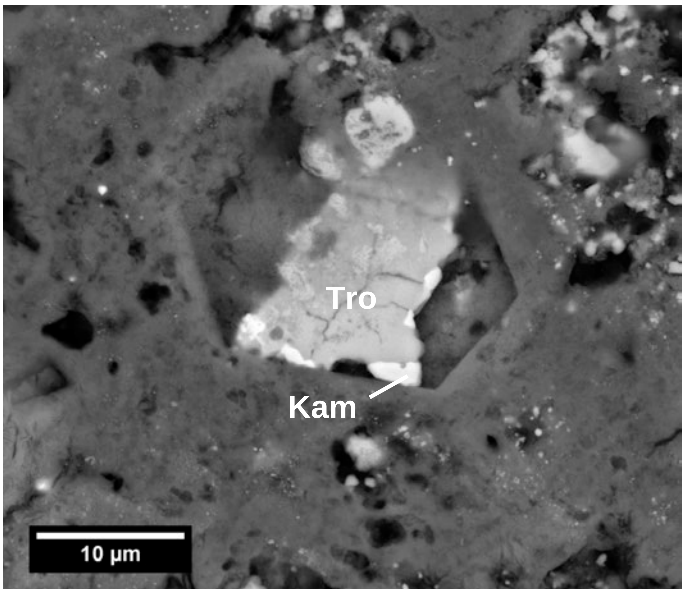

Figure 2. Formerly euhedral sulfide crystal in Y-86720 replaced by troilite (Tro) and partially converted to low-Ni kamacite (Kam).

Substantial mineralogical changes are observed in Y-86720 and B-7904, which contain almost exclusively troilite, which in part has been converted to low-Ni metallic iron (kamacite). Pentlandite appears to be absent in Y-86720, but B-7904 contains rare grains of Fe-rich pentlandite. Both contain small grains of Ni-rich metal (approaching 50 at% Ni in some cases).

Y-980115 shows a brecciated texture with internally fine grained clasts rich in phyllosilicates, magnetite and sulfides. The textures and particularly the morphology of magnetite and sulfide crystals are typical of CI chondrites. Large sulfides grains account for up to 2.8 vol% of the rock. Fe sulfide grains frequently show euhedral platelet shapes and reach sizes up to 70 µm. TEM-SAED patterns obtained from two apparently euhedral sulfide platelets extracted by FIB indicate that the sulfide is polycrystalline troilite and TEM imaging shows that the 'crystals' internally contain abundant grain boundaries meeting in 120° triple junctions. Pentlandite is present as internal grains within the platelets and SAED shows that it does not have a topotactic relationship with the surrounding polycrystalline troilite. The adjacent matrix is poorly crystalline but shows typical fibrous or scaly textures of phyllosilicates. EDS analyses of such aggregates indicate a typical serpentine composition, but SAED only showed diffuse rings with the larges *d*-value located at 0.465 nm. One better crystalline aggregate gave a diffraction pattern with largest *d*-value of 0.97 nm consistent with a talc group mineral; another showed polycrystalline rings consistent with olivine.

NWA 11024 displays typical fine-grained rims (FGRs) around chondrules. One rim sampled by FIB shows abundant Ni-rich metal grains < 1 µm in diameter with a composition centered about $Fe_{50}Co_3Ni_{47}$. The only present sulfide is troilite; Ni-poor metal and pentlandite are absent. The phyllosilicates originally present in the FGR have been converted to nanocrystalline olivine as indicated by SAED patterns. A second FIB obtained from a coarse phyllosilicate aggregate shows it to be a pseudomorph consisting entirely of nanocrystalline, Fe-rich olivine and minor amounts of Fe sulfide (probably troilite).

Discussion. The observations collected on a number of meteorites indicate that progressive thermal overprinting of CM/CI-like chondrites results in sulfur loss of pyrrhotite to form nearly stoichiometric troilite. Because pyrrhotite ($Fe_{1-x}S$) can be considered as an 'omission' solid solution between FeS and a hypothetical vacancy endmember VaS (Va = vacancy), the reaction can be written as $VaS \rightleftharpoons 0.5S_2$. Thus, sulfur loss progressively decreases the non-stoichiometry of $Fe_{1-x}S$ until FeS is reached. The preservation of pentlandite in Y-980115 suggests that it is stable at least until about this point. Further heating and increasing loss of sulfur probably leads to the decomposition of pentlandite to form Ni-rich metal as observed in NWA 11024. Preliminary thermodynamic calculations in the Fe-Ni-S system indicate that pentlandite with the composition $Fe_{4.5}Ni_{4.5}S_8$ is not stable with respect to $Fe_{50}Ni_{50}$ metal at temperatures above ~280 °C and a sulfur fugacity buffered by the presence of troilite. This needs further refinement for variable Ni/Fe ratios of pentlandite and the resulting metal. At highest temperatures troilite decomposes to form Ni-poor metal via the reaction $FeS \rightleftharpoons Fe + 0.5S_2$ as observed in B-7904 and Y-86720 of heating stage IV. Besides temperature the sulfur fugacity is therefore an important parameter that controls the decomposition. In all cases, the change of sulfide mineralogy requires at least partially open-system behavior such that S_2 (or H_2S) is lost from the rock, suggesting heating in a near-surface regolith or within a small meteoroid.

Potentially, the thermal decomposition of sulfide minerals can serve as another indicator of thermal processing on asteroid surfaces beside the dehydration of phyllosilicates. S-type chondritic regoliths that do not contain phyllosilicates may show heating effects by the presence of decomposed sulfides. However, the direct irradiation of sulfide surfaces by solar wind ions may produce similar effects at lower temperatures [11] and further investigations must establish differentiating criteria.

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References

[1] Akai, J. (1988) Geochim. Cosmochim. Acta, 52, 1593-1599. [2] Tomeoka, K. et al. (1989) Proc. National Institute of Polar Research Symposium on Antarctic Meteorites 2, 55-74. [3] Ikeda Y. (1992) Proc. National Institute of Polar Research Symposium on Antarctic Meteorites 5, 49-73. [4] Nakamura, T. (2005) J. Min. Pet. Science, 100, 260-272. [5] Harries, D. and Langenhorst F. (2013) Meteoritics & Planetary Science, 48, 879-903. [6] Kikuchi, K. et al. (2017) 8th Symposium on Polar Science/Antarctic Meteorites XXXX (abstract 00272). [7] Ebert, S. et al. (2018) submitted to Meteoritics & Planetary Science. [8] Nakamura T. et al. (2014) 5th Symposium on Polar Science/Antarctic Meteorites XXXVII (abstract 00315). [9] Nakamura, T. (2006) Earth and Planetary Science Letters. 242, 26-38. [10] Harries, D. et al. (2015) Nature Geoscience, 8, 97-101. [11] Matsumoto, T. et al. (2018) 81st Annual Meeting of The Meteoritical Society (abstract 6096).