The Fe/S ratio of pyrrhotite group sulfides in chondrites: An indicator of oxidation

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Introduction: Fe-sulfides are ubiquitous in chondrites and are sensitive indicators of formation and alteration conditions in the protoplanetary disk and minor Solar System bodies (e.g., Schrader et al., 2016). The compositions and textures of sulfides can be used to constrain the oxygen and sulfur fugacities, and the histories of aqueous alteration, thermal metamorphism, shock-impact processing, and cooling of the host rock (e.g., Kimura et al., 2011; Schrader et al., 2016, 2018; Harries and Zolensky, 2016; Schrader and Zega, 2019). The most abundant sulfides in astromaterials are the pyrrhotite group (ideally $Fe_{1-x}S$ where $0 \leq x \leq 0.125$, but x can be ≤ 0.2; i.e., FeS [troilite] to $Fe_{0.8}S$; e.g., Haldar, 2017), which can occur with pentlandite, $(Fe,Ni)_9S_8$, and pyrite, FeS_2 (e.g., Bullock et al., 2005; Schrader et al., 2016). The compositions of pyrrhotite in carbonaceous chondrites vary with the degree of aqueous alteration experienced; the at.% Fe/S ratio of pyrrhotite decreases with increasing degrees of aqueous alteration (i.e., Fe/S of pyrrhotite in CI < CM1 < CM2 [Bullock et al., 2005; Harries, 2018; Kimura et al., 2020]). However, Nakamura (2005) and Harries (2018) found troilite (FeS, Fe/S = 1) in aqueously altered and heated CM/CI-like chondrites. Here we discuss the Fe/S ratio of pyrrhotite in chondrite groups that cover a wide range of aqueous and thermal histories to evaluate its usefulness as an indicator of parent body processes and its application to returned samples. Minimally altered samples and those that have experienced varying types/degrees of secondary processing are included as: (1) asteroid Bennu is most like CM or CI chondrites (e.g., Hamilton et al., 2019); (2) asteroid Ryugu is most like heated CI, CM (e.g., Kitazato et al., 2019), or CY chondrites (King et al., 2019); and (3) both asteroids likely include impact-delivered xenoliths.

Samples and Analytical Procedure: We studied the sulfide compositions of 58 different chondrites; including CI (Alais, Ivuna, and Orgueil), an ungrouped C1 (MIL 090292), CY (B-7904, Y-82162, Y-86789, and Y-980115), CM1/2 (ALH 83100 and Kolang) CM2 (Aguas Zarcas, Mighei, and QUE 97990), stage I (A-881458) and stage II (Y-793321) heated CM2s (Nakamura, 2005), CM-like (Sutter's Mill), CO3.00 (DOM 08006), CR1 (GRO 95577), CR-an (Al Rais), CR2 (14 different meteorites), shock-heated CR2 (GRA 06100 and GRO 03116), $CV3_{OxA}$ (Allende), $CV3_{OxB}$ (Bali), and $CV3_{Red}$ (Vigarano), CK4 (ALH 85002 and Karoonda), CK5 (LAR 06868), CK6 (LEW 87009), H3.10 (NWA 3358), L3.05 (QUE 97008), L(LL)3.05 (MET 00452), LL3 (Semarkona and Vicência), LL4 (Hamlet and Soko-Banja), LL5 (Chelyabinsk and Siena), LL6 (Appley Bridge and Saint-Séverin), R3 (Meteorite Hills [MET] 01149), R3.6 (LAP 031275), R5 (LaPaz Icefield [LAP] 03639), and R6 (LAP 04840 and MIL 11207) chondrites. Some Fe/S ratios were determined from sulfide compositions that we previously published on LL, R, CK, CM, CR2, and CO3 chondrites (Schrader et al., 2015, 2016, 2018; Davidson et al., 2019a,b; Schrader and Zega, 2019). High-resolution images and chemical compositions were obtained with the JEOL-8530F Hyperprobe electron microprobe analyzer (EPMA) at Arizona State University, and the Cameca SX-100 EPMAs at the University of Arizona (UA) and at the Natural History Museum (NHM), London, following procedures described in Schrader and Zega (2019).

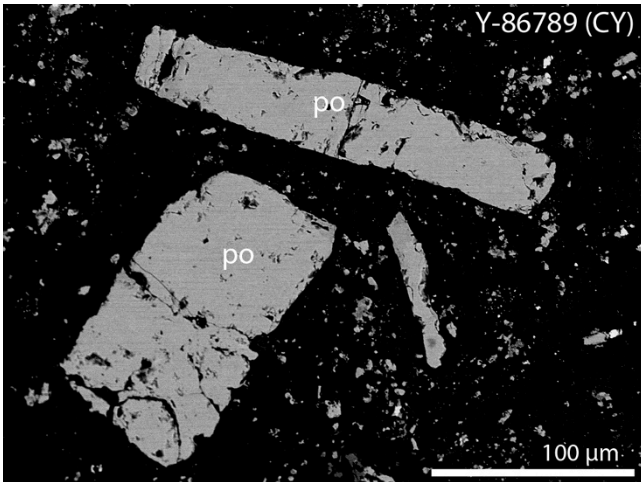

Figure 1. BSE of pyrrhotite (po) grains in Y-86789 (CY).

Results: Pyrrhotite group sulfides were identified in all samples except the CK4 ALH 85002, CK5, and CK6 chondrites. Pyrite was identified in all CK chondrites. To avoid analyses that could overlap with submicron-sized grains of pentlandite, we define Ni-poor pyrrhotite as pyrrhotite containing less than 1 wt.% Ni (Schrader and Zega, 2019); these analyses were used to determine the at.% Fe/S ratios. The pyrrhotite group sulfide troilite (Fe/S ≈ 1) was found in the H3.10, L3.05, all LL chondrites, the CO3.00, all CV3s, the CYs, the CR1, all CR2s, some CM2s, the CM-like chondrite Sutter's Mill, and the R3 chondrite. Fe-depleted pyrrhotite ($Fe_{1-x}S$; Fe/S from <1 to 0.8) was found in the CIs, CYs, the C1-ung, the CR-an Al Rais, some sulfides within CR2 chondrites, the CM1/2s, the CM2s, the CM-like Sutter's Mill, some sulfides in LL chondrites, one sulfide in the H3.10, the R3 to R6 chondrites, and a single grain in the CK4 Karoonda. No troilite was found in the CK chondrites and only a single grain of pyrrhotite was found in the CK4 Karoonda, which has the lowest Fe/S ratio analyzed here.

Discussion: The average Fe/S ratio of pyrrhotite varies between meteorite groups and between petrographic types within meteorite groups. The trend in average Fe/S ratio of all chondrites studied appears complicated, the order from lowest to highest average Fe/S ratio separated by petrographic type is: CK4 < CI < R6 < CM1/2 ≤ CR-an ≤ C1-ung ≤ R5 ≤ R3.6 ≤ R3 ≤ CM2 ≤ $CV3_{OxA}$ ≈ CR1 ≈ CR2 ≈ CY ≈ LL4 ≤ L3.05 ≤ LL5 ≤ LL3 ≈ $CV3_{OxB}$ ≤ H3.10 ≈ LL6 ≤ $CV3_{Red}$ ≤ L(LL)3.05 ≈ CO3.00. The average Fe/S ratio of pyrrhotite generally trends with the degree of aqueous alteration in unheated carbonaceous chondrites. It is likely that internal sample heterogeneities, thermal and aqueous alteration, and differences in sulfur and oxygen fugacities (e.g., the CK4) all contribute to the order of Fe/S ratios. For example, as previously noted by Nakamura (2005) and Harries (2018), trolite is present in thermally altered carbonaceous chondrites (e.g., the CYs studied here). Therefore, using the at.% Fe/S ratio of pyrrhotite as a universal proxy for the degree of aqueous or thermal alteration is not warranted. Comparing the average Fe/S ratio to the degree of oxiditation of each meteorite (e.g., Righter et al., 2006), we find a relationship between the average Fe/S ratio and the bulk meteorite oxidation state. The most reduced chondrites contain troilite and the most oxidized (via thermal or aqueous alteration) chondrites contain Fe-depleted pyrrhorite. The presence of troilite or Fe-depleted pyrrhotite in a chondrite is an indicator of the relative oxygen fugacity of its formation/alteration. This is the case whether the sample is unaltered, aqueously altered, and/or thermally metamorphosed, as oxidation can occur in the protoplanetary disk or in the parent body during aqueous or thermal alteration. While there are trends with the at.% Fe/S ratio of pyrrhotite with thermal and aqueous alteration in some meteorite groups, there is a universal trend with the Fe/S ratio with degree of oxidation. This finding has important implications for the analysis of sulfides in chondrites and returned samples.

References: Bullock E. S. et al., Mineralogy and texture of Fe-Ni sulfides in CI1 chondrites: Clues to the extent of aqueous alteration on the CI1 parent body, Geochim. Cosmochim. Acta, 69, 2687–2700, 2005.

Davidson J. et al., Re-examining thermal metamorphism of the Renazzo-like (CR) carbonaceous chondrites: Insights from pristine Miller Range 090657 and shock-heated Graves Nunataks 06100, Geochim. Cosmochim. Acta, 267, 240–256, 2019a.

Davidson J. et al., Mineralogy and petrology of Dominion Range 08006: A very primitive CO3 carbonaceous chondrite, Geochim. Cosmochim. Acta, 265, 259–278, 2019b.

Haldar S. K., Chapter 1 – Introduction. In Platinum-Nickel-Chromium Deposits, 1–35, 2017.

Hamilton V. E. et al. Evidence for widespread hydrated minerals on asteroid (101955) Bennu, Nature Astro., 3, 332–340, 2019.

Harries D. Sulfide mineralogy of heated CM/CI-like chondrites as indicator of asteroidal processes, 2018 Hayabusa Symposium (abstract), 2018.

Harries D. and Zolensky M. E., Mineralogy of iron sulfides in CM1 and CI1 lithologies of the Kaidun breccia: Records of extreme to intense hydrothermal alteration, Meteorit. Planet. Sci., 51, 1096–1109, 2016.

Kimura M. et al., Fe-Ni metal and sulfide minerals in CM chondrites: An indicator for thermal history, Meteorit. Planet. Sci., 46, 431–442, 2011.

King A. J. et al., The Yamato-type (CY) carbonaceous chondrite group: Analogues for the surface of asteroid Ryugu?, Geochem., 79, 125531, 2019.

Kitazato K. et al., The surface composition of asteroid 162173 Ryugu from Hayabusa2 near-infrared spectroscopy, Science, 364, 272–275, 2019.

Righter K. et al., Compositional relationships between meteorites and terrestrial planets. In: Lauretta, D., McSween Jr., H. (Eds.), Meteorites and the Early Solar System, II. University of Arizona Press, Tucson, pp. 803–828, 2006.

Schrader D. L. and Zega T. J., Petrographic and compositional indicators of formation and alteration conditions from LL chondrite sulfides, Geochim. Cosmochim. Acta, 264, 165–179, 2019.

Schrader D. L. et al., The formation and alteration of the Renazzo-like carbonaceous chondrites III: Towards understanding the genesis of ferromagnesian chondrules, Meteorit. Planet. Sci., 50, 15–50, 2015.

Schrader D. L. et al., Widespread evidence for high-temperature formation of pentlandite in chondrites, Geochim. Cosmochim. Acta, 189, 359–376, 2016.

Schrader D. L. et al., The background temperature of the protoplanetary disk within the first four million years of the Solar System, Earth Planet. Sci. Lett., 504, 30–37, 2018.

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