THE FE/S RATIO OF PYRRHOTITE IN CARBONACEOUS CHONDRITES RELEVANT TO BENNU AND RYUGU: AN INDICATOR OF PARENT ASTEROID AQUEOUS AND THERMAL ALTERATION.

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Introduction: Fe-sulfides are present in many meteorite types [e.g., 1,2] and are sensitive indicators of formation and alteration conditions in the Solar System. The compositions and textures of sulfides can be used to constrain the oxygen and sulfur fugacities of formation, and the histories of aqueous alteration, thermal metamorphism, shock-impact processing, and cooling of the host rock [e.g., 2–7]. The most abundant sulfides in known astromaterials are the pyrrhotite group (ideally $Fe_{1-x}S$ where $0 \leq x \leq 0.125$), which can occur with pentlandite $(Fe,Ni)_9S_8$ and pyrite FeS_2 [e.g., 2,6,8–13]. 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 [10,11,14]). Troilite (FeS, Fe/S ≅ 1) identified in aqueously altered and heated CM/CI-like chondrites was proposed to have formed by S loss during heating and decomposition of pyrrhotite into troilite and Ni-poor metal [14].

Here we determine the Fe/S ratio of pyrrhotite in carbonaceous chondrites with a wide range of aqueous and thermal histories, to evaluate its usefulness as an indicator of parent body processes. 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., 15]; (2) asteroid Ryugu is most like heated CI, CM [16,17], or CY chondrites [18]; and (3) both asteroids likely include impact-delivered xenoliths.

Samples and Analytical Procedure: We studied the sulfide compositions of samples of CI (Alais, Ivuna, and Orgueil), CM1/2 (Allan Hills [ALH] 83100), CM2 (Aguas Zarcas, Mighei, and Queen Alexandra Range [QUE] 97990), CM-like (Sutter's Mill), CY (Yamato[Y]-82162 and Y-980115), C1-ungrouped (Miller Range [MIL] 090292), CR1 (Grosvenor Mountains [GRO] 95577), CR-an (Al Rais), CR2 (16 meteorites), shock-heated CR2 (Graves Nunataks [GRA] 06100 and GRO 03116 [19]), CO3.00 (DOM 08006), $CV3_{OxA}$ (Allende), $CV3_{OxB}$ (Bali), and $CV3_{Red}$ (Vigarano) chondrites. Some Fe/S ratios were determined from sulfide compositions that we previously published; CM [2,20,this study], CR2 [12,19,21,this study], and CO3 [22] chondrites. Fe/S ratios of pyrrhotite in LL3 to LL6, L3.05, CK4 to CK6, and R3 to R6 chondrites are discussed separately in [23]. We obtained high-resolution images and chemical compositions with the Arizona State University JEOL-8530F Hyperprobe electron microprobe analyzer (EPMA) and the Cameca SX-100 EPMAs at the University of Arizona and at the Natural History Museum, London following procedures described in [7].

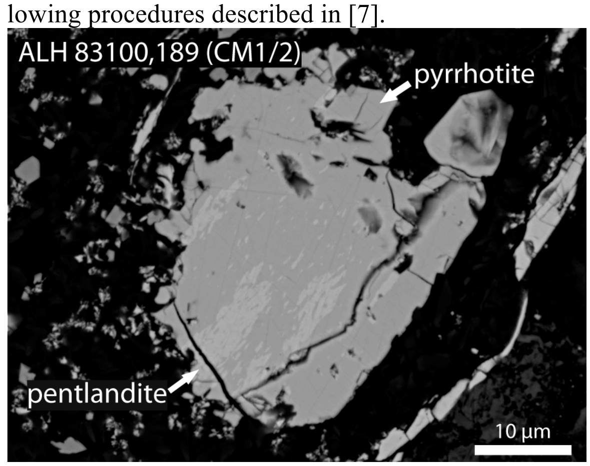

Figure 1. Pyrrhotite and pentlandite in ALH 83100.

Results: Pyrrhotite and/or troilite were identified in all samples studied. In some cases where pyrrhotite was likely present, pure pyrrhotite analyses were not possible to obtain due to submicron-sized grains of pentlandite intergrown with pyrrhotite at scales below the interaction volume of the EPMA (e.g., common in the CM2 Aguas Zarcas). To avoid analyses that could contain overlaps with submicron-sized grains of pentlandite, we define Ni-poor pyrrhotite as pyrrhotite containing less than 1 wt.% Ni [7]; these analyses were used to determine the at.% Fe/S ratios.

Troilite was found in the CO3.00, all CV3s, the CYs, the CR1, all CR2s, the CM2s QUE 97990 and Mighei, and the CM-like chondrite Sutter's Mill. Sulfides in the CR2 chondrites are dominantly troilite, however no troilite was found in the highly aqueously altered CR chondrite [e.g., 19] Al Rais.

Pyrrhotite ($Fe_{1-x}S$; Fe/S from <1 to 0.8) was found in the CIs, the CYs, the C1-ung, the CR-an Al Rais, some sulfides within CR2 and shock-heated CR2 chondrites, the CM1/2 (Fig. 1), the CM2s (except QUE 97990), and the CM-like Sutter's Mill.

Discussion: The average Fe/S ratio of pyrrhotite varies between meteorite groups and between petrographic types within meteorite groups. Typically, the average Fe/S ratio of pyrrhotite decreases with increasing aqueous alteration, consistent with [10,11,14,24]. Troilite is present in all minimally altered (e.g., CO3.00, CR2s, $CV3_{Red}$) and some thermally altered chondrites (e.g., CY). In contrast, pyrrhotite is the dominant sulfide in aqueously altered chondrites (e.g., CI and CM1/2 chondrites). R chondrite sulfides are an exception to this trend, which is likely due to high oxygen fugacity during thermal metamorphism [23].

The average Fe/S ratio of pyrrhotite generally trends with the degree of aqueous alteration in carbonaceous chondrites: CI < CM1/2 ≅ CR-an ≅ C1-ung ≅ CM-like ≅ CM2 < CY ≅ CR2 ≅ CR1 ≅ CV3 < CO3.00. While this overall trend can be attributed to differences in degree of aqueous alteration, it is likely that internal sample heterogeneities, group variations, thermal and aqueous alteration, and differences in sulfur and oxygen fugacities all contribute to the order of Fe/S ratios.

The CM and CR chondrites studied cover a range of aqueous alteration, providing a way to test how the Fe/S ratio of pyrrhotite varies with increasing degree of aqueous alteration within individual meteorite groups. Pyrrhotite in the more aqueously altered CM1/2 has a lower Fe/S ratio than in the CM2s. The least aqueously altered CM2 studied here, QUE 97990 [25], contains troilite and no pyrrhotite. Therefore, the average Fe/S ratio of pyrrhotite in the CM chondrites decreases with increasing degree of aqueous alteration.

There is also a trend in the average Fe/S ratio of pyrrhotite between the CR2 chondrites and Al Rais; Al Rais does not contain troilite and its average Fe/S is lower than that of all CR2 chondrites. Al Rais is recognized as the most aqueously altered CR chondrite, with the exception of the CR1 GRO 95577 [e.g., 26,27]. While most CR2 chondrites contain abundant troilite, there are also variations in the Fe/S ratios within individual CR2 chondrites; individual pyrrhotite grains in the CR2s Shişr 033 and North West Africa (NWA) 801 have Fe/S ratios as low as those seen in Al Rais, indicating heterogeneity in the degree of aqueous alteration or post-aqueous alteration mixing of lithologies via brecciation. However, the CR1 GRO 95577 does not contain pyrrhotite with low Fe/S ratios as expected, but instead contains troilite intergrown with pentlandite and as independent grains. No Fe,Ni metal was associated with the sulfides, contrary to the observations of [14]. The bulk δD of GRO 95577 [25] is significantly lower than other CR chondrites except for the shock-heated ones. These observations indicate that GRO 95577 was heated.

The CY chondrites were aqueously altered and then briefly heated to >500°C [18]. They contain abundant troilite and minor pyrrhotite, consistent with the observation that heating after aqueous alteration leads to the loss of pyrrhotite and formation of troilite.

Summary: The average Fe/S ratio of pyrrhotite is a useful parameter to understand both the aqueous and thermal history of chondrites. The production of pyrrhotite with low Fe/S ratios is likely the result of highly oxidizing conditions leading to the oxidation of Fe either during progressive aqueous alteration (e.g., CI and CM1/2; e.g., Fe oxidized into phyllosilicates) or thermal metamorphism (e.g., R chondrites; Fe oxidized into silicates and oxides [23]). The presence of troilite in highly aqueously altered carbonaceous chondrites (e.g., CY and the CR1) indicates heating. Sulfide textures and minor element compositions may provide a way to distinguish primary from secondary troilite and constrain its formation. These findings will prove useful for the analysis of sulfides in returned samples.

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