

EVALUATION OF REPORTED GRAPHITE IN THE R CHONDRITES LAP 02238/03645: RESOLUTION OF A REDOX RIDDLE. M. C. McCanta¹ and A. H. Treiman², ¹Tufts University (Geology Dept., Lane Hall, 2 North Hill Rd, Medford MA 02155, molly.mccanta@tufts.edu), ²Lunar and Planetary Institute (3600 Bay Area Blvd., Houston TX 77058, treiman@lpi.usra.edu).

Introduction: The R chondrites are unusual in having the highest $\Delta^{17}\text{O}$ values of all meteorites, and are distinct from other non-carbonaceous chondrites in containing magnetite rather than Fe-Ni metal, i.e., in being oxidized [e.g.,1]. This oxidation state is corroborated by the unique R chondrite LAP 04840 [2]; its high oxidation state is clear in the presence of biotite and amphibole that are rich in both OH and Fe^{3+} .

However, two recent Antarctic R chondrites, LAP 02238 and LAP 03645, present a redox riddle: both are reported to contain graphite. These meteorites are typical of R chondrites in having high $\Delta^{17}\text{O}$, and have typical petrographic and mineralogic characteristics: chondrules and chondrule fragments in a fine-grained matrix, a low chondrule/matrix ratio, common fayalitic olivine, and opaques dominated by magnetite, pyrrhotite, and pentlandite. However, the preliminary descriptions of these meteorites cited the presence graphite [3-4]. This material is easily recognized in thin section as platy black (opaque) material, generally associated with sulfides (Fig. 1).

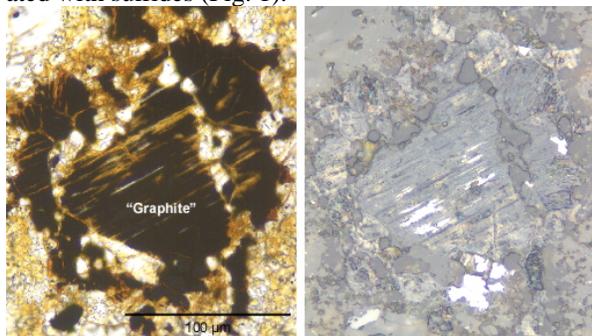


Figure 1. Photomicrographs of phase identified as graphite. A. Plane polarized light. B. Reflected light.

The presence of graphite in an equilibrated chondritic (ultramafic) mineral assemblage restricts oxygen fugacity to rather low values [5]. Under igneous conditions (1400°C), the presence of graphite suggests oxygen fugacities of lower than ~ 2 log units above the Iron-Wüstite buffer. Therefore, the presence of graphite in highly oxidized R chondrites seems paradoxical, and worthy of investigation.

Methods: We studied thin sections LAP 02238,10 and LAP 03645,11. Regions for study were identified using optical microscopy and then subject to probe, SEM, or Raman analysis to determine their chemical composition and distribution. Element maps were obtained at Johnson Space Center with their Cameca SX-100 electron probe. Energy-dispersive X-ray spectra

(EDS) were taken with the Tufts JEOL 6300 SEM. Spot Raman spectra were collected at Johnson Space Center with a Horiba HR-LabRam using 732 nm He-Ne laser light.

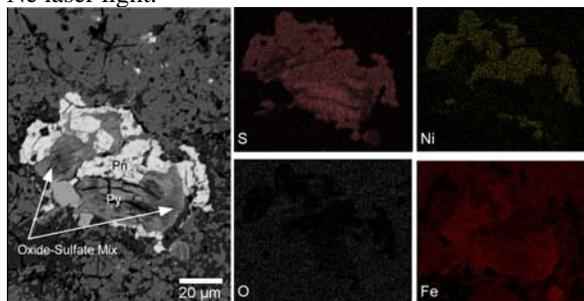


Figure 2. BSE image of sulfide-platy mineral intergrowth with corresponding X-ray maps showing S, Ni, O, and Fe concentrations. Pn = pentlandite; Py = pyrrhotite. The increase in O concentration delineates the oxide-sulfate material. Note the platy intergrowth occurs predominantly within the pyrrhotite.

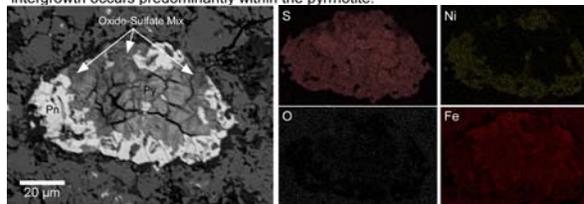


Figure 3. BSE image of sulfide-platy intergrowth with corresponding X-ray maps showing S, Ni, O and Fe concentrations. Pn = pentlandite; Py = pyrrhotite. The increase in O concentration delineates the oxide-sulfate material.

Results: Both thin sections contain platy opaque material, which we take to be the substance identified as graphite (Fig. 1) [3,4]. The platy material is associated with magnetite, pentlandite, and pyrrhotite (a common assemblage in R chondrites), and appears to be intergrown with or replacing the pyrrhotite (Figs. 2,3). Element maps and EDS spectra of the platy material (Figs. 2,3,4) show that it contains abundant Fe, S, and O (C peaks are due to the thin section C coat). Raman spectra of the platy material also did not show the peak at $\sim 1600\text{ cm}^{-1}$ that is characteristic of graphite and polymerized carbons (Fig. 5). Most of the Raman spectra are dominated by fluorescences, and thus uninformative. However, several are like that of Fig. 5, and are consistent with hematite. None of the spectra showed scattering characteristic of either sulfates or carbonates (at ~ 1020 and $\sim 1100\text{ cm}^{-1}$), although strong fluorescences may have masked these peaks.

EDS analysis (Fig. 4) and Raman spectra (Fig. 5) together, suggest that the platy material is a mixture of hematite and Fe-bearing sulfate(s); it is not graphite. This mineral assemblage has not been reported previously in R chondrites. The identity of the minerals containing S & O is not yet clear – they are not re-

solved in BSE imagery. Some regions contain detectable Si and Al (Fig. 4), but this could merely be from beam overlap with nearby silicate mineral grains. It is possible that additional Raman study (perhaps with other light wavelengths or different samples) will be more definitive. The material's platiness (Fig. 1) could be pseudomorphic after a preferred direction in the original pyrrhotite, or could be the tabular nature common in specular hematite.

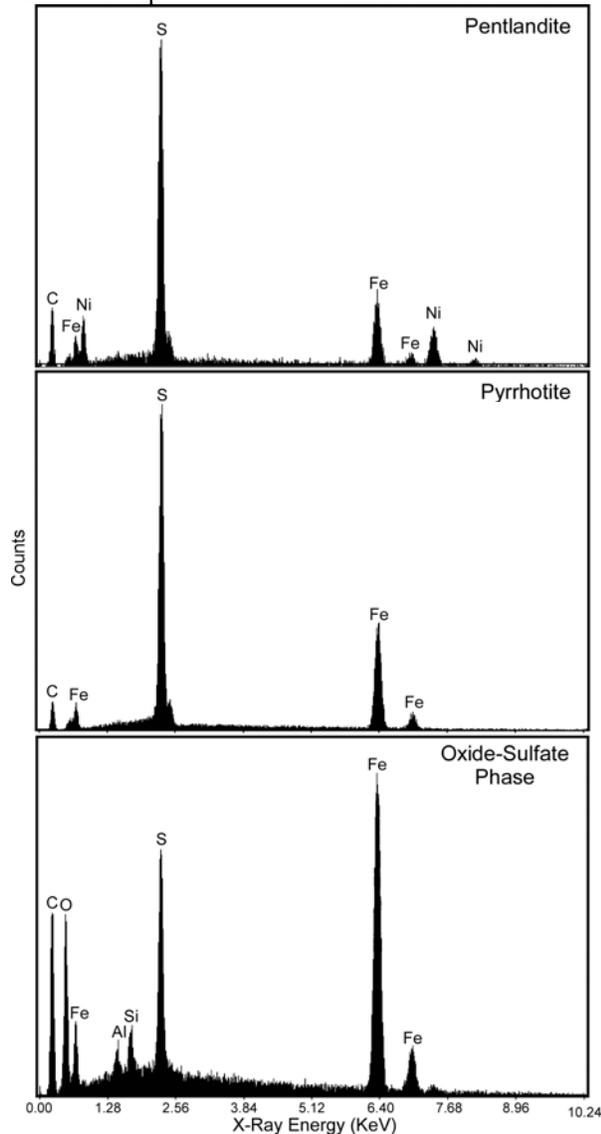


Figure 4. EDS spectra of S-rich phases in LAP 02238/03645. The Al and Si peaks in the oxide-sulfate spectra may be the result of beam overlap with surrounding phases. Carbon peaks result from the thin section C-coat.

Implications: The absence of graphite and presence of hematite in LAP 02238/03645 are consistent with a high oxidation state like those in other R chondrites. Thus recognition of a mixture of hematite and sulfate resolves the redox paradox implicit in the original meteorite descriptions.

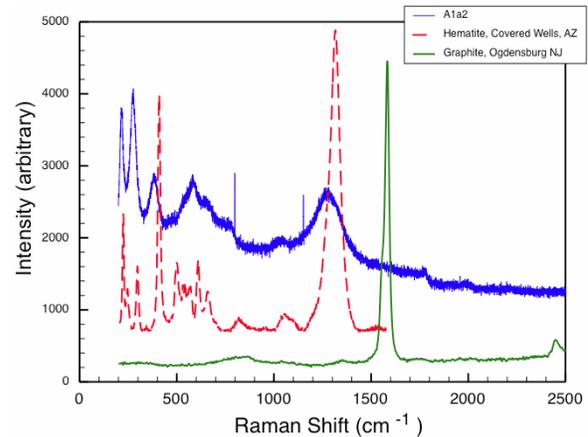


Figure 5. Raman spectrum of a spot in platy material (LAP 03645, A1a2), compared to spectra of hematite and graphite [6].

Mineral assemblages like this, e.g., hematite + jarosite, are common aqueous, acid-sulfate alterations of sulfide minerals, both in direct contact with the sulfides (as in LAP 02238/03645, Figs. 1-3) or at some distance as at Meridiani Planum, Mars [7]. Pyrrhotite and pentlandite have different alteration rates [8], so it is reasonable that some pentlandite might persist through this alteration.

If indeed the hematite and Fe sulfate(s) in LAP 02238/03645 are aqueous alteration products, the crucial question is whether they formed on Earth or on the parent R-chondrite asteroid. No other Antarctic R chondrites are reported to contain 'graphite' or to be weathered, but surely there are some weathering effects, which are now essentially unknown. The Fe-sulfate jarosite is a widespread, but rare, product of weathering in other Antarctic meteorites [9]. Hematite, however, forms rarely (if ever) in Antarctic weathering; goethite is the dominant Fe oxide (hydroxide) [10,11]. Therefore, the presence of hematite in LAP 02238/03645 could suggest that they were altered/weathered in a setting outside of Antarctica, which could thus be on their parent asteroid. This inference, which is generally consistent with the presence of hydrous phases in the LAP 04840 meteorite, is far from certain. Additional studies are in progress.

References: [1] Kallemeyn G. et al. (1996) *GCA.*, 60, 2243-2256. [2] McCanta M.C. et al. (2008) *GCA.*, 72, 5757-5780. [3] Satterwhite C. & Righter K. (2003) *Antarctic Meteorite Newsletter*. [4] Satterwhite C. & Righter K. (2005) *Antarctic Meteorite Newsletter*. [5] Holloway J.R. et al. (1992) *Eur. J. Mineral.*, 4, 105-114. [6] Downs R.T. (2006) <http://rruff.info>. [7] Elwood-Madden M. et al. (2004) *Nature* 821-823. [8] Blowes D.W. & Jambor J.L. (1990) *Appl. Geochem.*, 5, 327-346. [9] Zolensky M. E. & Gooding J. L. (1986) *Meteoritics* 21, 548-549. [10] Solberg T.C. & Burns R.G. (1989) *Proc. 19th LPSC* 313-322. [11] Bland P.A. et al. (2006) *MESS II*, 853-867.