

Speciation of Iron as a Monitor of Oxidation, Reduction and Sulfidation in Ordinary and Enstatite Chondrites. T. J. Fagan, H. Wakai, C. Niki and D. Kato, Department of Earth Sciences, Waseda University, Tokyo, Japan. (fagan@waseda.jp)

Introduction:

Chondrites formed in the solar nebula and hence contain clues about the conditions and processes of the nebula. Variations in the occurrence of Fe as FeO in silicates and oxides vs. metallic Fe in Fe,Ni-rich metals show that oxygen fugacities varied in the regions of the nebula where chondrites formed [1]. Iron is progressively oxidized along a sequence from EH & EL to H to L to LL to R chondrites, reflecting increasingly oxidized settings of formation in the solar nebula [2] (see Fig. 1).

This wide range in the distribution of Fe between silicates and metals is well established [3]; however, Fe also occurs in sulfide minerals in chondrites, raising the possibility that S fugacities also may have varied among the chondrite groups. In this project, we use speciation of Fe to address sulfidation as well as reduction and oxidation in enstatite (EH, EL), ordinary (H, L, LL) and Rumuruti-like (R) chondrites.

Methods:

FeO vs. Metallic Fe vs. FeS in Chondrite Samples. Three separate data sets were used to determine speciation of Fe in different samples of chondrites. Data (1) is based on modes and quantitative electron microprobe analyses of Fe-bearing minerals in the following set of chondrites: Bensour (LL6, fall); Mt. Tazerzite (L5, fall); Tamdakht (H5, fall); St. Marks (EH5, fall); Lewis Cliff 88180 (EH5, find); Northwest Africa 974 (E6, find); Northwest Africa 753 (R3, find). Meteorite falls were emphasized in order to limit the effects of terrestrial weathering; high petrologic types were preferred because coarse-grained samples with homogeneous mineral compositions are well suited for calculation of rock composition by modal recombination. The R- and E-chondrites are relatively rare, so some finds were used and the R-chondrite used here (NWA 753) is a type 3. Modes were determined from elemental X-ray maps of polished thin sections. Modes were counted manually from grids overlain on the elemental maps. Mineral compositions were determined by wavelength dispersive spectroscopy using a JEOL JXA electron microprobe at Waseda University.

In data sets (2) and (3), the speciation of iron among FeO, metallic Fe (Fe^0) and FeS was determined from wet chemical analyses of whole rocks. Data (2) is from analyses conducted by E. Jarosewich [4,5] on LL (n = 17), L (N = 57) and H (n = 31) finds, and 1 fall and 3 finds of E-chondrites. Data (3) is from analyses conducted by H. Haramura of NIPR (and compiled by Yanai and Kojima [6]) on Antarctic finds (59 LL, 158 L, 162 H, 6 E).

Mass Balance Model for Reactions in Chondrites.

Understanding Fe-speciation requires a model for the reactions that transfer Fe between the silicate, sulfide and metal subsystems within the whole-rock reacting systems for O, E and R chondrites. We use a linear algebraic approach to model whole-rock mass balance using independent reactions as vectors, and then combining the vectors as multi-dimensional reaction progress or “reaction space” [6,7].

Results:

Mass Balance Model. Potential variations in abundances of the major minerals in O, E, and R chondrites can be described as linear combinations of four independent reactions: (R1) $\text{NaAlSi}_3\text{O}_8 = \text{NaAlSi}_2\text{O}_6 + \text{SiO}_2$; (R2) $\text{Mg}_2\text{SiO}_4 + \text{SiO}_2 = 2 \text{MgSiO}_3$; (R3) $\text{FeSiO}_3 = \text{Fe-metal} + \text{SiO}_2 + 0.5 \text{O}_2$; (R4) $\text{FeSiO}_3 + 0.5 \text{S}_2 = \text{FeS} + \text{SiO}_2 + 0.5 \text{O}_2$. R1 does not appear to be important in most chondrites. R2 is very important as it describes variations in olivine vs. pyroxene, but it occurs entirely within the silicate subsystem. Reduction of FeO to Fe-metal occurs on R3, and sulfidation of FeO to FeS occurs on R4. The reactions as written above do not indicate that all Fe transferred from silicate to metal originates in pyroxene; nor do the model reactions indicate the true volatile species present during true reaction (e.g., in R3, oxygen lost from silicate might have been transferred to H_2O vapor instead of O_2). Rather the model reactions should be considered book-keeping tools to keep track of changes in abundances and compositions of minerals. R3 and R4 can be used as monitors of Fe transferred between the silicate, metal and sulfide subsystems (Figs. 2, 3).

Speciation of Fe in Data Sets (1), (2) and (3). The three data sets show internally consistent distributions of Fe among silicates, sulfides and metals among ordinary and enstatite chondrites. For most ordinary chondrites, 10 to 25% of Fe occurs in sulfides, and the progression from LL to L to H chondrites shows a wide range in the extent of reduction of FeO to Fe-metal on R3 (Figs. 2, 3). E-chondrites from Data (1) show that all Fe in these samples occur as FeS or Fe-metal. The presence of some FeO in E-chondrites in Data (2) and Data (3) is probably due to terrestrial weathering of meteorite finds. The only R-chondrite analyzed in this study (NWA 753) is in Data (1); modal recombination was determined for two areas, both showing all Fe in FeO or FeS (Fig. 2), consistent with previous interpretations of the R-chondrites as indicators of high oxygen and sulfur fugacities in the solar nebula [3].

The NIPR Antarctic finds (Data 3) show a

greater extent of scatter than the other data sets (compare Fig. 3 with Fig. 2). Most of the scatter appears to be from oxidation of FeS (negative progress on R4) or of Fe-metal (negative progress on R3) and is likely due to terrestrial weathering.

References:

[1] van Schmus W.R. and Wood J.A. (1967) *GCA*, 31, 747-765. [2] McSween H.Y., Jr. (1999) *Meteorites and their Parent Planets*, 310 p. [3] Weisberg M.K. et al (2006) in Lauretta D.S. and McSween H.Y. Jr. (editors) *Meteorites and the Early Solar System II*, p. 19-52. [4] Jarosewich E. (1990) *Meteorit. Planet. Sci.*, 31, 323-337. [5] Jarosewich E. (2006) *Meteorit. Planet. Sci.*, 41, 1381-1382. [6] Yanai K. and Kojima H. (1995) *Catalog of the Antarctic Meteorites*, NIPR, 230 p. [7] Thompson et al (1982) *Jour. Petrol.*, 23, 1-27. [8] Fagan T.J. and Day H.W. (1997) *Geology*, 25, 395-398.

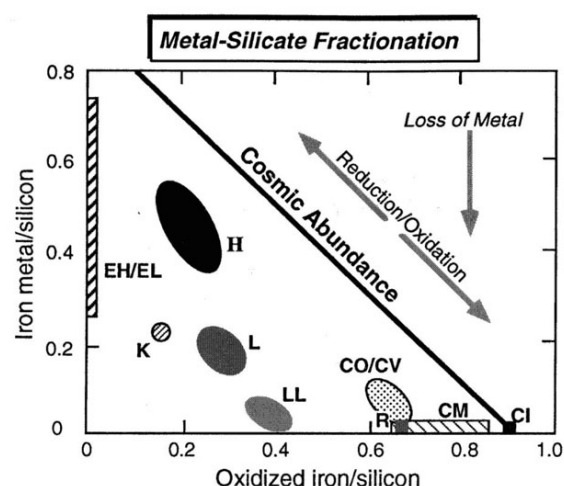


Fig. 1. Speciation of Fe into Fe,Ni-metal vs. silicates and oxides in several chondrite groups (from McSween, 1999 [2]). Iron abundances are presented as ratios of metallic Fe/Si and FeO/Si. All chondrites other than CI's have Fe/Si lower than the cosmic abundance. Increasing proportions of oxidized iron from EH/EL to H to L to LL to R reflect increasing $f(\text{O}_2)$ in nebular regions where these chondrite groups formed.

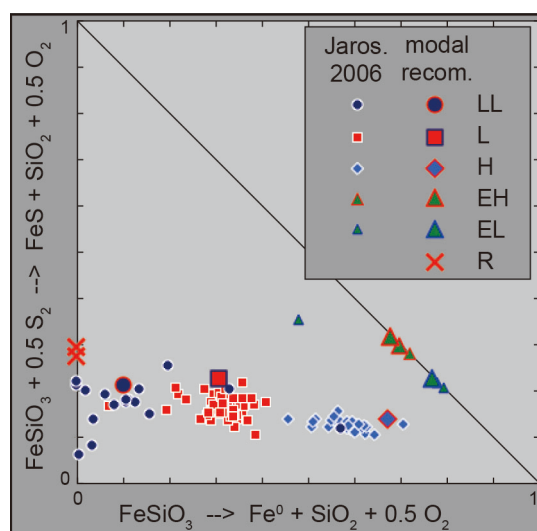


Fig. 2. Speciation of Fe into silicates, metals and sulfides for chondrites analyzed by modal recombination (this study) and by wet chemical techniques of Jarosewich [4,5]. Reaction progress on the horizontal axis shows speciation of all Fe in silicates (at origin) to all Fe in metal ($x = 1$). Progress on the vertical axis shows speciation of all Fe in silicates (at origin) to all Fe in sulfides ($y = 1$).

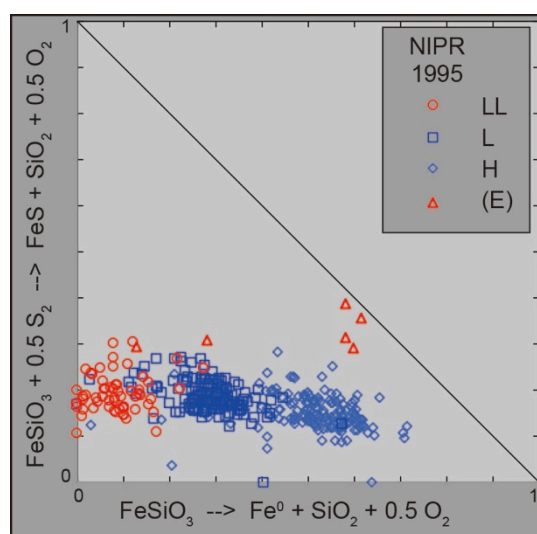


Fig. 3. Speciation of Fe into silicates, metals and sulfides for chondrites analyzed by wet chemical techniques by H. Haramura of NIPR [6]. See Fig. 2 for explanation of reaction progress along horizontal and vertical axes.