THE VALENCE STATE OF FE AND THE ORIGIN OF WATER IN CHONDRITES. S. Sutton[1], E.A. Cloutis[2] and C.M.O'D. Alexander[3], [1]CARS and Dept. Geophys. Sci., Univ. Chicago, IL 60439, USA (sutton@cars.uchicago.edu), [2]Department of Geography, University of Winnipeg, 515 Portage Avenue, Winnipeg, Manitoba, Canada R3B 2E9 (e.cloutis@uwinnipeg.ca). [3]DTM, Carnegie Institution of Washington, 5241 Broad Branch Road, Washington, DC 20015, USA (alexander@dtm.ciw.edu).

Introduction: The oxidation of Fe played a very important role during aqueous alteration of chondrites. The process of oxidation is most obvious in the CRs, Semarkona (LL3.0) and Paris (CM). In all of them, metal has clearly been converted to magnetite. In all other CMs and all CIs, the alteration of metal has almost gone to completion.

The oxidant was the water responsible for the aqueous alteration of the meteorites through reactions such as:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

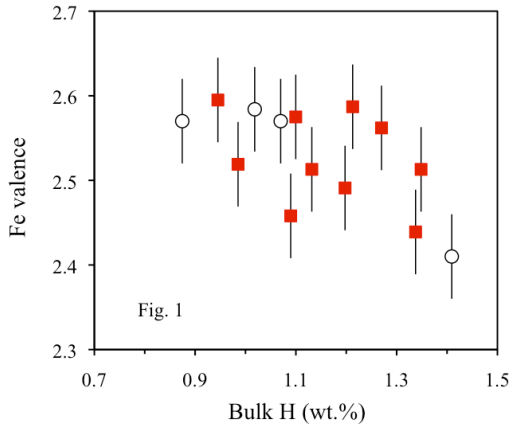
The likely consequences of this oxidation are that: (1) the water/rock ratios during alteration were higher than would be inferred from their present H_2O/OH contents [1, 2], (2) the internal pore pressures associated with the build-up of H_2 would have led to the catastrophic disruption of asteroids unless the H_2 was able to escape [3], and (3) the potential H isotopic mass fractionation associated with the generation and loss of the H_2 could have dramatically changed the H isotopic composition of chondrites [1, 2].

To quantitatively assess the consequences of the Fe oxidation requires the bulk or average initial and the current Fe valence states of the altered chondrites. The initial Fe valence states must be estimated from a study of the least altered meteorites and other primitive extraterrestrial materials [4]. The current bulk Fe valence states of chondrites have yet to be measured in any systematic way. The number of wet chemical analyses of primitive chondrites is limited [5]. Beck et al. [6] have measured the Fe valence states of small matrix fragments in a number of CM chondrites by Fe X-ray absorption near edge spectroscopy (XANES), but it is unlikely that their samples were representative of the bulk chondrites.

We report the bulk Fe valence states of a number of CM, CR, CI and O chondrites determined by Fe-XANES, and explore the implications of these results.

Samples and Techniques: The meteorites analyzed were: CI - Orgueil; CMs - ALH 84042, ALH 85013, Banten, Bells, DNG 06004, LEW 85312, LEW 87022, LEW 87148, LEW 90500, Murchison, Nogoya, QUE 99355, SCO 06043; CRs – GRO 95577, Renazzo and QUE 99177; and OC - Semarkona. The bulk Fe valence states of the chondrites were determined on ~30 mg aliquots of bulk meteorite powders that were previously used to determine bulk H, C and N elemental and isotopic abundances [2]. The aliquots were crushed to a grain size of <30 μm and dispersed between layers of Scotch tape. Fe-XANES spectra were collected in transmission mode at the GSECARS 13BMD station at the Advanced Photon Source.

The Fe-XANES spectra were fitted with a linear, least squares routine using 14 standard minerals. The proportions of the Fe associated with the phases given by the fits were then multiplied by the known Fe valences of the standards to get the average valence. The mineral standards used were: Fe-metal, FeO, pyrrhotite, San Carlos olivine, San Carlos CPX, San Carlos OPX, greenalite, chamosite, serpentine, cronstedtite, saponite, nontronite, magnetite and ferrihydrite. The estimated 1σ uncertainties in the measured valences are ~0.05 based on tests with physical mixtures.



Results: Of the meteorites studied, Orgueil is the most oxidized with a bulk valence of 2.84. The bulk valences for the CRs range from 1.42 in Renazzo to 2.62 in GRO 95577. The bulk valence for Semarkona is 2.10. For the CMs, the Fe valences are all very similar (2.4-2.6; Fig. 1). However, there is a weak inverse correlation with bulk H content, a proxy for the extent of alteration. This trend is apparent in both falls (open symbols) and Antarctic finds (filled red symbols).

Discussion: The expectation is that the bulk Fe valence should increase with the degree of alteration. This is consistent with Orgueil being the most oxidized of the chondrites measured, and with the increase in oxidation state from Renazzo to GRO 95577. Thus, the

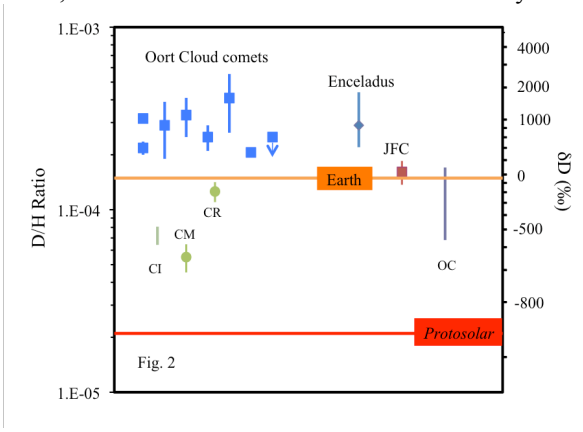
apparent decrease in oxidation state with increasing alteration in the CMs is surprising. The inverse correlation could reflect changes in fO_2 associated with systematic differences in PH_2 and/or temperature as a function of the degree of alteration.

The bulk Fe valences can also be used to estimate the water fractions lost when the Fe was oxidized, provided that the bulk Fe content and the initial bulk Fe valence are known or can be estimated. Unfortunately, there are no unaltered CIs, CMs, CRs or OCs. The least altered CRs are more metal-rich and must be closer in composition to the pre-alteration material, although some alteration of matrix even in these meteorites seems likely. Thus, for the CRs the upper limit for the initial bulk Fe valence is given by Renazzo (1.42). However, in the absence of unaltered meteorites, we have estimated the initial valence states by apportioning all S to FeS (Fe_{val}=2) and the remaining Fe to either all metal (Fe_{val}=0) or a 50:50 mix of metal and FeO (Fe_{val}=2). Using the respective bulk chondrite compositions, the estimated range of initial valences are: CI, Fe_{val}=1.1-1.6; CM, Fe_{val}=0.55-1.3; CR, Fe_{val}=0.19-1.1; and LL, Fe_{val}=0.43-1.2.

If we use the above ranges for the initial bulk Fe valences, then ~20-30 % of the initial water in Orgueil was consumed in the oxidation of Fe, and 75-85 % was consumed in Semarkona. The estimated losses from the CMs and CRs vary considerably if we use their current water/OH contents. However, [2] argued that in the CM and CR chondrites, Fe oxidation occurred in open hydrological systems before the swelling associated with the alteration of silicates caused the permeability to decrease dramatically. If correct, the most altered members of the two groups analyzed (the CM Nogoya and CR GRO 95577) provide minimum estimates of the amounts of water consumed. These minimum estimates are for the CM Nogoya, 38-50 %, and for the CR GRO 95577, 35-46 %. All of these estimates are lower limits if there was oxidation of S and/or organics at the same time as the oxidation of Fe.

Such large fractional losses of water could potentially have significantly increased the D/H ratio of the remaining water and, therefore, the bulk meteorites. Since the H isotopes are a possible indicator of the radial distance at which the ice accreted by chondrites formed, correcting the H isotopic compositions for this loss is of the first importance. The likely range of changes in H isotopic compositions can be estimated by assuming equilibrium H_2-H_2O H isotopic fractionation at the reaction site, Rayleigh loss of the H_2 after its formation, and alteration temperatures between 0°C and 200°C [1].

Based on these assumptions and the water fractions lost listed above, we have plotted the corrected the water H isotopic compositions for the various chondrite groups estimated by [2] in Fig. 2. Also included in Fig. 2 are the H isotopic compositions of: cometary ices (JFC=Jupiter family comet), Saturn's moon Enceladus, the bulk Earth and the initial bulk Solar System.



All the initial water H isotopic compositions are significantly lighter than estimated by [2], particularly for Semarkona whose water H isotopic composition decreased from a range of ~800-1200 ‰ to between -560 ‰ and 90 ‰. Despite the considerable uncertainty, this brings the initial H isotopic composition of Semarkona water into the range of the carbonaceous chondrites. The H isotopic composition of water in the solar nebula is expected to have increased with increasing radial distance from the Sun. This is consistent with the D-rich compositions of most comets. The uncorrected composition of Semarkona water is similar to that of most comets [2], yet it seems unlikely that the OCs formed in the outer Solar System.

It is predicted by two dynamical models of the orbital evolution of the planets that most or all primitive main-belt asteroids formed in the outer Solar System [7, 8]. These asteroids are thought to be the parent bodies of the primitive carbonaceous chondrites. However, with the exception of the CR chondrites, even the uncorrected water H isotopic compositions of the carbonaceous chondrites are significantly less D-rich than those of comets [2]. After the corrections, even the CRs are less D-rich than all known comets (Fig. 2).

References: [1] Alexander C. M. O'D. *et al.*, (2010) *Geochim. Cosmochim. Acta* **74**, 4417. [2] Alexander C. M. O'D. *et al.*, (2012) *Science* **337**, 721. [3] Wilson L. *et al.*, (1999) *Meteor. Planet. Sci.* **34**, 541. [4] Ogliore R. C. *et al.*, (2010) *Earth Planet. Sci. Lett.* **296**, 278. [5] Jarosewich E., (1990) *Meteoritics* **25**, 323. [6] Beck P. *et al.*, (2012) *Geochim. Cosmochim. Acta* **99**, 305. [7] Levison H. F. *et al.*, (2009) *Nature* **460**, 364. [8] Walsh K. J. *et al.*, (2011) *Nature* **475**, 206.