TAKING THE MYSTERY OUT OF UREILITES: ATTRIBUTING CORRELATED Fe/Mg AND Δ^{17}O TO ISOTOPICALLY HEAVY ICE IN THE PARENT BODY

I. S. Sanders[1] and E. R. D. Scott[2], [1]Department of Geology, Trinity College, Dublin 2, Ireland; isanders@tcd.ie, [2]Hawaii Institute of Geophysics and Planetology, University of Hawaii, Honolulu HI 96822, USA; escott@hawaii.edu.

Introduction: Ureilites are enigmatic meteorites [1]. They comprise a group of over 300 ultramafic achondrites that typically contain coarse olivine and low-Ca pyroxene (mostly pigeonite), possible augite, and interstitial graphite and metal [1-3]. Their chemistry is roughly chondritic with strong depletions of plagiophile elements and minor depletions of siderophiles. Most ureilites are regarded as partial melt residues formed during ultra-metamorphism of a carbon-rich chondritic asteroid >200 km across [4]. That body was catastrophically broken up while it was still young and very hot, and the cool fragments reaccreted into one or more rubble piles [5]. Pigeonite was quenched from ~ 1250°C and olivine margins were reduced and clouded with metal blebs, but olivine cores survived.

Ureilites are puzzling because they clearly come from a single body [5, 6], yet they differ significantly from one meteorite to another in their Fe/Mg and oxygen isotope ratios. Molar Fe/Mg in olivine cores varies between 0.05 and 0.33, while Mn/Mg is constant. Oxygen isotopes lie on a slope ~ 1 line close to the carbonaceous chondrite anhydrous mineral (CCAM) line on a δ^{17}O – δ^{18}O diagram [7], and Δ^{17}O varies from -2.5 to -0.2. Moreover, the Fe/Mg ratios and Δ^{17}O values of olivine cores are positively correlated.

It is not clear how these trends, and their correlation, arose. Many authors, e.g. [6-8], believe that they are a legacy of nebular processes, captured during heterogeneous accretion of the ureilite parent body, but the precise nature of these processes is not clear.

Others, e.g. [9], point out that reduction of Fe-bearing olivine by carbon ('smelting') during partial melting in the parent body must have led to an outward radial decrease in Fe/Mg, but this process seems to imply a fortuitous pre-existing radial gradient in Δ^{17}O.

Here we take a different approach. The correlation beween Fe/Mg and Δ^{17}O in ureilites is also seen in equilibrated bulk H, L and LL [e.g. 8] and also R chondrites. We hope that by identifying its origin in chondrites we may shed light on its origin in ureilites.

The Fe/Mg - Δ^{17}O correlation in chondrites: This correlation is popularly regarded as having been inherited from the nebula [7]. However, growing evidence from *unequilibrated* chondrites suggests that it was developed during low-temperature aqueous alteration in the parent bodies. Kita et al. [10] showed that Δ^{17}O in chondrule phenocrysts in Semarkona (LL3.0) is ~ 0.5‰. However, Δ^{17}O in the bulk rock is ~1.3‰,

and chondrule glass has Δ^{17}O as high as 5‰. It seems clear that water with highly elevated Δ^{17}O (perhaps 20‰ [10]) has infiltrated the rock and raised the bulk Δ^{17}O from ~0.5‰ (the value in the original pristine chondrules) to ~1.3‰. An even greater increase, from ~0.5‰ to ~2.3‰, was reported for R chondrites [11]. The aqueous alteration is associated with oxidation of metal and formation of magnetite with high Δ^{17}O (~5‰ in Semarkona) [12, 13]. Thus oxidized iron and Δ^{17}O were simultaneously increased. This would explain their correlation in equilibrated H, L, LL and R chondrites. CV chondrites also show evidence that the more aqueously altered and oxidized types (the dark inclusions) have the highest Δ^{17}O [14].

The isotopically heavy water evidently came from accreted ice whose composition lay close to the CCAM line. It may have been isotopically extreme, to judge from the composition (δ^{17}O = δ^{18}O = +180‰) of the cosmic symplectite grains in the pristine ungrouped carbonaceous chondrite, Acfer 094 [15].

As iron was oxidized, any unoxidized siderophile elements were presumably concentrated in the residual metal, thus explaining the increase of Co in kamacite going from H to LL chondrites [16]. In R chondrites, where all iron metal disappeared, stranded siderophile elements appear as exotic metal nuggets [17].

The Fe/Mg - Δ^{17}O correlation in ureilites: In light of the above observations we propose the following model. The ureilite body was chondritic (though it was not, in fact, carbonaceous [18]) and it accreted metal, carbon and ice. The ice was enriched in ^{17}O and ^{18}O and was close to the CCAM line. During the earliest stages of heating, the ice melted and reacted with the metal to produce iron oxides enriched in ^{17}O and ^{18}O. These oxides, in their turn, combined with silicates at higher temperatures to produce isotopically heavy Fe-enriched olivine. Thus the Fe/Mg ratio and the Δ^{17}O of the olivine were both dependent on the amount of iron metal that had earlier been oxidized.

We acknowledge that our proposal glosses over the complex sequence of prograde metamorphic reactions that would have taken place from the time of initial aqueous alteration to final equilibration. For example, the H$_2$O vapour probably contained C since iron carbides were produced in Semarkona [12]. Also, magnetite in Semarkona falls well to the left of the slope-1 line [13] and yet bulk ureilites, like bulk CV chondrites, lie close to the line, implying that other phase(s)

(framework and sheet silicates?) lay to the right of the line to compensate. Nevertheless, it seems plausible to suggest that once isotopically heavy oxygen atoms had become preferentially attached to iron atoms, then many of those Fe-O chemical bonds would have survived intact during metamorphism, preserving the link between $\Delta^{17}O$ and Fe/Mg in ureilites. After all, oxygen diffusion is sluggish and has been implicated in preserving isotopic heterogeneity in the parent body despite the magmatic temperatures reached [9].

Fe-Mn-Mg relations in ureilites and parent body heterogeneity: While oxidation of iron metal may hold the key to the correlation between $\Delta^{17}O$ and Fe/Mg, it is not clear how the ureilite parent body came to be heterogeneous. Why did it not end up uniformly oxidized and shifted to identical higher $\Delta^{17}O$ and Fe/Mg values? We do not know but, importantly, the variation in Fe/Mg with constant Mn/Mg in ureilite olivines implies that metallic iron must have been removed, or added, locally.

As a first possible cause of heterogeneity we speculate that the extent of aqueous oxidation of metal may have varied from place to place depending on the local availability of water. We suggest that excess, unreacted metal was later lost as melt, resulting in the observed variation in Fe/Mg with constant Mn/Mg.

The availability of water may have varied for two reasons. Firstly, ice may have accreted to the parent body unevenly. Ice-rich chondritic volumes (layers?) would then have become more oxidized than ice-poor volumes. Alternatively, the availability of water may have been a function of 'plumbing' in the parent body, such that metal was substantially oxidized in zones with fluid flow, but remained largely unaltered where little water could permeate. This alternative, interestingly, does not require an initially heterogeneous body.

Another possible source of hetereogeity is nebular metal-silicate fractionation and uneven accretion of metal. In this case metal-rich layers and metal-poor layers would both have become substantially oxidized, with little metal left to be removed as melt. This scenario involves addition, not subtraction, of metal to yield the Fe-Mn-Mg relations, and is consistent with the near-chondritic siderophile element concentrations in ureilites. The nebular metal-silicate fractionation was possibly caused by earlier oblique collisions of molten planetesimals when plumes of debris, variably depleted in metal, were recycled to the disk [19].

A third possible cause of heterogeneity is the 'smelting' of Fe-bearing olivine by carbon which leads to metal loss and radial variation in Fe/Mg [9]. On the face of it 'smelting' does not explain the variable $\Delta^{17}O$ in ureilites. However, we suspect that reduction of FeO to metal, and release of CO gas, would have been part of the complex sequence of metamorphic changes during heating, and were not confined to reactions at the highest temperatures. In this case, the issue of oxygen isotope variation needs more careful consideration. Is it perhaps conceivable that the isotopically heavy oxygen added to Fe during oxidation may have been preferentially lost as CO gas during later reduction? If so, the high $\Delta^{17}O$ and high Fe/Mg established during low temperature oxidation would both decline in tandem during high-temperature reduction, and so retain their correlation.

Lodranites and other primitive achondrites: A correlation between $\Delta^{17}O$ and olivine Fe/Mg (with constant Mn/Mg) is also seen in lodranites, though it is spread over a narrower range of values than in ureilites. It too has been attributed to early aqueous alteration [20]. Brachinites and winonaites, however, show a more limited range of $\Delta^{17}O$ [20] despite a wide range of total Fe/Mg. The latter reflects variable metal; the ratio of FeO/MgO is restricted [8]. In the last two meteorite groups uneven metal accretion or patchy coalescing of molten metal may have occurred, and aqueous alteration was presumably negligible.

Conclusions: Oxygen isotope systematics and oxidation of metal in unequilibrated chondrites suggests that aqueous alteration of iron in the ureilite parent body led to the correlation there of $\Delta^{17}O$ and Fe/Mg. Heterogeneity in the ureilite body may have resulted from variable availability of ice, uneven exposure to migrating water, differences in the amount of accreted metal, or depth-related reduction of FeO by carbon.

References: [1] Mittlefehldt D. et al. (1998) *Reviews in Mineralogy 36*:4-1 – 4-195. [2] Krot A. N. et al. (2012) *Treatise on Geochemistry update* 1.05. [3] Goodrich C. A. et al. (2004). *Chemie der Erde 64*, 283–327. [4] Walker D. and Grove T. (1993) *Meteoritics 28*, 629-636. [5] Downes H. et al. (2008) *GCA 72*, 4825–4844. [6] Scott E. R. D et al. (1993) *Geophysical Research Letters 20*, 415–418. [7] Clayton R. N. and Mayeda T. K. (1988) *GCA 52*, 1313-1318. [8] Goodrich C. A. and Delaney J. S. (2000) *GCA 64*, 149-160. [9] Goodrich C. A. et al. (2007) *GCA 71*, 2876–2895. [10] Kita et al. (2010) *GCA 74*, 6610-6635. [11] Kita et al. (2013) *Meteoritics & Planet. Sci. 48,* abstract #5149. [12] Krot A. N. et al. (1997) *GCA 61*, 219-237. [13] Choi B-G. et al. (1998) *Nature 392*, 577-579. [14] Clayton R. N. and Mayeda T. K. (1999) *GCA 63*, 2089-2104. [15] Sakamoto N. et al. (2007) *Science 317*, 231-233. [16] Rubin A. E. (1990) *GCA 54*, 1217-1232. [17] Bischoff A. et al. (2011) *Chemie der Erde 71,* 101–133. [18] Warren P. H. (2011) *GCA 75*, 6912–6926. [19] Sanders I. S. and Scott E. R. D. (2012) *Meteoritics & Planet. Sci. 47,* 2170–2192. [20] Greenwood R. C. et al. (2012) *GCA 94*, 146–163.