RELATIONSHIPS AMONG OXIDATION STATE, BULK CHEMISTRY, OXYGEN-ISOTOPIC COMPOSITION, PETROLOGIC TYPE AND CHONDRULE SIZE IN ORDINARY CHONDRITES.

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Variations in oxidation state

Each ordinary-chondrite (OC) group comprises chondrites of different petrologic types and exhibits a narrow range in oxidation state, bulk chemical composition, oxygen-isotopic composition and chondrule size. Relationships among these properties reflect both nebular [1] and asteroidal [2] processes.

There are variations in oxidation state (as exemplified by olivine Fa) among OC. For example, some H5 chondrites have essentially non-overlapping olivine compositional distributions [3]. My analyses of H5 chondrites that have the same cosmic-ray exposure age of ~7.5 Ma (a peak that includes ~45% of H chondrites [4]) show that some of these rocks have significant differences in their olivine Fa contents: e.g., Fa17.2-18.1 (n=26) in TIL82415; Fa18.1-19.2 (n=28) in ALH79046. (Both meteorites are shock-stage S2.) These rocks have been metamorphosed and shocked to the same degree; they were both launched from the same parent body during the same event. Thus, these H chondrites were probably within a few kilometers of each other from the time they accreted ~4.5 Ga ago until they were ejected from their parent asteroid ~7.5 Ma ago. Their differences in olivine Fa content most likely reflect stochastic nebular sampling of materials that controlled the rocks' final redox states.

The dominant redox process among OC was oxidation: even at the lowest degrees of metamorphism, there is evidence of oxidation. Metal grains in Semarkona (LL3.0) contain P, Cr and Si in solid solution, but those in Bishunpur (LL3.1) and Krymka (LL3.2) contain Si and Cr, but no P [5]. Metal grains in more-metamorphosed type-3 OC (e.g., Tieschitz, H/L3.6) do not contain P, Cr and Si in solid solution, but instead contain micrometer-size inclusions of phosphate, chromite and silica [5].

Oxidation state and bulk chemistry

Chondrite properties derived from the solar nebula include bulk concentrations of non-mobile elements involved in the metal-silicate fractionation. There are negative correlations between bulk Ni/Si and olivine Fa in H (r=-0.47, n=18, 95% confidence level) and L (r=-0.44, n=17, 91% confidence level) chondrites [6]. Bulk Ir/Si is negatively correlated with Fa in H chondrites (r=-0.40, n=18, 90% confidence level) [6]. In a more recent data set [7], I found negative correlations for H5 and H6 chondrites between atomic Ir/Mn and Fa (r=-0.66, n=16, 99.5% confidence level) and between atomic Ir/Cr and Fa (r=-0.57, n=16, 98% confi-

dence level). (The lower significance of the Ir/Cr-Fa correlation may be due to the fact that Cr is not as strongly lithophile as Mn and thus was not fractionated from siderophile elements to the same extent.)

The correlations between oxidation state and bulk elemental ratios affected by the metal-silicate fractionation suggest that the oxidizing agent was associated with silicate. The metal-silicate fractionation affected the amount of silicate incorporated into OC; individual chondrites that incorporated a greater proportion of silicate also acquired more of the oxidizing agent.

The oxidizing agent may have been water; Choi et al. [8] inferred that water was the agent responsible for converting some of the metal in Semarkona into magnetite. This is consistent with the evidence for minor aqueous alteration in type-3 OC: the presence of phyllosilicates, Ni-rich sulfide and smectite [9,10], fayalite-silica associations [11] and carbide-magnetite assemblages [12].

Oxidation state and O-isotopic composition

The H-L-LL sequence shows systematic increases in mean oxidation state and mean $\Delta^{17}O$ composition: H4-6 (Fa 18.8 mol%, $\Delta^{17}O = 0.73$‰), L4-6 (Fa 24.7 mol%, $\Delta^{17}O = 1.07$‰), LL4-6 (Fa 29.4 mol%, $\Delta^{17}O = 1.26$‰) [13,14]. The correlation between Fa and $\Delta^{17}O$ is not restricted to the mean values of the three OC groups. There are 14 H chondrites for which olivine Fa data [13; Rubin, 2004, unpub. data] and O-isotope data [14] are available: these parameters are positively correlated (r=0.74, 99.4% confidence level). The H-chondrite trend line plots close to the line that connects the mean values of the three OC groups.

The L and LL chondrites do not show a correlation between olivine Fa and $\Delta^{17}O$ perhaps because the larger chondrules in these groups ensure that the ~100-mg samples typically used in the O-isotopic analyses [14] are dominated by relatively few chondrules (each of which can vary significantly from the mean in O-isotopic composition).

It seems plausible that the water that OC inherited from the nebula also affected their bulk O-isotopic compositions. Choi et al. [8] inferred that LL water had very high $\Delta^{17}O$ (i.e., ~+7‰). If H_2O was the main OC oxidant, it follows that LL chondrites incorporated the greatest amount of nebular water, L chondrites incorporated an intermediate amount, and H chondrites incorporated the least. This produced the correlations

among OC between $\Delta^{17}O$ and oxidation state. (The correlation of oxidation state is stronger with $\Delta^{17}O$ than with $\delta^{18}O$ or $\delta^{17}O$ in part because the O-isotopic compositions of individual minerals lie along a mass-fractionation line, and stochastic variations in their modal abundances in individual OC will cause changes in $\delta^{18}O$ and $\delta^{17}O$, but not $\Delta^{17}O$ [14].)

Oxidation state and petrologic type

Scott et al. [15] and Rubin [13] reported systematic increases in olivine Fa with petrologic type. However, published olivine Fa data are not perfect measures of bulk oxidation state. Electron microprobe analysis (EMPA) is typically confined to relatively coarse ($\geq$5 μm) grains. The mean olivine Fa content of an incompletely equilibrated OC, determined by EMPA, is appreciably lower than it would otherwise be if the small ferroan olivine grains in the matrix were included. With increasing metamorphism, the small ferroan olivine grains approach equilibrium with the coarser grains (which were mainly derived from chondrules) and the mean olivine Fa content of the chondrite (as determined by EMPA) increases. This can account for the correlation between olivine Fa and petrologic type.

Petrologic type and O-isotopic composition

Clayton et al. [14] noted that OC O-isotopic compositions tend to vary with petrologic type. This correlation is probably due to whole-rock metamorphism. With increasing metamorphism, water is driven out of chondrites. This is shown by the lower amounts of indigenous water in chondrites of higher petrologic type; e.g., mean LL3 falls contain a total of 1.18±0.46 wt.% H_2O^+ (n=4) whereas mean LL6 falls contain a total of 0.26±0.14 wt.% H_2O^+ (n=5) [16]. If the water was enriched in heavy O isotopes [8], loss of this water during metamorphism would cause OC of higher petrologic type to develop lower $\delta^{18}O$ and $\delta^{17}O$ abundances, consistent with observation. (The inverse correlations between petrologic type and $\delta^{18}O$ and $\delta^{17}O$ are stronger than with $\Delta^{17}O$ because loss of water moves the bulk O-isotopic composition along a mass-fractionation line; this affects $\delta^{18}O$ and $\delta^{17}O$, but not $\Delta^{17}O$.)

Chondrule size, oxidation state and O-isotopic composition

If nebular water acquired by OC was associated with silicate, it is likely that the water was contained within phyllosilicates. Although kinetic constraints prevent gas-solid reactions from forming nebular phyllosilicates at low ambient temperatures [17], Petaev and Wood [18] proposed that phyllosilicates could condense from solar gas at 330-400 K if ≤0.2% of the condensate were continuously removed. It also seems possible that non-equilibrium phases such as phyllosilicates could condense at low ambient temperatures

if H_2O-bearing gas became enriched in such elements as Al, Fe, Mg, Si, O, Na and K that were evaporated from dustballs during chondrule formation [e.g., 19].

The phyllosilicate abundance among fine-grained nebular materials may have increased through time by one of these processes [18, 19]. I suggest that H chondrites agglomerated first and incorporated the lowest abundances of $\Delta^{17}O$-rich phyllosilicates. L and LL chondrites agglomerated later and acquired higher abundances, thereby accounting for the O-isotopic differences among the OC groups.

Mean chondrule size increases from H to L to LL; FeO-poor chondrules tend to be smaller than FeO-rich chondrules. The majority of low-FeO chondrules formed before the majority of high-FeO chondrules in each OC group [20]. Most low-FeO and high-FeO chondrules contain primary sulfide [21] and must have experienced final melting at ambient nebular temperatures <600 K (the 50%-condensation temperature of S). It is possible that chondrule precursor aggregates were growing larger through time via low-velocity collisions. The chondrules in H chondrites may have formed before those in L and LL chondrites and, hence, formed from smaller precursors. The early agglomeration of H chondrites (and subsequent agglomeration of L and LL chondrites) would thus account for the correlations in OC between mean chondrule size, bulk oxidation state and bulk $\Delta^{17}O$ content.

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