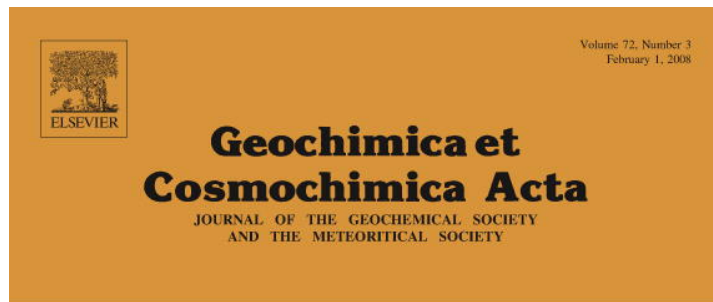


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Size scales over which ordinary chondrites and their parent asteroids are homogeneous in oxidation state and oxygen-isotopic composition

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Abstract

Literature data demonstrate that on a global, asteroid-wide scale (plausibly on the order of 100 km), ordinary chondrites (OC) have heterogeneous oxidation states and O-isotopic compositions (represented, respectively, by the mean olivine Fa and bulk $\Delta^{17}\text{O}$ compositions of equilibrated samples). Samples analyzed here include: (a) two H5 chondrite Antarctic finds (ALHA79046 and TIL 82415) that have the same cosmic-ray exposure age (7.6 Ma) and were probably within ~ 1 km of each other when they were excavated from the H-chondrite parent body, (b) different individual stones from the Holbrook L/LL6 fall that were probably within ~ 1 m of each other when their parent meteoroid penetrated the Earth's atmosphere, and (c) drill cores from a large slab of the Estacado H6 find located within a few tens of centimeters of each other. Our results indicate that OC are heterogeneous in their bulk oxidation state and O-isotopic composition on 100-km-size scales, but homogeneous on meter-, decimeter- and centimeter-size scales. (On kilometer size scales, oxidation state is heterogeneous, but O isotopes appear to be homogeneous.) The asteroid-wide heterogeneity in oxidation state and O-isotopic composition was inherited from the solar nebula. The homogeneity on small size scales was probably caused in part by fluid-assisted metamorphism and mainly by impact-gardening processes (which are most effective at mixing target materials on scales of ≤ 1 m).

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1. INTRODUCTION

Each of the three main ordinary-chondrite (OC) groups, H, L and LL, has a distinct range in oxidation state (e.g., Keil and Fredriksson, 1964; Müller et al., 1971; Wasson, 1972; Rubin, 1990; McSween and Labotka, 1993) and O-isotopic composition (Clayton et al., 1991). Because diffusion of Mg and Fe in olivine is relatively rapid (e.g., Buening and Buseck, 1973; Freer, 1981; Chakraborty, 1997), the mean olivine Fa content of an equilibrated (petrologic types 4–6) OC can be used as a viable indicator of the bulk oxidation state of the rock (Prior, 1916; Mueller and Olsen,

1967; Rubin, 1990; McSween and Labotka, 1993). A useful measure of the O-isotopic composition of OC whole rocks is the bulk $\Delta^{17}\text{O}$ value (the deviation of $^{17}\text{O}/^{16}\text{O}$ relative to the terrestrial fractionation line); it is typically expressed in parts per thousand (per mil or ‰) and measured relative to standard mean ocean water (SMOW).

Relationships in OC between olivine Fa and $\Delta^{17}\text{O}$ were explored by Wasson (2000) and Rubin (2005, 2006). Rubin reported a significant positive correlation between these two properties among equilibrated H-chondrite falls and inferred that a single nebular component was mainly responsible for the mean oxidation states and O-isotopic compositions of OC.

The ranges among individual meteorites in each OC group in mean olivine Fa (~ 3 –6 mol%; Rubin, 1990) and bulk $\Delta^{17}\text{O}$ (~ 0.3 –0.5‰; Clayton et al., 1991) indicate that

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on an asteroid-wide scale (plausibly on the order of 100 km), these properties are heterogeneous. In contrast, replicate analyses of individual meteorites indicate that these properties are relatively homogeneous on centimeter to decimeter scales. The transition between heterogeneity and homogeneity must therefore occur between the 10^2 - and 10^{-4} -km-size scales. In order to constrain this transition and determine if small-scale homogeneities reflect nebular or parent-body processes, we analyzed selected OC samples that represent materials derived from different-sized asteroidal regions.

2. ANALYTICAL PROCEDURES

Olivine compositions were determined with the JEOL JXA-8200 electron microprobe at UCLA using natural standards, an accelerating voltage of 15 keV, a 15 nA sample current, 20-s counting times, and ZAF corrections. For each meteorite, the centers of unfractured olivine grains $\geq 10 \mu\text{m}$ in size were analyzed; the grains were distributed among different chondrules and chondrule fragments throughout the thin sections.

Four widely spaced parallel cylindrical 1-cm-diameter drill cores were made through a $36 \times 51 \times 4$ cm slab of the Estacado H6 chondrite at the Natural History Museum in London. The drill plugs were cut into slices with a diamond saw prior to crushing. In order to preserve any millimeter-scale inhomogeneities, the samples were not finely ground.

Meteorite pieces were crushed with a mortar and pestle for O-isotopic analysis. The two Antarctic meteorite finds (ALHA79046 and TIL 82415) were visibly oxidized, and, hence, some samples of these rocks were acid-treated. The other find (Estacado) appeared unoxidized under a microscope and was not acid-treated. Four different individuals of the Holbrook fall were selected for analysis; samples from these individuals that were located away from the fusion crust were crushed and were not treated with acid. Acid treatment of the crushed rocks involved three minutes of reaction with 6 N HCl at 70 °C, followed by five rinses with distilled water (each rinse consisted of 5 min in a sonic vibrator). Samples were dried at 60 °C for ~15 h. Pieces of the crushed samples with masses of 1–2 mg (and planar dimensions on the order of 1 mm²) were picked for O-isotopic analyses.

Oxygen-isotopic compositions were determined by an infrared-laser fluorination technique following a modification of the procedures of Young et al. (1998) using a Delta-plus Finnigan stable-isotope ratio mass spectrometer. San Carlos olivine standards (1.06–2.48 mg) were analyzed daily. The analytical precision for $\Delta^{17}\text{O}$ values with this technique is 0.02‰.

We calculated the O-isotopic ratios using the following procedure. The $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values refer to the per-mil deviation in a sample ($^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$, respectively) from SMOW, expressed as $\delta^{18}\text{O} = [(^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{SMOW}} - 1] \times 10^3$. The delta-values were converted to linearized values by calculating:

$$\delta^{18}\text{O}' = \ln[(\delta^{18}\text{O} + 10^3)/10^3] \times 10^3$$

in order to create straight-lined mass-fractionation curves. The $\Delta^{17}\text{O}'$ -values were obtained from the linear δ -values by the following relationship:

$$\Delta^{17}\text{O}' = \delta^{17}\text{O}' - 0.528 \times \delta^{18}\text{O}'.$$

3. RESULTS

ALHA79046 and TIL 82415 are two H5 chondrites that have the same cosmic-ray exposure (CRE) age (7.6 Ma; Graf and Marti, 1995) but very different olivine Fa compositional distributions (Fa 18.1–19.2 mol% and Fa 17.2–18.1 mol%, respectively; Rubin, 2005). The O-isotopic compositions of these meteorites determined in the present study are listed in Table 1. The $\Delta^{17}\text{O}$ values of the individual acid-washed samples of ALHA79046 range from 0.76 to 0.81‰; the two samples that did not undergo acid washing have values of 0.69 and 0.72‰. The acid-washed samples of TIL 82415 range from 0.69 to 0.94‰; the two unwashed samples have values of 0.64 and 0.67‰.

The olivine Fa compositions and O-isotopic compositions of samples from the H6 Estacado slab and of individual specimens of the L/LL6 Holbrook fall are listed in Table 2. The Estacado samples have near-identical olivine Fa contents (18.5–18.6 mol%) and $\Delta^{17}\text{O}$ values (0.75–0.77‰). The Holbrook samples have statistically indistinguishable olivine Fa contents (25.6–25.8 mol%) and a narrow range of $\Delta^{17}\text{O}$ values (1.25–1.32‰).

4. DISCUSSION

To determine the size scales over which OC are homogeneous with respect to oxidation state and O-isotopic composition, we found it necessary to study selected meteorites from different OC groups and to assume that all OC parent bodies had broadly similar evolutionary histories. Conclusions derived from a study of one OC group are taken to apply in a general sense to all OC groups.

4.1. Global size scale (~100 km)

It is likely that the majority of the different members of each OC group were derived from the same parent asteroid. This is supported by the narrow ranges in properties of the individual meteorites in each group. These properties include chondrule size, bulk chemical composition, gas-retention age, and CRE age.

4.1.1. Chondrule size

Nelson and Rubin (2002) measured chondrules in four moderately to highly unequibrated LL3 chondrites and found the following mean apparent diameters (i.e., diameters measured in petrographic thin sections): LL3.0 Semarkona (610 μm , $n = 380$), LL3.1 Bishunpur (590 μm , $n = 86$), LL3.1 Krymka (520 μm , $n = 91$), LL3.4 Piancaldoli (600 μm , $n = 87$). The mean values vary by $\leq 15\%$ [although Nelson and Rubin (2002) also measured chondrule sizes in LL3.8 LEW 88175, chondrule outlines in this

Table 1
Olivine Fa and O-isotopic compositions of two Antarctic H5 chondrites, both with cosmic-ray exposure (CRE) ages of 7.6 Ma

Meteorite	Fa (mol%)	Sample	Mass (mg)	$\delta^{17}\text{O}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	<i>n</i>
ALHA79046	18.5 ± 0.3 (<i>n</i> = 28) 18.1–19.2	UCLA 1718					
ALHA79046		ALHA79046,8 acid-washed sample A	1.16	3.23 ± 0.01	4.58 ± 0.02	0.81 ± 0.01	8
ALHA79046		ALHA79046,8 acid-washed sample B	1.41	3.64 ± 0.01	5.33 ± 0.01	0.82 ± 0.01	5
			1.22	3.19 ± 0.01	4.60 ± 0.01	0.76 ± 0.01	12
ALHA79046		ALHA79046,8 acid-washed sample C	1.85	3.22 ± 0.01	4.61 ± 0.01	0.79 ± 0.01	5
ALHA79046		ALHA79046,8 no acid	1.52	2.80 ± 0.00	4.00 ± 0.00	0.69 ± 0.01	15
			1.46	2.99 ± 0.01	4.30 ± 0.01	0.72 ± 0.01	7
				Mean = 2.90	Mean = 4.15	Mean = 0.70	
TIL 82415	17.7 ± 0.3 (<i>n</i> = 26) 17.2–18.1	UCLA 1693					
TIL 82415		TIL 82415,18 acid-washed sample A	1.57	3.32 ± 0.01	4.98	0.69 ± 0.01	5
			1.89	3.59 ± 0.01	5.02	0.94 ± 0.01	5
				Mean = 3.46	Mean = 5.00	Mean = 0.82	
TIL 82415		TIL 82415,18 acid-washed sample B	1.66	3.07 ± 0.01	4.39	0.75 ± 0.01	14
			1.19	3.12 ± 0.01	4.34	0.83 ± 0.01	10
				Mean = 3.10	Mean = 4.36	Mean = 0.79	
TIL 82415		TIL 82415,18 acid-washed sample C	1.49	3.03 ± 0.01	4.38	0.74 ± 0.01	16
			1.16	3.21 ± 0.01	4.41	0.88 ± 0.01	12
				Mean = 3.12	Mean = 4.40	Mean = 0.81	
TIL 82415		TIL 82415,18 no acid	2.11	2.81 ± 0.03	4.12	0.64 ± 0.03	5
			2.17	3.25 ± 0.01	4.89	0.67 ± 0.02	4
				Mean = 3.03	Mean = 4.50	Mean = 0.66	

Thin sections from UCLA Leonard Collection. The sample of ALHA79046 is from the Smithsonian Institution; the sample of TIL 82415 is from the Antarctic Meteorite Working Group and NASA-Johnson Space Center. Olivine Fa data from Rubin (2005); CRE age data from Graf and Marti (1995). O-isotope data from the present study. The analytical uncertainty is the standard error, defined as the standard deviation of the difference between the measured and the true value, i.e., the deviation of the error of the analysis. It is calculated by taking the standard deviation and dividing it by the square root of the number of samples/measurements. The “*n*” in the right-hand column is the number of times oxygen gas was analyzed in the mass spectrometer wherein $1n = 20$ cycles of sample-standard comparison.

moderately texturally equilibrated rock are difficult to discern, rendering the mean diameter of 440 μm ($n = 75$) somewhat uncertain].

Chondrules in other chondrite groups have different mean diameters, ranging from 150 μm in CO to 1000 μm in CV chondrites (Table 2 of Rubin, 2000).

4.1.2. Bulk chemical composition

Each OC group is remarkably homogeneous in bulk chemical composition. For example, Kallemeyn et al. (1989) analyzed 22 H chondrites (21 falls and one unweathered find) by instrumental neutron activation analysis (INAA). They found that the mean Mg- and CI-normalized abundances of lithophile elements (Al, Ca, Sc, La, Sm, Eu, Yb, Lu, V, Mg, Cr, Mn, Na, K) in these 22 meteorites have a narrow range (0.90–0.95 \times CI) and a low standard deviation (0.91 \pm 0.01). Other chondrite groups have different, but similarly narrow, ranges in bulk chemical composition (e.g., Wasson and Kallemeyn, 1988).

4.1.3. Gas-retention ages

Heymann (1967) found that about two-thirds of L chondrites suffered He losses during a major collisional event \sim 520 Ma ago. Subsequent studies confirmed this impact event (e.g., Turner, 1988; McConville et al., 1988; Bogard et al., 1976, 1995; Keil et al., 1994; Haack et al., 1996), but revised the timing to \sim 470 Ma ago (Korochantseva et al., 2006). Because this single collision affected the majority of L chondrites, it is clear that these rocks were present on the same parent body at that time.

4.1.4. Cosmic-ray exposure ages

Approximately 45% of H chondrites, mainly those of petrologic types 4 and 5, plot within a cluster peaking at 7–8 Ma (Graf and Marti, 1995) in CRE age. These meteorites were launched from the same parent asteroid by an impact event \sim 7.5 Ma ago. An analogous situation occurs in LL chondrites: about a third of these meteorites fall within a cluster peaking at \sim 15 Ma (Graf and Marti, 1994). Among L chondrites, Marti and Graf (1992) found that

Table 2
Mean olivine Fa and O-isotopic compositions of samples of the Estacado H6 find and the Holbrook L/LL6 fall

Meteorite	Sample	Thin section	Fa (mol%)	Mass (mg)	$\delta^{17}\text{O}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	<i>n</i>
Estacado	BM 1906,259 core A	BM 1906,259-A	18.6 ± 0.4 (<i>n</i> = 23)	1.30	3.03 ± 0.01	4.29 ± 0.01	0.76 ± 0.01	5
Estacado	BM 1906,259 core B	BM 1906,259-B	18.6 ± 0.4 (<i>n</i> = 27)	1.59	3.10 ± 0.01	4.42 ± 0.01	0.77 ± 0.01	5
				1.36	2.90 ± 0.01	4.07 ± 0.01	0.75 ± 0.01	5
					Mean = 3.00	Mean = 4.24	Mean = 0.76	
Estacado	BM 1906,259 core D	BM 1906,259-D	18.5 ± 0.4 (<i>n</i> = 33)	1.72	2.93 ± 0.01	4.14 ± 0.01	0.75 ± 0.01	5
Holbrook	AMNH 1128 273 g	UCLA 1881	25.8 ± 0.2 (<i>n</i> = 23)	1.36	3.87 ± 0.01	4.96 ± 0.01	1.25 ± 0.009	6
				1.67	3.87 ± 0.01	4.91 ± 0.01	1.28 ± 0.007	19
					Mean = 3.87	Mean = 4.94	Mean = 1.26	
Holbrook	AMNH 1137 113 g	UCLA 1882	25.6 ± 0.1 (<i>n</i> = 17)	1.19	3.90 ± 0.01	4.99 ± 0.01	1.27 ± 0.007	13
				1.58	3.97 ± 0.01	5.01 ± 0.01	1.32 ± 0.009	6
					Mean = 3.94	Mean = 5.00	Mean = 1.30	
Holbrook	AMNH 1154 89.6 g	UCLA 1883	25.6 ± 0.3 (<i>n</i> = 17)					
Holbrook	AMNH 1160 94.0 g	UCLA 1884	25.7 ± 0.1 (<i>n</i> = 24)					
Holbrook	AMNH 1173 408 g	UCLA 1885	25.7 ± 0.3 (<i>n</i> = 14)					
Holbrook	AMNH 1174 101.0 g	UCLA 1886	25.6 ± 0.2 (<i>n</i> = 19)	1.83	3.91 ± 0.01	4.93 ± 0.01	1.31 ± 0.009	6
Holbrook	AMNH 1175 77.6 g	UCLA 1887	25.6 ± 0.1 (<i>n</i> = 20)					
Holbrook	AMNH 4351 52.8 g	UCLA 1888	25.6 ± 0.1 (<i>n</i> = 19)	1.65	3.88 ± 0.01	4.87 ± 0.01	1.31 ± 0.009	5

Samples and thin sections: BM, The Natural History Museum, London; AMNH, American Museum of Natural History; UCLA, UCLA Leonard Collection. Olivine Fa data and O-isotope data from the present study. The original masses of the individual Holbrook stones (52.8–408 g) are listed in the second column. The fifth column lists the masses of Estacado and Holbrook analyzed for O isotopes. The analytical uncertainty is the standard error, defined as the standard deviation of the difference between the measured and the true value, i.e., the deviation of the error of the analysis. It is calculated by taking the standard deviation and dividing it by the square root of the number of samples/measurements. The “*n*” in the right-hand column is the number of times oxygen gas was analyzed in the mass spectrometer wherein *n* = 20 cycles of sample-standard comparison.

L5 and, especially, L6 samples cluster within a peak at ~40 Ma; this is a strong indication of a major collisional event on the L parent body at that time.

4.1.5. Heterogeneity in OC of oxidation state and O-isotopic composition

If we make the plausible assumption (certainly a good working model) that all H chondrites were derived from the same parent asteroid, then a survey of the oxidation states of equilibrated samples (as reflected by their olivine Fa content) and bulk O-isotopic compositions will show to what degree the parent asteroid was homogeneous with respect to these properties.

Fig. 1a shows that the olivine Fa contents of the 29 H4-6 chondrites analyzed by Rubin (1990) are relatively heterogeneous: mean values range from 17.3 to 20.2 mol% with an average composition of 18.8 ± 0.8 mol%. Oxygen isotopes are also relatively heterogeneous (Fig. 1b); for the 22 H4-6 falls analyzed by Clayton et al. (1991), mean $\Delta^{17}\text{O}$ values range from 0.56 to 0.88‰ and average 0.73 ± 0.09 ‰.

The same general trends also hold for equilibrated L and LL chondrites. The L4-6 chondrite mean olivine Fa contents range from 23.0 to 25.8 mol% with a mean of 24.7 ± 0.8 mol%; the LL4-6 range is 26.6–32.4 mol% with a mean of 29.4 ± 1.6 mol% (Rubin, 1990). For the 21 L4-6 falls analyzed by Clayton et al. (1991), mean $\Delta^{17}\text{O}$ values range from 0.80 to 1.25‰ and average 1.08 ± 0.10 ‰. For the 20 LL4-6 falls, the mean $\Delta^{17}\text{O}$ values range from 1.02 to 1.44‰ and average 1.26 ± 0.12 ‰.

Therefore, on a global scale, OC asteroids are heterogeneous with respect to oxidation state and O-isotopic

composition. This size scale is plausibly on the order of 100 km, the scale inferred for OC parent bodies by Wood (1979) based on metallographic cooling rates and the thermal diffusivity of OC material. [Gaffey and Gilbert (1998) suggested that the 185-km-diameter asteroid 6 Hebe (Tedesco et al., 1992) was the H-chondrite parent body].

4.2. Kilometer size scale

As mentioned above, ~45% of H chondrites were launched as meter-size objects from their parent asteroid during a major collisional event ~7.5 Ma ago. Other H chondrites with shorter CRE ages may have been launched as larger fragments that were whittled down to meter-size bodies during subsequent collisions. Anders (1978) estimated that the 7.5-Ma-collisional event excavated material with a volume on the order of 1 km³. [To calculate the amount of material excavated during this cratering event (after integrating the mass distribution to larger masses), Anders used the fraction of chondrite falls equivalent to that of H chondrites with CRE ages of 7–8 Ma, the estimated annual terrestrial influx of chondrites, and the dynamical mean life against planetary capture.]

Fig. 2, modified from Rubin (2005), shows the olivine compositional distributions of two H5 chondrites (ALHA79046 and TIL 82415) that have identical CRE ages of 7.6 Ma. Both chondrites are shock-stage S2 and have similar modal abundances of metallic Fe–Ni (15.2 and 16.8 wt.%, respectively) and troilite (6.0 and 5.4 wt.%, respectively) (Table 1 of Rubin, 2005). Both chondrites were very likely launched from the same parent asteroid

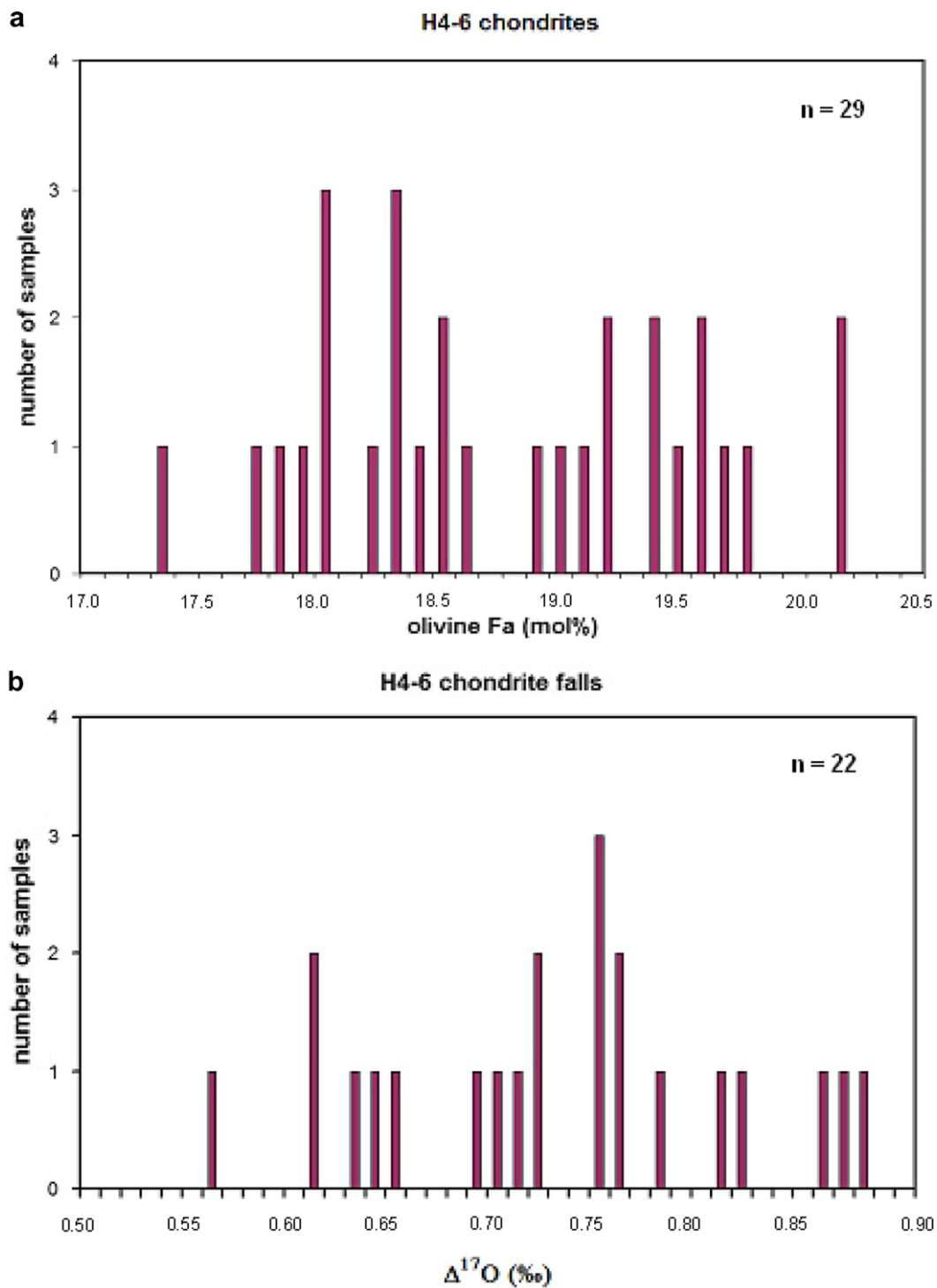


Fig. 1. Global compositional variations among H chondrites. (a) Variations in the mean olivine composition (mol% Fa) among the 29 equilibrated H chondrites analyzed by Rubin (1990). (b) Variations in the mean bulk $\Delta^{17}\text{O}$ compositions of the 22 equilibrated H-chondrite falls analyzed by Clayton et al. (1991).

during the same cratering event and, hence, were within ~ 1 km of each other on the asteroid prior to the impact. The olivine data for these two meteorites overlap only at the extremes of the distributions: Fa 17.2–18.1 in TIL 82415 and Fa 18.1–19.2 mol% in ALHA79046 (Table 1).

Statistical tests reported by Rubin (2005) show that these populations are significantly different; the confidence level of this conclusion exceeds 99.999%. It is clear that at the ~ 1 -km-size scale, H chondrites differ in their olivine compositions.

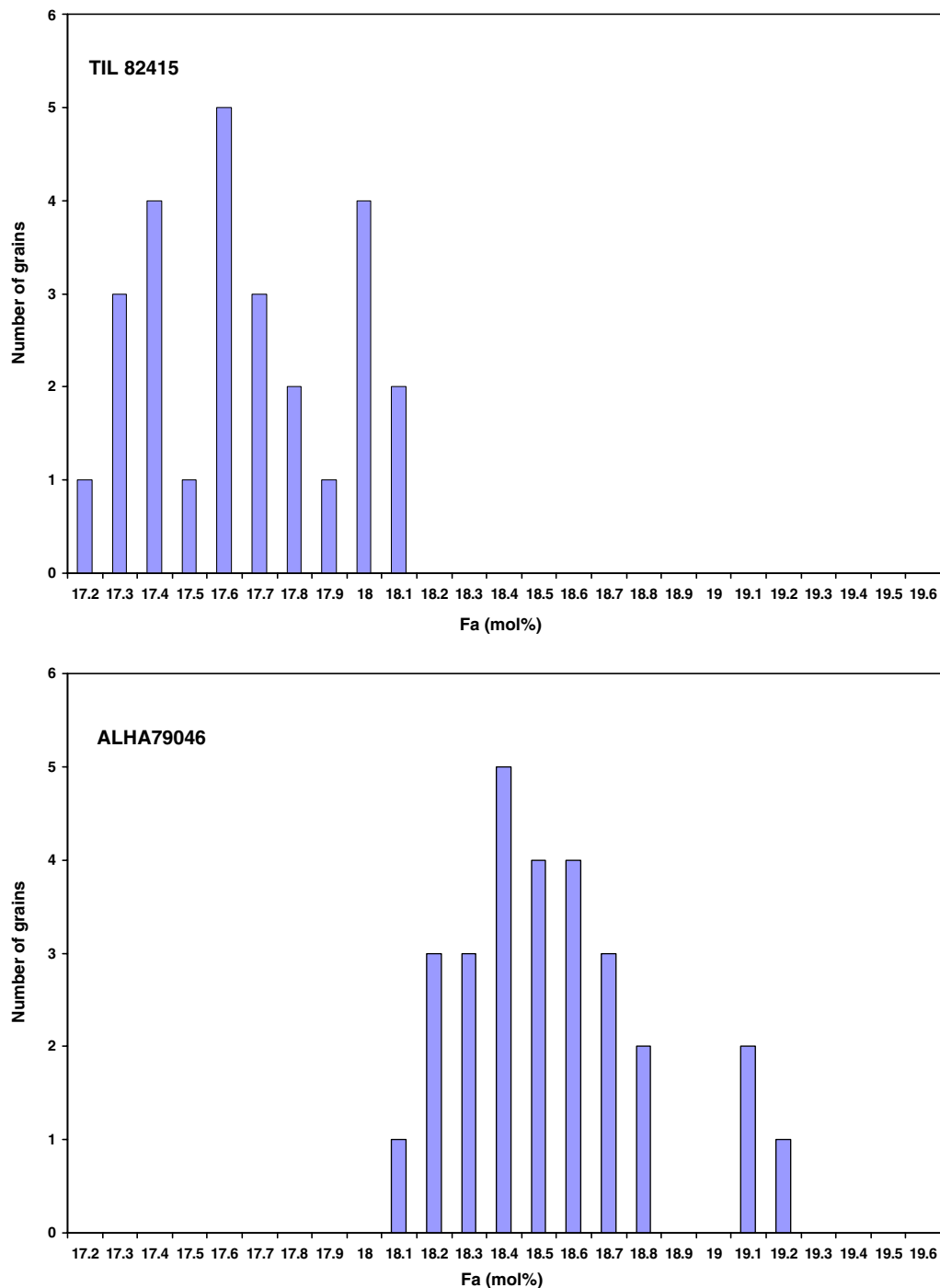


Fig. 2. Diagram modified from Rubin (2005) of the olivine compositional distributions (mol% Fa) of two Antarctic H5 chondrites that have identical cosmic-ray exposure (CRE) ages of 7.6 Ma. The distributions are distinct, overlapping only at their extreme values. Although these rocks were launched from their parent asteroid during the same collisional event and, hence, were in relatively close proximity (probably on the order of 1 km) beforehand, they have very different mean oxidation states.

The O-isotopic compositions of several 1- to 2-mg-size samples of ALHA79046 and TIL 82415 were determined as part of this study (Table 1). For each meteorite, three acid-washed samples and one unwashed sample were analyzed. The mean $\Delta^{17}\text{O}$ values of the acid-treated samples are not significantly different: $0.80 \pm 0.01\text{‰}$ and

$0.81 \pm 0.02\text{‰}$, respectively. In contrast, comparison of the untreated samples shows that the $\Delta^{17}\text{O}$ value of ALHA79046 (0.70‰) is higher than that in TIL 82415 (0.66‰). Because these Antarctic finds have experienced terrestrial weathering, the acid-washed samples are likely to yield more accurate values. Additional H5 chondrites

with ~ 7.5 -Ma CRE ages (e.g., Changde, LEW 85320, Shuangyang, Vengerovo) should be analyzed to confirm O-isotopic homogeneity.

4.3. Meter size scale

Although Grady (2000) lists Holbrook as L6, there is reason to question this classification. The mean olivine composition of Holbrook (Fa 25.6 mol%; Table 2) falls near the upper range of L4-6 chondrites (Fa 23.0–25.8; Rubin, 1990), but the mean kamacite Co content (10.4 mg/g Co; Rubin, 1990) falls in between the ranges for equilibrated L and LL chondrites (7.0–9.5 mg/g and 14.2–370 mg/g Co, respectively). The O-isotopic compositions of the different Holbrook individuals ($\Delta^{17}\text{O} = 1.25$ – 1.32‰ ; Table 2) lie at and just beyond the extreme upper end of the range of equilibrated L chondrites (0.80– 1.25‰), but well within the range of equilibrated LL chondrites (1.02– 1.44‰ ; Clayton et al., 1991). Because of such ambiguities, Holbrook was classified as L/LL6 by Rubin (1990). This classification is accepted here.

Holbrook fell in Navajo County, Arizona in 1912 as a large shower; about 14,000 individuals with a mass totaling 218 kg were recovered (Grady, 2000). If we assume that 15% of the original mass of Holbrook was recovered from this semi-arid area and that, prior to atmospheric entry, the meteoroid was a sphere with some porosity and thus had a bulk density of 3.2 g cm^{-3} (Table 2 of Britt et al., 2002), we can calculate that the object had a pre-atmospheric diame-

ter of 95 cm. Given the uncertainties, this can be rounded off to ~ 1 m. Analysis of a moderate number of random samples of Holbrook should indicate whether olivine Fa and bulk $\Delta^{17}\text{O}$ are heterogeneous on the meter size scale.

We examined eight individual Holbrook stones with original masses of 53–408 g (Table 2). The mean olivine Fa values of the individual stones are essentially identical, ranging from $25.6 \pm 0.1 \text{ mol}\%$ to $25.8 \pm 0.2 \text{ mol}\%$. Oxygen-isotope ratios were determined for four of the samples. They also indicate homogeneity: $\Delta^{17}\text{O}$ ranges from 1.26‰ to 1.31‰ with an average $\Delta^{17}\text{O}$ value of $1.30 \pm 0.02\text{‰}$ (Table 2). If we assume that Holbrook is representative of equilibrated ordinary chondrites, we can conclude that, on the meter scale, OC are homogeneous in oxidation state and O-isotopic composition.

4.4. Decimeter size scale

Estacado H6 was found in semi-arid Hale County, Texas in 1883 as a single 290 kg stone (Grady, 2000). The distances between the drill cores in the Estacado slab (Fig. 3) are in the decimeter range: AB = 17 cm, AD = 34 cm, BD = 36 cm. All of the core samples are more than 3 cm from the surface of the meteorite.

The olivine compositions in the cores are essentially identical; mean core olivine Fa values range from 18.5 to 18.6 mol% (Table 2). The O-isotopic compositions of the cores are also essentially identical; mean core $\Delta^{17}\text{O}$ values range from 0.75 to 0.76‰ with an average of

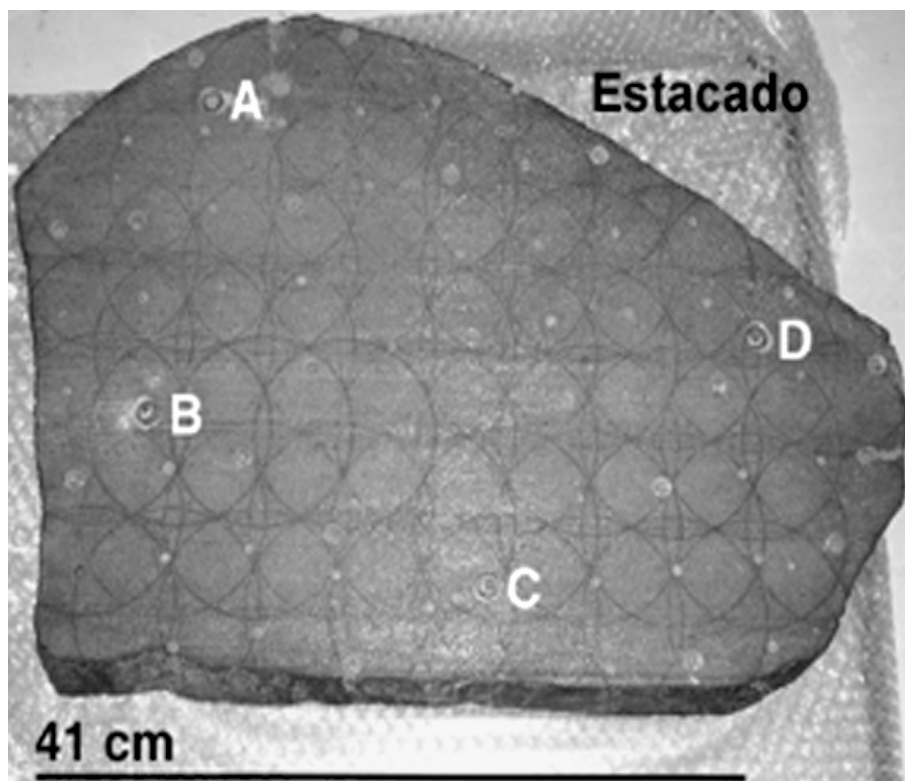


Fig. 3. Slab of the Estacado H6 chondrite (sample BM 1906,259) from the Natural History Museum in London. The locations of the four drill cores (A, B, C, D) are shown on the slab. The circular patterns were drawn on the slab during a previous, unrelated study.

$0.76 \pm 0.01\%$ (Table 2). It follows that, at the decimeter scale, OC are homogeneous in oxidation state and O-isotopic composition.

4.5. Centimeter size scale

The area subtended by a meteorite slice on a typical 1-inch (2.54 cm) round thin section is 1.0–2.0 cm². Rubin (1990) analyzed randomly distributed olivine grains in OC thin sections. He analyzed 20 or more grains in 20 different equilibrated H and L chondrites. The average standard deviation of these 20 sets of analyses is 0.4 ± 0.2 mol% Fa; the small ranges indicate relative homogeneity in oxidation state on the centimeter scale.

Clayton et al. (1991) analyzed replicates of 10 equilibrated OC falls; in most cases, the samples were probably located within a few centimeters of each other (or, at most, a few tens of centimeters) in the whole rock. The average spread of the replicate analyses in $\Delta^{17}\text{O}$ is $0.09 \pm 0.08\%$; six of the 10 analyses have a spread of $\leq 0.05\%$. The observed ranges are of the same order as the estimated analytical uncertainty in $\Delta^{17}\text{O}$ in the analyses (0.08%; Clayton and Mayeda, 1983). (However, there is uncertainty about the degree of uncertainty; the analytical uncertainty was determined on the basis of the analysis of replicate samples.)

4.6. Parent-body conditions producing homogeneity in oxidation state and O-isotopic composition

The three major OC groups constitute a chondritic clan and reflect points on a continuum of properties inherited from the solar nebula. These properties include bulk siderophile/lithophile element ratios (Müller et al., 1971; Wasson and Kallemeyn, 1988), oxidation state (e.g., McSween and Labotka, 1993), chondrule size (Rubin, 2000), and O-isotopic composition (Clayton et al., 1991). Each group has a limited range in these properties relative to the entire OC clan; nevertheless, there is appreciable diversity within each group.

For example, the mean olivine Fa contents of individual meteorites among the three OC groups range from 17.3 to 32.4 mol%, a span of ~ 15 mol% (Rubin, 1990); the Fa range within each group is much less, i.e., on the order of 3 mol% (Keil and Fredriksson, 1964; Rubin, 1990). Because the variability of olivine Fa within an individual equilibrated OC is typically ≤ 1 mol% (e.g., Rubin, 1990, 2005),

it is clear that each OC group reflects moderate compositional variability.

An analogous situation pertains to the O isotopes. The mean $\Delta^{17}\text{O}$ contents of individual meteorites among the three OC groups range from 0.56 to 1.44‰, a span of $\sim 0.9\%$ (Clayton et al., 1991). The $\Delta^{17}\text{O}$ range within each OC group is on the order of 0.3–0.4‰. As mentioned above, the variability (or analytical uncertainty) in $\Delta^{17}\text{O}$ within an individual equilibrated OC is about 0.08‰. Thus, the compositional diversity within each group is substantially greater than that in any individual member of the group and significantly less than that of the entire OC clan.

The global heterogeneity in oxidation state and O-isotopic composition reflects the moderate diversity of these properties inherited from the solar nebula by each OC asteroid during chondrite agglomeration and parent-body accretion of planetesimals. It is clear that these properties were derived from the nebula because oxidation state (represented by mean olivine Fa in equilibrated OC) inversely correlates with bulk siderophile/lithophile ratios (i.e., Ni/Si, Ir/Si, Ir/Mn, Ir/Cr, Ir/Mg, Ni/Mg, As/Mg, Ga/Mg) that reflect the nebular metal-silicate fractionation event (Müller et al., 1971; Rubin, 2005).

This heterogeneity in oxidation state persists from the global scale (surmised to be on the order of 100 km) down through the kilometer-size scale (Table 3). Oxygen isotopes are also heterogeneous on the global scale, but appear to be homogeneous on the kilometer scale. Another way to represent the different size scales is with a relative probability plot (Fig. 4). The decimeter and meter scales have narrow ranges of probable $\Delta^{17}\text{O}$ distributions, whereas the range is wider for the kilometer scale and much wider for the 100-km scale.

The homogeneity in oxidation state and O-isotopic composition on scales ≤ 1 m (Table 3) may be (1) a primary nebular effect dating back to planetesimal formation, (2) a simple post-accretion, metamorphic effect, or (3) a post-metamorphic effect reflecting impact gardening that resulted in mixing and local homogenization of compositionally diverse materials. These alternatives are discussed below.

(1) Chondrules in individual unequilibrated chondrites exhibit large heterogeneities in oxidation state and O-isotopic composition (e.g., Gooding et al., 1983; Clayton et al., 1983; McSween, 1985). Different proportions of type-I chondrules (low-FeO objects that tend to be small and ¹⁶O rich) and type-II chondrules (high-FeO objects that tend to be large and ¹⁶O poor) among unequilibrated members of

Table 3
Compositional homogeneity of OC at different size scales

Size range (km)	10 ²	10 ⁰	10 ⁻³	10 ⁻⁴	10 ⁻⁵
Samples	Entire OC asteroid	H chondrites from the 7.5-Ma cratering event	Individual L/LL6 stones from large meteorite shower	Separate regions on a large H6 slab	Thin section studies; replicate samples analyzed for O isotopes
Oxidation state	Heterogeneous	Heterogeneous	Homogeneous	Homogeneous	Homogeneous
O-isotopic composition	Heterogeneous	Apparently homogeneous	Homogeneous	Homogeneous	Homogeneous

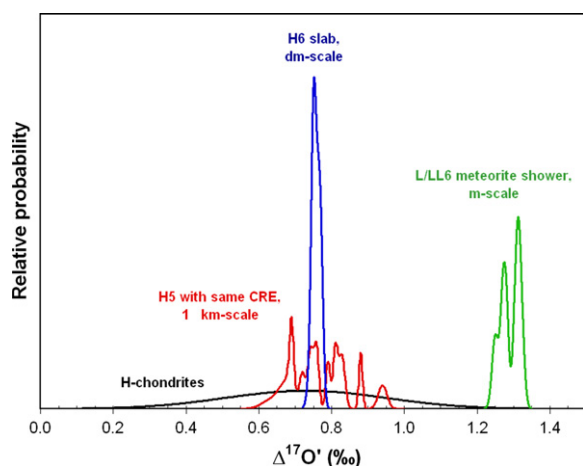


Fig. 4. Relative probability plot for OC at different size scales. There are narrow ranges of probable $\Delta^{17}\text{O}'$ distributions at the dm- and m-scales, a wider range of distributions for the km-scale (H5 samples), and a much wider range for the ~ 100 -km global scale (H-chondrite group). The H6 slab is Estacado, the L/LL6 shower is Holbrook, and the H5 samples with the same CRE (cosmic-ray exposure) age are TIL 82415 and ALHA79046. The probability density function describes the probability of finding a $\Delta^{17}\text{O}'$ value within a defined range. The probability that $\Delta^{17}\text{O}'$ assumes a value within a given interval [a, b] on the x-axis is equal to the area under the density function from a to b. Because the probability density function represents the entire sample space, the area under the function must equal unity.

the OC groups could account for mean group differences in oxidation state and O-isotopic composition (e.g., Zanda et al., 2006). Each individual chondrite may also have a distinct proportion of type-I and type-II chondrules (Fig. 4 of Zanda et al., 2006) and thus exhibit a unique oxidation state and O-isotopic composition (properties that can be readily determined in equilibrated samples). It is also possible that 1- to 10-meter-size batches of chondritic material have distinct proportions of type-I and type-II chondrules; each batch could thus have inherited its unique mean bulk compositional properties from the solar nebula. However, there is no evidence at present that this is the case.

(2) Thermal metamorphism to petrologic type 6 may have caused chondritic meteorites to reach maximum temperatures near 1220 K (e.g., Huss et al., 2006). Equilibration occurred as cations and anions diffused through this material. The Arrhenius relation applies:

$$D = D_0[\exp(-Q/RT)]$$

where D is the diffusion coefficient, D_0 is the pre-exponential factor, Q is the activation energy, R is the universal gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature.

The diffusion length L is related to D and time t via the equation:

$$L^2 = D \cdot t$$

The Fe–Mg interdiffusion rates for olivine measured by Chakraborty (1997) yield values for D_0 of $5.38 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and Q of $226,000 \text{ J mol}^{-1}$. Volume diffusion through a hypothetical meter-size, defect-free olivine grain would

take about 30 Ga. However, it is grain boundary diffusion, not volume diffusion, that governs the rate of equilibration of chondritic material. This type of diffusion is roughly 10 orders of magnitude faster than volume diffusion (Suzuki and Mishin, 2004). If water is present along grain boundaries, as seems likely (Rubin, 2005) because two-thirds of type-6 OC falls still retain detectable indigenous water (Table 2 of Jarosewich, 1990), then diffusion rates can be further enhanced by factors of 5–30 (Yund, 2004). These factors indicate that meter-size blocks of chondritic material could equilibrate at 1220 K during fluid-assisted metamorphism at times on the order of one year. If the chondritic material consisted largely of millimeter-size grains, then fluid-assisted grain-boundary diffusion of Fe–Mg could occur on far shorter time scales.

However, self-diffusion of oxygen is a much slower process. If we assume dry conditions, an activation energy Q of $477,000 \text{ J mol}^{-1}$, a pre-exponential factor D_0 of $8.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, and an oxygen fugacity equivalent to the iron–wüstite buffer (Ryerson et al., 1989), then it would take ~ 1 Ga for oxygen to diffuse through a $1 \mu\text{m}$ olivine grain at 1220 K. Larger grains would take longer than the age of the Solar System for complete oxygen self diffusion under anhydrous conditions.

In contrast, under hydrothermal conditions, diffusion is much faster. Using the empirical model of Fortier and Gilletti (1989) for estimating diffusion coefficients under hydrothermal conditions with a water pressure of 100 MPa, we find that at 1073 K, O would diffuse through a $1 \mu\text{m}$ olivine grain in about 1 day and through a 1-mm-size olivine grain in ~ 3000 years. Although it would take ~ 3 Ga for O to diffuse through a defect- and fracture-free meter-size olivine grain under these conditions, meter-size materials on asteroids are very likely to be fractured and brecciated.

This indicates that if there was sufficient water present, it is possible that the homogeneity in O-isotopic composition on meter-size scales among OC materials was caused at least in part by post-accretion metamorphism. However, the amount of water available is unknown.

(3) Impact gardening could cause homogenization of material on meter-size scales. Evidence for the latter process comes from Williams et al. (1985) who studied the Nulles H-chondrite regolith breccia and found that all of the light-colored equilibrated clasts in this meteorite are H6 material and that the meteorite matrix consists mainly of crushed H6 debris. In the case of Nulles, it seems likely that post-metamorphic impacts homogenized the local parent-body environment.

Although compositionally aberrant mafic-silicate grains have been reported in many equilibrated OC (Scott et al., 1985; Rubin, 1990), some of these grains may have developed their anomalous compositions through localized olivine–orthopyroxene–metal reactions during post-metamorphic cooling (a process that can change olivine Fa contents by up to 2 mol%; Reiserer et al., 2006). Nevertheless, a few of the aberrant olivine and low-Ca pyroxene grains reported by Scott et al. (1985) differ from the mean group Fa or Fs contents by more than 4 mol%. In addition, Rubin (1990) reported compositionally anomalous kamacite grains in many equilibrated OC that have Co concen-

trations that differ from the individual meteorite's mean Co value by ~3–9 wt.%. The occurrence of these compositionally aberrant grains is indicative of post-metamorphic impact-mixing in asteroids (Scott et al., 1985; Rubin, 1990). The grains were probably mixed into comminuted post-metamorphic debris that was subsequently lithified by small-scale impact events. Similar impact-gardening processes occur at meter size scales in the lunar regolith (e.g., McKay et al., 1991).

Heterogeneity in mean olivine Fa and bulk $\Delta^{17}\text{O}$ among equilibrated OC at global size scales is consistent with this analysis. Impact gardening is ineffective at mixing compositionally diverse components across distances substantially larger than a few meters on OC parent bodies.

5. CONCLUSIONS

The heterogeneity of oxidation state and O-isotopic composition among ordinary chondrites (OC) depends on the size scale. On a global scale (probably on the order of 100 km), each OC group is heterogeneous in both properties. For example, olivine Fa in each group varies by ~3 mol%; $\Delta^{17}\text{O}$ varies by 0.3–0.4‰. On the kilometer scale (as determined by studies of different H5 chondrites launched from their parent asteroid during a major collision ~7.5-Ma ago that excavated ~1 km³ of material), there is heterogeneity in olivine Fa (but apparently not in O isotopes). On a meter size scale (as determined by analyses of different individual stones from the large shower of L/LL6 Holbrook), the oxidation state and O-isotopic composition are homogeneous. This homogeneity persists to smaller size scales—on the decimeter scale (as measured in different regions of a large slab of the Estacado H6 chondrite) and on the centimeter scale (as measured in thin sections and sample replicates).

Inhomogeneities in oxidation state and O-isotopic composition on the global scale were inherited from the solar nebula. The homogeneity in these properties on scales ≤ 1 m probably resulted from fluid-assisted metamorphism and/or post-metamorphic impact gardening processes that caused mixing and local homogenization of compositionally diverse materials. The latter process is probably more important.

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