Oxygen isotope variation in primitive achondrites: The influence of primordial, asteroidal and terrestrial processes

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Abstract

A detailed oxygen isotope study of the acapulcoites, lodranites, winonaites, brachinites and various related achondrites has been undertaken to investigate the nature of their precursor materials. High levels of terrestrial alteration displayed by many of these samples have been mitigated by leaching in ethanolamine thioglycollate (EATG) solution. Due to their high metal and sulphide content, acapulcoite, lodranite and winonaite samples show much greater isotopic shifts during weathering than brachinites. As observed in previous studies, Antarctic weathered finds are displaced to lighter oxygen isotope compositions and non-Antarctic finds to heavier values.

Leached primitive achondrite residues continue to show high levels of oxygen isotope heterogeneity. This variation is reflected in the 2σ error on group mean $\Delta^{17}O$ values, which decrease in the following order: acapulcoite–lodranite clan > brachinites > winonaites. On an oxygen three-isotope diagram, the acapulcoite—lodranite clan define a limited trend with a slope of 0.61 ± 0.08 and an intercept of -1.43 ± 0.27 ($R^2 = 0.78$). A broad positive correlation between $\Delta^{17}O$ and olivine fayalite contents displayed by both acapulcoite and lodranite samples may be the result of early aqueous alteration and subsequent dehydration. Winonaites experienced a greater degree of differentiation than the acapulcoite–lodranite clan and define a distinct mass fractionation line, with a slope of 0.53 ± 0.01 and an intercept of -0.53 ± 0.04 ($R^2 = 1$). A number of samples currently classified as acapulcoites (NWA 725, NWA 1052 and Dho 1222) have oxygen isotope compositions indicating that they are winonaites. The relatively high level of oxygen isotope heterogeneity displayed by the brachinites supports their designation as primitive achondrites. A number of ungrouped olivine-rich achondrites (Divnoe, NWA 4042, NWA 4363, NWA 4518, NWA 5400, Zag (b)) as well as the unique plagioclase-rich achondrites GRA 06128 and GRA 06129 have similar oxygen isotope compositions to the brachinites. It remains unclear whether the brachinites and related olivine-rich achondrites are from a single or multiple parent bodies. The primitive achondrites and related samples represent material from at most only 18 parent bodies, compared to an estimated 65 for the iron meteorites. This suggests that asteroidal mantle material is underrepresented in the meteorite record. Early fragmentation of differentiated asteroids, followed by preferential destruction of their silicate-rich mantles, offers a possible explanation for this discrepancy.

On an oxygen three-isotope diagram, primitive chondrule-bearing winonaites (Dho 1222, NWA 725, NWA 1052, NWA 1463, Mt. Morris (Wisconsin)) plot close to the Young & Russell (Y&R) slope 1 line, with more evolved samples extending away from it towards the CCAM line. A similar relationship is shown by the CR chondrites. The acapulcoite–lodranite clan plots between the slope 1 and CCAM lines. However, the precursor material to the clan may have had a composition close to the slope 1 line prior to parent body processing. These relationships support the view that primordial oxygen isotope variation in the early solar system is best represented by the slope 1 (Y&R) line.

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1. INTRODUCTION

Primitive achondrites exhibit near-chondritic bulk compositions and non-chondritic textures (Weisberg et al., 2006). They are generally considered to represent meteorites that have experienced high-grade metamorphism, which in some cases resulted in partial melting (Benedix et al., 1998; Weisberg et al., 2006; Touboul et al., 2009). Consequently, primitive achondrites bridge the gap between chondrites and differentiated achondrites (Benedix et al., 1998; Weisberg et al., 2006; Floss et al., 2008; Touboul et al., 2009). In contrast to the more highly processed differentiated achondrites, primitive achondrites often retain compositional, isotopic and textural features that provide evidence about the nature of their precursor materials (McCoy et al., 2006). As a result, the study of this important class of meteorites has the potential to increase our understanding of the diversity of primitive materials present in the early solar system.

There is an ongoing debate about which meteorite groups should be considered to be primitive achondrites. Weisberg et al. (2006) suggest that there is unambiguous evidence in favour of including the acapulcoites, lodranites, winonaites, silicate-bearing IAB and IIICD irons as primitive achondrites. These authors also consider the brachinites and ureilites to be primitive achondrites, but recognise that there is uncertainty about whether these groups represent residues or cumulates. Weisberg et al. (2006) cite chondritic-like, lithophile-element abundances in Brachina as evidence in favour of considering the brachinites to be primitive achondrites. A cumulate origin for the brachinites and ureilites is proposed by Mittlefehldt (2005, 2008). Hutchison (2004) also notes that the high degree of crystal–liquid fractionation indicated by ureilite mineralogy poses a problem for their designation as primitive achondrites.

In this paper, we present the results of a detailed oxygen isotope study of acapulcoites, lodranites, winonaites and brachinites. We have also analysed a number of ungrouped meteorites that show affinities to the primitive achondrites. Oxygen isotopes are a powerful tool for understanding the origin of these meteorites, providing insight into possible genetic relationships between diverse solar system materials (Clayton and Mayeda, 1996). In particular, oxygen isotopes can highlight linkages between primitive and more evolved lithologies (Franchi, 2008), a relevant example being the possibility that the CR chondrites were parental to the acapulcoite–lodranite clan (Rubin, 2007). In addition, the degree of partial melting of precursor materials can be studied by examining the level of isotopic heterogeneity preserved in each of the primitive achondrite groups (Clayton and Mayeda, 1996; Greenwood et al., 2007). Some preliminary results of this work were reported by Greenwood et al. (2007, 2008a,b). A summary of the main mineralogical and compositional features displayed by the primitive achondrite groups examined in this study is given in the Electronic annex.

2. ANALYTICAL TECHNIQUES

2.1. Leaching of weathered finds

Compared to the more abundant, differentiated achondrites of the HED group (1082 entries on the Meteoritical Bulletin Database, of which 61 are falls), the primitive achondrites contain few falls (158 entries on the Meteoritical Bulletin Database, of which only 3 are falls). This paucity of falls is compounded by the fact that many primitive achondrite finds show evidence of extensive terrestrial weathering. This presents a significant problem when attempting to define primary levels of oxygen isotope heterogeneity in these lithologies. One approach is to remove weathering products by undertaking leaching of meteorite finds. In this investigation, a high proportion of the samples studied have been leached, using a solution of ethanolamine thioglycollate (EATG) (Cornish and Doyle, 1984; Martins et al., 2007). Tests undertaken on a suite of variably weathered H chondrites collected in the Tenere region of Niger indicated that the EATG-wash method was efficient at removing Fe-rich alteration products, without disturbing the primary oxygen isotope composition of the samples (Martins et al., 2007). EATG treatment is preferred to conventional leaching in dilute HCl, as this latter method can partially remove indigenous glass and feldspathic-rich material. Individual samples were leached in EATG for variable periods. The minimum leaching time was 2 hours, after which samples were given a series of washes in isopropanol and distilled water and then centrifuged, with more weathered samples requiring a second 2-hour treatment in EATG.

2.2. Oxygen isotopes

Oxygen isotope analysis was carried out at The Open University, using an infrared laser-assisted fluorination system (Miller et al., 1999). All analyses were obtained on whole-rock samples (0.5–2 mg). After fluorination, the O_2 released was purified by passing it through two cryogenic nitrogen traps and over a bed of heated KBr. O_2 was analysed using a Micromass Prism III dual inlet mass spectrometer. Analytical precision (1σ), based on replicate analyses of both international (NBS-28 quartz, UWG-2 garnet (Valley et al., 1995)) and internal standards, is approximately $\pm0.04\permil$ for $\delta^{17}O$, $\pm0.08\permil$ for $\delta^{18}O$ and $\pm0.024\permil$ for $\Delta^{17}O$ (Miller et al., 1999). All sample powders analysed in this study were drawn from larger homogenised aliquots, obtained by crushing interior whole-rock chips with a minimum mass of about 100 mg. The precision (1σ) quoted for individual meteorite samples are based on replicate analyses.

Oxygen isotopic analyses are reported in standard δ notation, where $\delta^{18}O$ has been calculated as: $\delta^{18}O = [(^{18}O/^{16}O_{sample}/^{18}O/^{16}O_{ref}) - 1] \times 1000$ ($\permil$) and, similarly, for $\delta^{17}O$ using the $^{17}O/^{16}O$ ratio. $\Delta^{17}O$, which represents the deviation from the terrestrial fractionation line, has been calculated using the linearised format of Miller (2002):

$$\Delta^{17}O = 1000\ln(1 + \delta^{17}O/1000) - \lambda 1000\ln(1 + \delta^{18}O/1000)$$

$\lambda = 0.5247$, and was determined using 47 terrestrial whole-rock and mineral separate samples (Miller et al., 1999; Miller, 2002). Shaded boxes, rather than distinct error bars, have been used on a number of figures (Figs. 1, 3, 4a, b, 6) to illustrate the 2σ variation of the mean $\delta^{18}O$ and

Δ^{17}O values for various meteorite groups. Since δ^{18}O and Δ^{17}O are correlated values, rectangular boxes are not strictly valid as a means of representing the variation in these parameters. However, they are used here as a simple graphical means of illustrating the extensive differences in oxygen isotope variation seen both between weathered and EATG-washed primitive achondrite samples, and between the various differentiated and primitive achondrite groups.

3. RESULTS

Full oxygen isotope results for untreated primitive achondrite samples and EATG residues analysed in this study are given in Table 1 and shown in Figs. 1–9. Detailed results for each individual primitive achondrite group and various ungrouped samples are presented below.

3.1. Acapulcoite – lodranite clan

Acapulcoite and lodranite samples show a wide variation in their oxygen isotope compositions, ranging from 0.93‰ to 7.73‰ with respect to δ^{18}O, and −0.69‰ to −1.53‰ with respect to Δ^{17}O (Table 1, Fig. 1). However, in terms of the δ^{18}O variation, high and low portions of the range are defined by the untreated hot and cold desert samples. The most extreme case is that of NWA 2866, which has a δ^{18}O value of 7.73‰ for the untreated sample, compared to 4.97‰ for the EATG residue (Table 1). Tie-lines connecting untreated samples to their respective EATG residues (Fig. 1) reveal that non-Antarctic finds are displaced to higher δ^{18}O and Δ^{17}O values, whereas untreated Antarctic finds are shifted to lower δ^{18}O values and higher Δ^{17}O values. Similar patterns of isotopic displacement in weathered hot and cold desert finds have been documented in other meteorite groups, including carbonaceous (Greenwood and Franchi, 2004) and ordinary chondrites (Bland et al., 2000).

Weathering, both in hot and cold desert environments, has the effect of incorporating terrestrial oxygen into a sample and, as a result, Δ^{17}O values are shifted towards the terrestrial fractionation line. The extent to which this takes place will depend on the degree of weathering and, hence, will tend to increase the degree of dispersion seen in untreated samples. A detailed discussion of the processes involved in the terrestrial alteration of meteorites is given in the Electronic annex.

While EATG residues for acapulcoites and lodranites show greatly reduced variation in terms of δ^{18}O values compared to untreated finds, the level of Δ^{17}O variation is only slightly reduced (Fig. 1). The Δ^{17}O variation of the EATG residues is most likely a reflection of the intrinsic primary variation within the acapulcoite–lodranite clan, as inherited from their chondritic source material. This inference is supported by a plot of oxygen isotope variation in the individual lithologic groups of the acapulcoite–lodranite clan (Fig. 2). There is essentially no difference between the isotopic variation in lodranites compared to acapulcoites (Fig. 2). Again, this suggests that the oxygen isotopic variation inherited from the precursor material was not completely lost during subsequent parent body processing, i.e. aqueous alteration, metamorphism and partial melting (see Section 4.2.1).

3.2. Winonaites

Like the acapulcoites and lodranites, untreated winonaites display a wide variation in their oxygen isotope compositions, ranging from −1.47‰ to 7.37‰ with respect to δ^{18}O and −0.24‰ to −0.60‰ with respect to Δ^{17}O (Table 1, Fig. 3). However, compared with untreated samples, EATG residues show much reduced variation both in terms of δ^{18}O and Δ^{17}O. In a similar manner to the acapulcoites and lodranites, untreated Antarctic winonaites are shifted to lower δ^{18}O values and slightly displaced to less negative Δ^{17}O values than their EATG residues (Fig. 3). The most extreme example of this behaviour is displayed by the untreated aliquot of Y-791058, which is nearly 7‰ lighter than its EATG residue (Table 1, Fig. 3). Unlike the acapulcoites and lodranites, the non-Antarctic winonaite finds do not show a consistent shift to higher δ^{18}O values compared to their EATG residues. In particular, the untreated Winona sample (from NHM, London) is nearly 4‰ lighter than its EATG residue. However, Winona is a unique, extremely weathered find that was discovered in 1928 in a stone cist, in the ruins of the Elden pueblo near Winona, Arizona (Mason and Jarosewich, 1967). The meteorite had been carefully buried and one possibility is that the stone was transported from more northerly latitudes by migrating Native American inhabitants. To a lesser extent, Tierra Blanca shows similar behaviour to Winona, with the untreated sample being about 1‰ lighter than its EATG residue (Table 1, Fig. 3). Both Winona and Tierra Blanca are very weathered North American finds. One further possibility to explain their distinct alteration characteristics is that they may have high terrestrial residence ages and, consequently, experienced much colder weathering conditions than those prevailing nowadays. Other non-Antarctic winonaite finds show much smaller isotopic shifts compared to their EATG residues than either Winona or Tierra Blanca. In these examples, the untreated residue tends to be shifted slightly to higher δ^{18}O and less negative Δ^{17}O values than their respective EATG residues (Table 1, Fig. 3), similar to the variation seen in the acapulcoite–lodranite clan and other meteorite groups (Bland et al., 2000; Greenwood and Franchi, 2004).

3.3. Brachinites

Compared to the untreated acapulcoite, lodranite and winonaite samples, the brachinites show more restricted δ^{18}O variation (ranging from 3.08‰ to 5.04‰), but similar levels of Δ^{17}O variation to the untreated winonaites (−0.39‰ to −0.11‰) (Table 1, Fig. 4a and b). However, unlike these other groups, individual untreated brachinites display only minor isotopic shifts when compared to their respective EATG residues (Fig. 4a). In keeping with the results from other groups, there is a tendency for the untreated Antarctic finds to be displaced to lower δ^{18}O values than their EATG residues, and for untreated

Table 1
Oxygen isotope composition of primitive achondrites.

Sample	Treatment	N	Source	Weathing	$\delta^{17}O$‰	1σ	$\delta^{18}O$‰	1σ	$\Delta^{17}O$‰	1σ	Notes
Brachinites											
ALH 84025,10	Untreated	2	MWG-NASA-JSC	A/Be	2.19	0.04	4.71	0.05	−0.28	0.01	
ALH 84025,10	EATG residue	2		A/Be	2.26	0.07	4.89	0.17	−0.30	0.01	
Brachina	Untreated	2	BM 1995,M3	NR	1.26	0.07	3.16	0.05	−0.39	0.05	
Brachina	EATG residue	2		NR	1.22	0.10	3.08	0.18	−0.39	0.00	
Eagles Nest	Untreated	2	AMNH	NR	2.21	0.01	4.56	0.01	−0.18	0.02	
Eagles Nest	EATG residue	1		NR	2.09		4.36		−0.19		
EET 99402,34	Untreated	2	MWG-NASA-JSC	B	2.17	0.02	4.40	0.01	−0.14	0.02	
EET 99407,11	Untreated	2	MWG-NASA-JSC	B	2.17	0.08	4.36	0.12	−0.11	0.02	
EET 99407,11	EATG residue	2		B	2.20	0.01	4.47	0.00	−0.14	0.02	
Hughes 026	Untreated	2	AMNH	NR	2.12	0.07	4.44	0.13	−0.20	0.00	
Hughes 026	EATG residue	2		NR	2.08	0.02	4.35	0.03	−0.20	0.01	
Nova 003	Untreated	2	BM 1993,M11	NR	2.23	0.07	4.78	0.12	−0.27	0.01	
Nova 003	EATG residue	2		NR	1.88	0.24	4.13	0.45	−0.28	0.01	
NWA 595	Untreated	2	UCLA	W3/4	2.46	0.02	5.04	0.04	−0.18	0.01	
NWA 595	EATG residue	2		W3/4	2.35	0.14	4.81	0.25	−0.17	0.01	
NWA 1500	Untreated	2	R. Bartoschweitz	NR	2.17	0.02	4.67	0.04	−0.28	0.00	1
NWA 1500	EATG residue	2		NR	1.97	0.01	4.35	0.03	−0.30	0.02	1
NWA 3151	Untreated	2	A. Irving–Washington Uni.	NR	2.25	0.03	4.70	0.07	−0.21	0.01	
Mean of all samples		18			2.07	0.33	4.40	0.52	−0.24	0.08	
Mean of all EATG residues		8			2.01	0.35	4.30	0.55	−0.25	0.09	
Mean of all untreated samples		10			2.12	0.32	4.48	0.51	−0.22	0.08	
Winonaites											
Dhofar 1222	Untreated	2	MHN-PARIS	W2/3	1.38	0.12	3.50	0.21	−0.45	0.01	3
Fortuna	Untreated	3	Humbolt University, Berlin	W0/W1	2.17	0.23	5.07	0.50	−0.49	0.03	
Fortuna	EATG residue	2		W0/1	2.05	0.03	4.87	0.07	−0.50	0.01	
HaH 193	Untreated	2	BM	W3	2.32	0.07	5.32	0.11	−0.47	0.01	
HaH 193	EATG residue	2		W3	1.95	0.04	4.71	0.09	−0.52	0.01	
Mount Morris (Wisconsin)	Untreated	2	Open University	NR	1.72	0.00	4.19	0.05	−0.48	0.02	2
Mount Morris (Wisconsin)	EATG residue	1		NR	1.25		3.45		−0.56		2
NWA 516	Untreated	2	UCLA	W3	2.66	0.36	6.04	0.74	−0.50	0.03	
NWA 516	EATG residue	2		W3	2.42	0.10	5.77	0.18	−0.60	0.01	
NWA 725–1457	Untreated	2	S. Turecki	NR	1.38	0.12	3.52	0.18	−0.46	0.02	
NWA 725	Untreated	2	BM 2002,M23	NR	1.40	0.20	3.49	0.35	−0.43	0.02	3
NWA 725	EATG residue	2		NR	1.03	0.05	2.92	0.11	−0.50	0.01	3
NWA 1052	Untreated	2	Vanni Moggi Cecchi	W1	1.35	0.07	3.30	0.16	−0.37	0.01	3
NWA 1052	EATG residue	2		W1	1.01	0.09	2.84	0.21	−0.48	0.01	3
NWA 1463	Untreated	6	Royal Ontario Museum	NR	1.46	0.16	3.58	0.35	−0.42	0.03	
NWA 1463	EATG residue	2		NR	1.25	0.15	3.30	0.27	−0.48	0.00	
Pontlyfni (Fall)	Untreated	2	BM 1975,M6	W0	2.72	0.21	6.18	0.32	−0.52	0.04	
QUE 94535,21	Untreated	2	MWG-NASA-JSC	C	0.13	0.15	1.14	0.28	−0.47	0.01	
QUE 94535,21	EATG residue	2		C	1.71	0.03	4.28	0.05	−0.53	0.01	

Table 1 (*continued*)

Sample	Treatment	N	Source	Weathering	$\delta^{17}O\permil$	1σ	$\delta^{18}O\permil$	1σ	$\Delta^{17}O\permil$	1σ	Notes
Sahara 02029	Untreated	2	MHN-PARIS	W2	3.51	0.04	7.37	0.03	−0.35	0.02	
Sahara 02029	EATG residue	2		W2	3.37	0.28	7.21	0.50	−0.40	0.02	
Tierra Blanca	Untreated		BM 1999, M37	NR	2.71	0.02	5.62	0.00	−0.24	0.02	
Tierra Blanca	EATG residue	2		NR	3.07	0.02	6.71	0.03	−0.45	0.01	
Winona	Untreated	3	BM 1930, 974	NR	0.41	0.15	1.22	0.28	−0.24	0.01	
Winona	Untreated	2	Open University	NR	0.92	0.12	2.42	0.27	−0.35	0.02	
Winona	EATG residue	2		NR	2.17	0.15	5.15	0.22	−0.53	0.03	
Y-8005	Untreated	1	NIPR	NR	0.44		1.73		−0.47		
Y-8005	EATG residue	2		NR	1.91	0.11	4.64	0.18	−0.52	0.02	
Y-74025	Untreated	2	NIPR	B	1.71	0.06	4.28	0.10	−0.53	0.01	
Y-74025	EATG residue	2		B	2.13	0.01	5.09	0.03	−0.53	0.00	
Y-75305	Untreated	1	NIPR	NR	1.29		3.41		−0.50		
Y-75305	EATG residue	2		NR	1.92	0.10	4.63	0.17	−0.51	0.01	
Y-791058	Untreated	1	NIPR	NR	−1.18		−1.47		−0.41		
Y-791058	EATG residue	2		NR	2.21	0.17	5.25	0.32	−0.53	0.00	
Mean of all samples		34			1.70	0.95	4.14	1.83	−0.46	0.08	
Mean of all EATG residues (includes fall)		16			2.01	0.68	4.81	1.28	−0.51	0.04	
Mean of all untreated samples		18			1.43	1.08	3.54	2.07	−0.42	0.08	
Acapulcoite–lodranite clan											
Acapul/lodranite											
EET 84302,45	Untreated	2	MWG-NASA-JSC	B/C	0.21	0.05	2.73	0.10	−1.22	0.01	
EET 84302,45	EATG residue	2		B/C	0.33	0.09	2.90	0.28	−1.19	0.05	
FRO 93001	Untreated	2	Open University	W1 (low)	0.44	0.22	2.81	0.41	−1.04	0.00	
LEW 86220	Untreated	2	SI	NR	0.65	0.14	3.41	0.22	−1.13	0.03	
Acapulcoites											
Acapulco (Fall)	Untreated	2	BM 1978,M25	W0	0.91	0.09	3.51	0.16	−0.93	0.00	
ALHA78230	Untreated	1	NIPR	NR	0.86		3.72		−1.09		
ALHA78230	EATG residue	2		NR	0.86	0.06	3.68	0.06	−1.07	0.03	
ALHA81187,39	Untreated	2	MWG-NASA-JSC	B/C	−0.14	0.06	1.94	0.16	−1.16	0.03	
ALHA81187,39	EATG residue	2		B/C	0.24	0.03	2.72	0.09	−1.19	0.02	
ALHA81261,30	Untreated	2	MWG-NASA-JSC	A/B	0.78	0.12	3.55	0.23	−1.08	0.00	
ALHA81261,30	EATG residue	2		A/B	0.85	0.12	3.71	0.18	−1.10	0.02	
Dhofar 125	Untreated	1	Humbolt University, Berlin	W1/2	0.92		3.97		−1.16		
Dhofar 125	EATG residue	2		W1/2	0.49	0.05	3.59	0.08	−1.39	0.01	
Dhofar 290	Untreated	2	Vernadsky Institute	NR	0.95	0.25	3.61	0.58	−0.94	0.06	
Dhofar 290	EATG residue	2		NR	0.73	0.07	3.52	0.14	−1.12	0.00	
Dhofar 312	Untreated	2	Vernadsky Institute	W3	1.57	0.02	5.13	0.05	−1.12	0.01	
Dhofar 312	EATG residue	2		W3	0.58	0.13	3.72	0.23	−1.37	0.01	
FRO 95029	Untreated	1	Open University	W1	−0.05		2.00		−1.10		
GRA 98028,29	Untreated	2	MWG-NASA-JSC	C	−0.08	0.03	1.81	0.08	−1.03	0.02	
Monument draw	Untreated	2	BM 2002, M22	NR	1.04	0.04	3.78	0.06	−0.94	0.00	
Monument draw	EATG residue	2		NR	0.89	0.01	3.76	0.03	−1.08	0.02	

Sample	Treatment	N	Source	Class							
NWA 2775	Untreated	2	Stan Turecki	NR	0.89	0.01	3.01	0.03	−0.69	0.03	
NWA 2775	EATG residue	2		NR	0.94	0.01	3.42	0.02	−0.85	0.00	
NWA 2866	Untreated	3	Ted Bunch	W3	3.23	0.26	7.73	0.44	−0.81	0.05	
NWA 2866	EATG residue	1		W3	1.42		4.97		−1.18		
NWA 2871	Untreated	2	Stan Turecki	W3	1.23	0.05	4.30	0.06	−1.02	0.02	
NWA 2871	EATG residue	2		W3	0.49	0.02	3.28	0.06	−1.23	0.01	
NWA 3008	Untreated	2	Min. Museum, Hamburg	W2	0.81	0.06	3.33	0.13	−0.93	0.01	
NWA 3008	EATG residue	2		W2	0.64	0.06	3.10	0.07	−0.99	0.02	
TIL 99002	Untreated	2	Palatine Harper College	A	0.89	0.03	3.82	0.05	−1.11	0.01	
Y-74063	Untreated	1	NIPR	B	0.69		2.88		−0.81		
Y-74063	EATG residue	2		B	1.13	0.04	3.77	0.05	−0.84	0.01	
Lodranites											
FRO 03001	Untreated	2	University of Siena	W0	0.54	0.07	3.01	0.05	−1.03	0.04	
FRO 03001	EATG residue	2		W0	0.49	0.29	2.98	0.54	−1.07	0.00	
FRO 90011	Untreated	1	Open University	NR	0.52		2.97		−1.04		
Gibson	Untreated	2	SI	NR	0.91	0.10	3.97	0.18	−1.17	0.01	
GRA 95209,243	Untreated	2	MWG-NASA-JSC	B	−0.86	0.15	1.03	0.31	−1.39	0.01	
GRA 95209,243	EATG residue	2		B	−0.24	0.03	2.33	0.03	−1.46	0.02	
LEW 88280,28	Untreated	2	MWG-NASA-JSC	B	0.83	0.09	3.36	0.20	−0.93	0.02	
LEW 88280,28	EATG residue	2		B	0.78	0.04	3.33	0.03	−0.96	0.02	
Lodran (Fall)	Untreated	2	BM 1985,M84	W0	0.92	0.02	3.56	0.08	−0.95	0.03	
MAC 88177,12	Untreated	2	MWG-NASA-JSC	B/C	0.29	0.09	2.64	0.17	−1.09	0.00	
MAC 88177,12	EATG residue	2		B/C	0.60	0.01	3.28	0.04	−1.11	0.01	
NWA 2235	Untreated	2	NIPR	W1	1.52	0.16	4.55	0.36	−0.87	0.03	
NWA 2235	EATG residue	2		W1	0.91	0.03	3.79	0.08	−1.08	0.01	
Y-74357	Untreated	1	NIPR	NR	−0.25		1.93		−1.26		
Y-74357	EATG residue	2		NR	0.45	0.17	3.35	0.28	−1.31	0.02	
Y-75274	Untreated	2	NIPR	C	−0.41	0.36	2.14	0.66	−1.53	0.01	
Y-75274	EATG residue	3		C	0.03	0.33	2.79	0.75	−1.43	0.07	
Y-791491	Untreated	1	NIPR	NR	−0.44		0.93		−0.92		
Y-791491	EATG residue	3		NR	0.76	0.13	3.26	0.21	−0.94	0.01	
Mean of all samples		51			0.64	0.62	3.30	1.04	−1.09	0.18	
Mean of all EATG residues (includes falls)		23			0.66	0.36	3.41	0.51	−1.12	0.18	
Mean of all untreated samples		28			0.63	0.79	3.22	1.34	−1.06	0.18	
Ungrouped achondrites											
Dhofar 732	Untreated	2		NR	2.57	0.07	5.84	0.17	−0.49	0.02	
Dhofar 732	EATG residue	2		NR	2.19	0.01	5.17	0.00	−0.52	0.01	
Divnoe	Untreated	2	AMNH	NR	2.29	0.01	4.89	0.03	−0.28	0.00	
Divnoe	EATG residue	2		NR	2.26	0.01	4.86	0.00	−0.28	0.01	
LEW 88763,18	Untreated	2	MWG-NASA-JSC	B	0.10	0.04	2.47	0.10	−1.19	0.01	4
NWA 4042	Untreated	5	Humbolt University, Berlin	W2	2.54	0.15	5.18	0.28	−0.17	0.02	

N = Number of replicate analyses.

Notes: (1) official classification = ungrouped achondrite; (2) official classification = IAB-an; (3) official classification = acapulcoite; (4) official classification = brachinite.

Abbreviations: AMNH, American Museum of Natural History, New York; BM, Natural History Museum, London; MHN-Paris, Natural History Museum, Paris; MWG-NASA-JSC, Meteorite Working Group NASA; NIPR, National Institute of Polar Research, Japan, Johnson Space Center; SI, Smithsonian Institution, Washington.
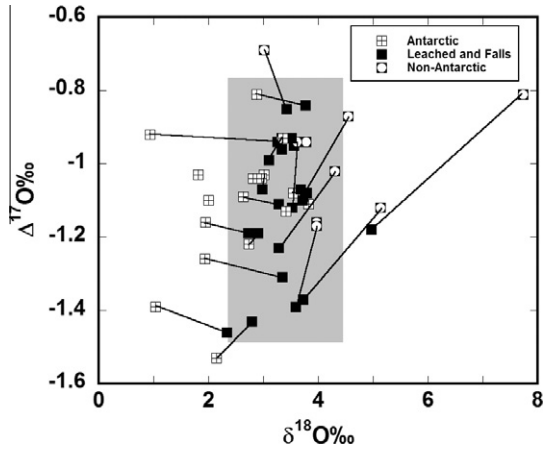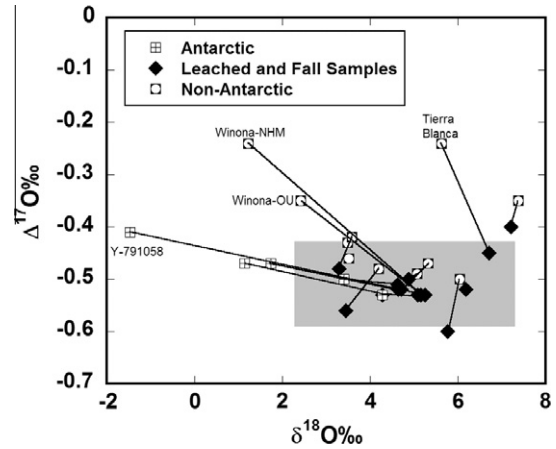
Fig. 1. Oxygen isotope variation in the acapulcoite–lodranite clan. Compared to EATG leached residues, Antarctic finds are displaced towards lower $\delta^{18}O$ values, whereas non-Antarctic finds are displaced to higher $\delta^{18}O$ values. The diagram also shows that, not only are the untreated samples displaced to more extreme $\delta^{18}O$ values compared to their respective EATG residues, but are also generally displaced to less negative $\Delta^{17}O$ values, consistent with the source of the contamination being terrestrial in origin. Tie-lines are drawn between untreated samples and their respective EATG residues. The light grey shaded box shows the 2σ variation on the mean $\delta^{18}O$ and $\Delta^{17}O$ values for the EATG residues and fall samples.
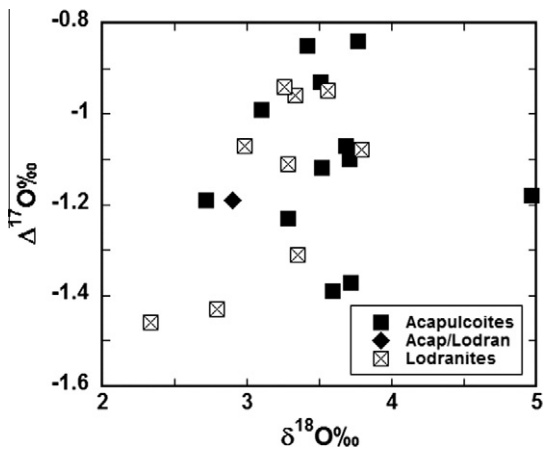
Fig. 2. Oxygen isotope variation for EATG residues and falls of the various groups of the acapulcoite–lodranite clan.

non-Antarctic finds to be displaced to higher $\delta^{18}O$ values (Fig. 4a).

Brachina plots away from other brachinite samples on Fig. 4a and b. This is reflected in the 2σ variation of the mean $\delta^{18}O$ and $\Delta^{17}O$ values of the brachinites (including Brachina) (light grey box Fig. 4a and b), compared to the much more restricted values if Brachina is excluded (dark grey box Fig. 4a and b). Brachinites are known to be a diverse group of meteorites and it has been suggested that they may not all have formed by the same processes, or be derived from a single parent body (Weisberg et al., 2006). These issues are discussed further in Section 4.2.3.

Fig. 3. Oxygen isotope variation in the winonaites. Compared to EATG leached residues, Antarctic finds are displaced towards lower $\delta^{18}O$ values. Non-Antarctic finds show less distinct trends than seen in the acapulcoite–lodranites (see text for further discussion). The light grey shaded box shows the 2σ variation on the mean $\delta^{18}O$ and $\Delta^{17}O$ values for the EATG residues and fall samples.

3.4. Ungrouped and misclassified primitive achondrites

Certain ungrouped achondrites display characteristics similar to those shown by members of the well-defined primitive achondrite groups discussed above. In addition, there are also individual members of the main primitive achondrite groups that appear to have oxygen isotope compositions incompatible with their official classifications. The oxygen isotope compositions of a number of these ungrouped or anomalous primitive achondrites are given in Table 1 and plotted in Figs. 4b and 5. In Table 1, NWA 1500 is included in the brachinites and NWA 725, NWA 1052, Dho 1222 are members of the winonaite group, based on the evidence presented in this and other recent studies. However, their official classifications are somewhat different (see notes to Table 1 for further details).

Three ungrouped achondrites (Divnoe, NWA 4042 and NWA 1500) analysed in this study show mineralogical similarities to the brachinites (Fig. 4b). Divnoe is an olivine-rich achondrite, with a generally coarse, but variable grain-size (up to 2000 μm) (Petaev et al., 1994; Mittlefehldt et al., 1998). While there has been debate about the relationship between Divnoe and the other principal primitive achondrite groups (McCoy et al., 1992; Petaev et al., 1994; Weigel et al., 1996, 1997; Mittlefehldt et al., 1998) in terms of its oxygen isotope composition, Divnoe plots within the inner brachinite field close to ALH 84025 (Fig. 4b). This relationship might be taken as evidence that Divnoe should be reclassified as a brachinite (see Section 4.2.3 for further discussion).

NWA 4042 is an olivine-rich achondrite, comprising 93.3% equigranular olivine ($Fa_{20.3}$), 4.6% low-Ca pyroxene ($Fs_{16.2}$) and minor metal, pyrrhotite and chromite (Connolly, 2006). In terms of its oxygen isotope composition, NWA 4042 plots just outside the inner brachinite field (Fig. 4b).
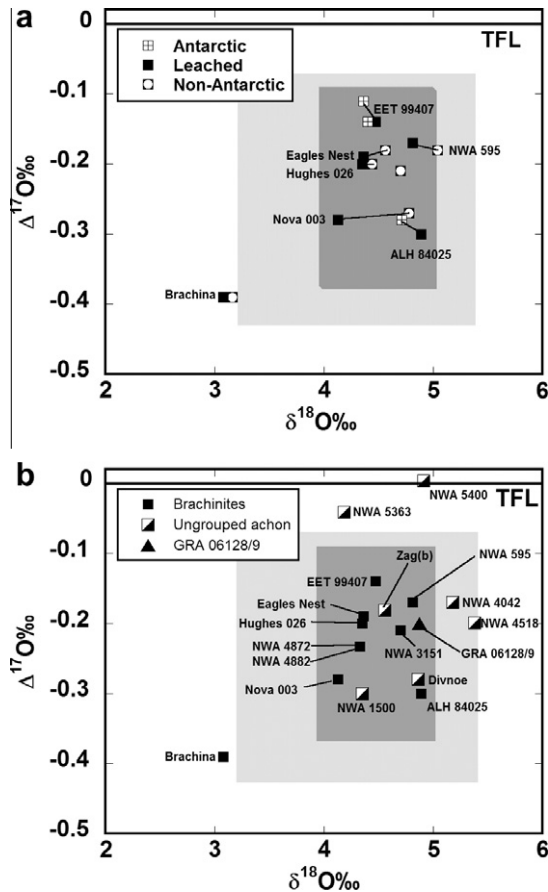
Fig. 4. Oxygen isotope variation in brachinites. The light grey shaded boxes shows the 2σ variation on the mean $\delta^{18}O$ and $\Delta^{17}O$ values for all the EATG residues including Brachina. The dark grey shaded boxes shows the 2σ variation on the mean $\delta^{18}O$ and $\Delta^{17}O$ values for all the EATG residues excluding Brachina. (a) Brachinites only. (b) Oxygen isotope variation in brachinites compared to related olivine-rich achondrites. All brachinite analyses this study, except NWA 4872 and NWA 4882 (Rumble et al. (2008)). References for other primitive achondrite oxygen isotope analyses are given in the text.

Fig. 5. Oxygen isotope variation in ungrouped and misclassified primitive achondrites. All of the analysis plotted are for EATG leached residues except for NWA 4042, Dho 1222 and LEW 88763 which were untreated. Also shown for comparison are analyses of EATG leached residues for the main primitive achondrite groups.
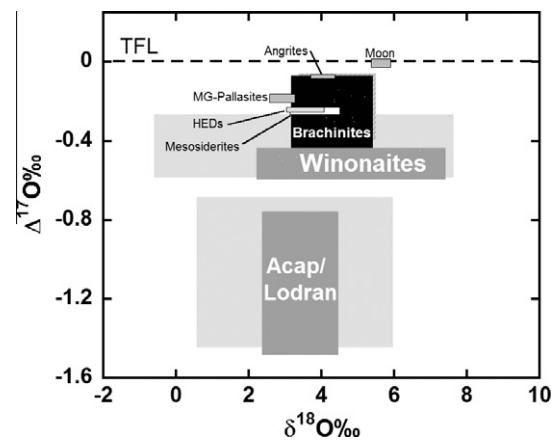

Fig. 6. Diagram showing the 2σ variation on the mean $\delta^{18}O$ and $\Delta^{17}O$ values for EATG leached residues of the principal primitive achondrite group compared to untreated samples and differentiated achondrites. Dark shaded box labelled "Acap/Lodran": acapulco-ite–lodranite clan EATG residues, associated light shaded box: untreated acapulcoite–lodranite samples. Dark shaded box labelled "Winonaites": winonaite EATG residues, associated light shaded box: untreated winonaite samples. Black box: brachinite EATG residues; striped shaded box (mainly hidden behind brachinite residue box): untreated brachinite samples. TFL: Terrestrial Fractionation Line. Differentiated achondrite boxes, as labelled on diagram. (Data for differentiated achondrites: Greenwood et al. (2005, 2006) and Hallis et al. (2010).

NWA 1500 is an olivine-rich achondrite that was originally classified as a basaltic ureilite (Bartoschewitz et al., 2003), but was subsequently redefined as an ungrouped achondrite, on the basis that it displays an essentially non-ureilitic mineralogy (Mittlefehldt and Hudon, 2004; Goodrich et al., 2006). In terms of its oxygen isotope composition, NWA 1500 plots within the inner brachinite field on Fig. 4b.

As demonstrated by Benedix et al. (1998), an oxygen isotope analysis is required to unambiguously distinguish winonaites from members of the acapulcoite–lodranite clan (see Electronic annex for further discussion). It is therefore unsurprising that misclassification can occur when such an analysis has not been undertaken. NWA 725, NWA 1052, and Dhofar 1222 are clear examples of this problem. All three meteorites have been classified as acapulcoites, but have oxygen isotope compositions consistent with being winonaites (Fig. 5). The petrographic characteristics of

these samples are also consistent with their designation as winonaites (Grossman, 2001; Russell, 2005; Rubin, 2007).

Dhofar 732 is an orthopyroxene-rich achondrite, with an oxygen isotope composition that plots in the winonaite field (Fig. 5). While it shows a number of similarities to the winonaites (e.g. very low FeO/MgO and FeO/MnO ratios), it also displays some differences (e.g. low Na mesostasis) (Demidova et al., 2004). The possibility that Dhofar 732
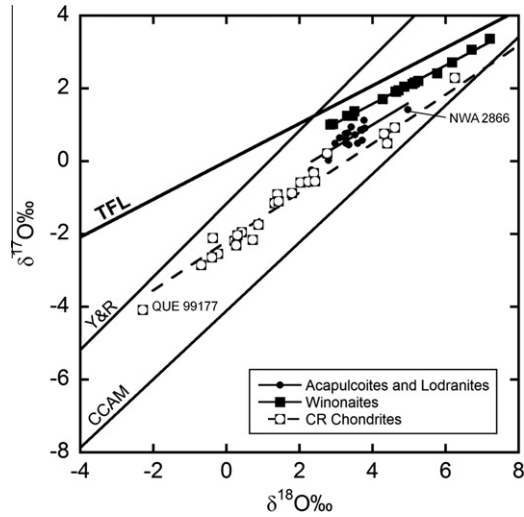
Fig. 7. $\delta^{17}O‰$ vs. $\delta^{18}O‰$ for acapulcoite–lodranite clan and winonaites (this study), CR chondrites (Clayton and Mayeda, 1999; Schrader et al., 2011). Key: TFL: Terrestrial Fractionation Line; Y&R: slope 1 line (Young and Russell, 1998); CCAM: carbonaceous chondrite anhydrous mineral line (Clayton et al., 1977; Clayton and Mayeda, 1999).
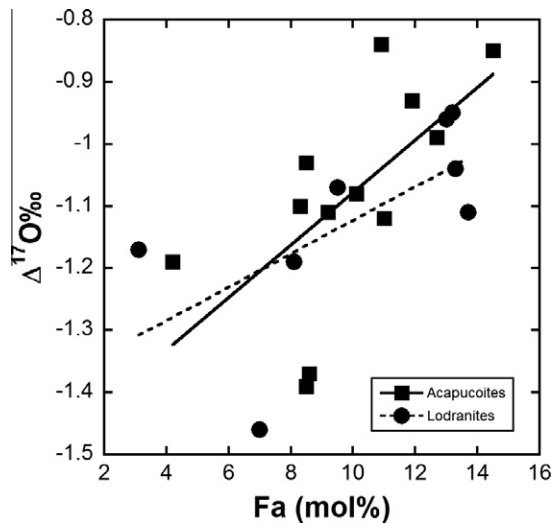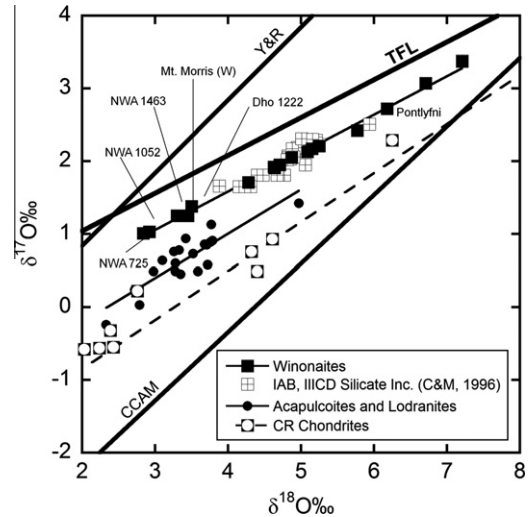

Fig. 9. Oxygen isotope composition ($\delta^{17}O‰$ vs. $\delta^{18}O‰$) of winonaites (this study) and IAB, IIICD silicate inclusions (Clayton and Mayeda, 1996). The composition of acapulcoite–lodranite clan samples (this study) and CR chondrites (Clayton and Mayeda, 1999; Schrader et al., 2011) are shown for comparison. Named winonaite samples are those which have been found to contain relict chondrules. Key: TFL: Terrestrial Fractionation Line; Y&R: slope 1 line (Young and Russell, 1998); CCAM: carbonaceous chondrite anhydrous mineral line (Clayton et al., 1977; Clayton and Mayeda, 1999).

Fig. 8. $\Delta^{17}O‰$ vs. Fa (mol%) for acapulcoites and lodranites. The best fit lines through both the lodranite and acpulcoite data have R^2 values of 0.40.

is related to the winonaites appears feasible, but further detailed study is required to test this suggestion.

LEW 88763 is currently classified as a brachinite, but has an oxygen isotope composition that is distinct from other members of the group (Fig. 5) (see Section 4.2.3 for further discussion).

4. DISCUSSION

4.1. Terrestrial alteration of primitive achondrites

The Meteoritical Bulletin Database currently lists 27 brachinite specimens, 24 winonaites and 98 acapulcoite–

lodranites, the majority of which were located and classified within the last ten years. However, despite this rapid increase in numbers, there remain only three recognised primitive achondrite falls, namely Pontlyfni, Acapulco and Lodran. The high levels of terrestrial contamination shown by many primitive achondrites are a major issue, when trying to define primary levels of oxygen isotope heterogeneity in these lithologies. We have attempted to overcome this problem by using a leaching treatment (Section 2.1).

The oxygen isotope results for EATG treated residues are compared to non-treated samples in Fig. 6. For the acapulcoites and lodranites, untreated samples show almost three times the level of $\delta^{18}O$ variation compared to that of the EATG residues. In contrast, EATG residues show only slightly reduced $\Delta^{17}O$ variation compared to untreated samples (Section 3.1). Similar characteristics are seen in the winonaite samples (Fig. 6), with the $\delta^{18}O$ range of the untreated samples being about twice that of the EATG residues. The reduced $\Delta^{17}O$ variation of winonaite EATG residues compared to acapulcoite–lodranite samples indicates that their parent body was more extensively differentiated than that of the acapulcoites and lodranites. Brachinites display only slight differences in $\Delta^{17}O$ and $\delta^{18}O$ variation between the untreated samples and EATG residues (Fig. 6). This behaviour undoubtedly reflects their low metal and sulphide content when compared to the winonaites, acapulcoites and lodranites. In relatively unaltered acapulcoites and lodranites, the content of Fe,Ni metal varies between about 4 and 28 vol.% and the content of troilite from <1 to 5 vol.% (Palme et al., 1981; Rubin, 2007). Due to the extensive weathering suffered by most

winonaite samples, there is some uncertainty about the primary modal content of metal and sulphide in these meteorites (Benedix et al., 1998). However, relatively unweathered examples have Fe,Ni metal in the range 1.5–12.3 vol.% and sulphide in the range 9.1–19.9 vol.% (Benedix et al., 1998). In comparison, brachinites generally contain only trace amounts of metal and between 2 and 7 vol.% sulphide (Nehru et al., 1992; Weisberg et al., 2006).

Based on thermodynamic calculations, Gooding (1986) predicted that Fe,Ni metal should be more susceptible to Antarctic weathering than sulphide, which in turn should also be more susceptible than silicates. This general order of weathering susceptibility is consistent with the results of detailed studies of meteorite alteration in both hot and cold desert environments (Lee and Bland, 2004; Al-Kathiri et al., 2005; Bland et al., 2006). The greater oxygen isotope shifts in weathered vs. treated samples for the acapulcoite–lodranite clan and winonaites, when compared to the brachinites (Fig. 6), is consistent with the theoretical and observational evidence that metal and sulphide are more susceptible to terrestrial alteration than silicates (Gooding, 1986; Lee and Bland, 2004). Bland et al. (2000) found that ~25% alteration of L chondrite finds is required before any shift in primary oxygen isotope values can be detected. However, the results of the present study seem at odds with this conclusion and suggest instead that oxidation of metal and sulphide, even during the earliest stages of terrestrial weathering, necessarily involves the incorporation of a terrestrial oxygen component within a meteorite find. A more detailed discussion of terrestrial weathering processes in meteorites is presented in the Electronic annex.

4.2. Primitive achondrite precursor materials

Even after the influence of weathering has been mitigated by EATG leaching, primitive achondrites display much greater oxygen isotope variation than differentiated groups (Clayton and Mayeda, 1996). This is reflected in the 2σ errors of the mean $\Delta^{17}O$ values, which decrease in the following order: acapulcoites–lodranites > brachinites > winonaites (Fig. 6, Table 2). Clayton and Mayeda (1996) suggested that these relatively high levels of oxygen isotope variation reflect primary heterogeneity in the precursor materials, which in the case of the primitive achondrites was not completely homogenised by later parent body processes. In contrast, differentiated achondrite groups (HEDs, mesosiderites, SNCs, angrites, main-group pallasites and lunar rocks) define a series of mass-dependent fractionation lines on Fig. 6. The simplest interpretation of the oxygen isotope variation displayed by the differentiated achondrites is that their parent bodies underwent early extensive melting and isotopic homogenisation (Clayton and Mayeda, 1996; Greenwood et al., 2005). Subsequent processing would then be controlled by a simple mass-dependent fractionation law, i.e. $\delta^{17}O = 0.52\delta^{18}O$ (Clayton and Mayeda, 1996). Recent Hf–W chronometry suggests that the parent bodies of the primitive achondrites accreted slightly later than those of the differentiated achondrites and, therefore, had a lower content of the short-lived heat producing isotopes ^{26}Al and ^{60}Fe (Schulz et al., 2010). A

Table 2
Mean oxygen isotope composition of primitive achondrites, differentiated achondrites and ordinary chondrites.

	$\delta^{18}O\%$	2σ	$\Delta^{17}O\%$	2σ
Brachinites				
EATG residue (Inc. Brachina)	4.30	1.10	−0.25	0.18
EATG residue (ex. Brachina)	4.48	0.54	−0.23	0.14
Untreated samples	4.48	1.02	−0.22	0.16
Winonaites				
EATG residue	4.81	2.56	−0.51	0.08
Untreated samples	3.54	4.14	−0.42	0.16
Acapulcoite–lodranite clan				
EATG residue	3.41	1.02	−1.12	0.36
Untreated samples	3.22	2.68	−1.06	0.38
Differentiated achondrites[*]				
HEDs	3.56	0.52	−0.24	0.01
Mesosiderites	3.84	0.70	−0.25	0.02
Angrites	4.02	0.33	−0.07	0.01
Pallasites	2.91	0.32	−0.18	0.02
SNCs	4.68	0.67	0.3	0.03
Lunar rocks	5.64	0.24	−0.01	0.02
Ordinary chondrites[**]				
H equilibrated	4.08	0.44	0.73	0.18
L equilibrated	4.7	0.48	1.07	0.18
LL equilibrated	5.04	0.48	1.26	0.24

[*] Data for differentiated achondrites: Franchi et al. (1999), Greenwood et al. (2005,2006), and Hallis et al. (2010).
[**] Data for ordinary chondrites: Clayton et al. (1991).

brief summary of the various dating studies undertaken on the primitive achondrites is given in the Electronic annex.

In the following sections, we review the evidence, including our oxygen isotope data, for the composition and character of the likely source materials of the acapulcoite–lodranite clan, winonaites and brachinites.

4.2.1. Acapulcoite–lodranite clan
Refractory lithophile and siderophile element abundances in acapulcoites are similar to those in CI chondrites, suggesting that the precursor to the clan was a carbonaceous chondrite (Rubin, 2007). Based on their generally high metal content, Rubin (2007) suggested a possible match to the CR chondrites. However, due to the low sulphide content of CR chondrites compared to acapulcoites, Rubin (2007) concluded that a direct parent-daughter relationship was unlikely. Instead, he proposed a CR-like chondrite parent that was richer in sulphide and slightly more enriched in metal than normal CR samples.

CR chondrites are isotopically heterogeneous meteorites consisting of ^{16}O-rich anhydrous silicates and ^{16}O-poor phyllosilicates (Weisberg et al., 1995; Clayton and Mayeda, 1999). On a three-isotope diagram (Fig. 7), the combined CR data of Clayton and Mayeda (1999) and Schrader et al. (2011) define a trend with a slope of 0.67 ± 0.02 and an intercept of -2.20 ± 0.07 ($R^2 = 0.98$). This variation is generally interpreted as being the result of increasing degrees of parent body aqueous alteration, with less altered material lying closer to the slope 1 line of Young and

Russell (1998) and progressively more altered material plotting further away from it.

EATG-washed acapulcoite and lodranite samples define a more limited trend to the left of the CRs (Fig. 7), with a slope of 0.61 ± 0.08 and an intercept of -1.43 ± 0.27 ($R^2 = 0.78$). Taken at face value, the fact that the CR chondrites and acapulcoite–lodranite clan define distinct trends on Fig. 7 might be taken as evidence that the two groups do not share a common parent. However, the slope of the acapulcoite–lodranite line is strongly controlled by the analysis of NWA 2866, which is very highly weathered (Fig. 7) (Section 3.1). If this analysis is excluded, the best fit line for the remaining samples has a slope of 0.70 ± 0.10 and an intercept of -1.74 ± 0.34 ($R^2 = 0.74$). The extension of this line would intersect that for the CR chondrites to the left of Y&R slope 1 line (Fig. 7). A convergence of the two lines close to or on the slope 1 line is feasible, given the relatively large error on the modified acapulcoite–lodranite line (slope = 0.70). These relationships suggest that a common precursor for both the CR chondrites and acapulcoite–lodranite clan cannot be excluded on the basis of the oxygen isotope data.

McCoy et al. (1997) found that lodranites display a broad positive correlation between olivine Fa content and $\Delta^{17}O$, with more recent studies indicating that this trend is also shown by the acapulcoites (Rumble et al., 2005; Irving et al., 2007). In Fig. 8, $\Delta^{17}O$ values obtained in this study are plotted against the respective Fa content for individual acapulcoites and lodranites given by Rubin (2007). In keeping with the results of earlier studies, Fig. 8 shows that Fa content and $\Delta^{17}O$ values are positively correlated in both the acapulcoites and lodranites. Separate best fit lines through the acapulcoite and lodranite data both have R^2 values of 0.40, consistent with a fairly weak relationship between Fa content in olivine and whole-rock $\Delta^{17}O$ values. McCoy et al. (1997) suggest that this correlation is a characteristic inherited from the chondritic precursor and reflects nebular, rather than parent body processes. In support of this possibility, McCoy et al. (1997) point out that similar correlations are displayed by ureilites and ordinary chondrites.

The fact that both the acapulcoites and lodranites show similar trends suggests that the correlation between $\Delta^{17}O$ values and olivine Fa contents predates the onset of thermal metamorphism. An alternative explanation to the nebular model proposed by McCoy et al. (1997) is that the chondritic precursor material to the acapulcoites and lodranites may have experienced a stage of mild aqueous alteration, prior to the onset of metamorphism. In this scenario, precursor material that experienced a greater degree of interaction with high $\Delta^{17}O$ fluids would have had a higher $\Delta^{17}O$ value and a higher content of Fe-rich phyllosilicates than less aqueously altered material. Thermal metamorphism would result in dehydration of the Fe-rich phyllosilicate, leading to the formation of Fe-rich olivine, in a manner analogous to that proposed for some Allende dark inclusions (Kojima and Tomeoka, 1996). However, unlike Allende, discrete Fe-rich olivines are absent from either the acapulcoites or lodranites, possibly reflecting the higher grade of metamorphism and partial melting that they

experienced (McCoy et al., 1992, 1997). The 0.61 slope defined by the acapulcoite–lodranite clan is similar to that observed in carbonaceous chondrites groups that have experienced extensive aqueous alteration, such as the CMs and CRs (Clayton and Mayeda, 1999; Schrader et al., 2011). Since nebular processes alone tend to result in variation with a slope of close to 1 on an oxygen three-isotope diagram (Section 4.4), the shallower slope shown by the acapulcoite–lodranite clan on Fig. 7 is consistent with the possibility that they experienced an early phase of aqueous alteration, prior to the onset of thermal metamorphism. Experimental work has demonstrated that dehydration of phyllosilicates results in a significant shift to higher $\delta^{18}O$ and $\delta^{17}O$ values in the solid residue (Mayeda and Clayton, 1998). Thus, if the acapulcoite–lodranite clan did experience an aqueous alteration-dehydration cycle, their precursor material would have had a composition much closer to the slope 1 line than is indicated by present values.

4.2.2. Winonaites

On an oxygen three-isotope diagram (Fig. 9), winonaite analyses show much less scatter than the acapulcoite–lodranite clan and essentially define a mass fractionation line with a slope of 0.53 ± 0.01 and an intercept of -0.53 ± 0.04 ($R^2 = 1$). This indicates that the winonaite parent body experienced a greater level of homogenisation than that of the acapulcoites and lodranites. Oxygen isotope analyses of IAB and IIICD silicate inclusions are also plotted in Fig. 9 (Clayton and Mayeda, 1996). While these show slightly greater scatter with respect to $\delta^{17}O$ than our winonaite analyses, the two datasets display considerable overlap, consistent with the suggestion that both groups are genetically related (Bild, 1977; Clayton and Mayeda, 1996; Benedix et al., 1998).

Relict chondrules have been recognised in a number of winonaites, including NWA 1463, Pontlyfni and Mount Morris (Wisconsin) (Benedix et al., 1998, 2003). Rubin (2007) indicates that Dhofar 1222 contains ~4 vol.% relict chondrules. Although this meteorite is currently classified as an acapulcoite, its oxygen isotope composition indicates that it is a member of the winonaite group (Fig. 9). Likewise, NWA 725 and NWA 1052 contain relict chondrules and, although also classified as acapulcoites, have oxygen isotope compositions consistent with being winonaites (Fig. 9). The link between winonaites and precursor chondritic material is particularly strong in the case of NWA 1463, which texturally resembles a petrologic type 5 chondrite (Benedix et al., 2003). It therefore appears that members of the winonaite group span the transition from strongly metamorphosed chondrites to primitive achondrites.

Chondrule-bearing winonaites (NWA 725, NWA 1052, NWA 1463, Dhofar 1222, Mt. Morris (Wisconsin)) plot at lower $\delta^{18}O$ values than other members of the group, which typically display equigranular textures (Benedix et al., 1998). The chondrule-bearing winonaite fall, Pontlyfni ($\delta^{18}O = 6.18\permil$), is a clear exception to this trend, being isotopically heavier than most other members of the group. If the chondrule-bearing winonaites that plot at

low $\delta^{18}O$ values (Fig. 9) are indicative of the oxygen isotope composition of the chondritic precursor material, this might suggest that the bulk of winonaites and IAB silicate inclusions, which plot at higher $\delta^{18}O$ values, are either depleted in a mafic-rich component, or conversely enriched in feldspathic material. If this inference is correct, it would appear to confirm the suggestion that, prior to its break-up, the original winonaite–IAB parent body had already undergone at least the early stages of differentiation into a crust and mantle (Benedix et al., 1998). While recalculated modal data (Benedix et al., 1998) for winonaites (plag + mafics = 100%) does show some variation (plagioclase: 9–18 vol.%, mafics: 82–91 vol.%), there is no simple relationship with $\delta^{18}O$ values. This may reflect the difficulty of completely removing all traces of terrestrial weathering by leaching and/or uncertainties in the modal data, given that winonaites are relatively fine-grained heterogeneous samples (Benedix et al., 1998).

Winonaites and silicate inclusions in IAB irons display clear textural evidence for the mobility of Fe,Ni–FeS and basaltic partial melts (Benedix et al., 2005). This indicates that peak temperatures on the winonaite–IAB parent asteroid were in excess of both the Fe,Ni–FeS eutectic temperature ($\sim$950 °C) and basaltic partial melting temperature ($\sim$1050 °C), and may have been as high as 1450 °C (Benedix et al., 2005). Variable differences between the closure temperatures recorded by the two pyroxene and olivine-chromite geothermometers indicate that the winonaites and IAB irons experienced large fluctuations in cooling rate on a local scale. This evidence has been cited in support of a model involving catastrophic break-up and subsequent reassembly of a partially molten winonaite–IAB–IIICD parent body (Benedix et al., 2000, 2005). However, recent Hf–W data suggests that the low degrees of partial melting in the winonaites can be explained by the relatively late accretion of the winonaite–IAB–IIICD parent body (Schulz et al., 2010). The Hf–W data also indicates a later metamorphic event at $14.3^{+2.6}_{-2.2}$ Ma (Schulz et al., 2010). This suggests that partial melting and disruption of the winonaite parent body may have been distinct events. See Electronic annex for further discussion.

4.2.3. Brachinites and related olivine-rich primitive achondrites

The mineralogy and texture of the brachinites are in sharp contrast to either the acapulcoite–lodranite clan or the winonaites. Brachinites are olivine-dominated, oxidised assemblages that lack distinct evidence as to the nature of their precursor chondritic materials, such as the presence of relict chondrules. There is currently disagreement about whether the brachinites should be designated as a primitive achondrite group. Thus, while Nehru et al. (1996) and Goodrich (1998) consider brachinites to be chondrite partial melt residues, and hence *bona fide* primitive achondrites, it has also been suggested that they are magmatic cumulates (Warren and Kallemeyn, 1989; Mittlefehldt et al., 2003).

As discussed in Section 3.3, Brachina has an oxygen isotope composition that is distinct from the other brachinites (Fig. 4a and b). However, even if Brachina is excluded, the oxygen isotope variation displayed by brachinites is considerably greater than any group of differentiated achondrites (Table 2). Thus, the brachinites (excluding Brachina) have a $\Delta^{17}O$ value of -0.23 ± 0.14 (2σ), whereas in comparison the HEDs and angrites are more homogeneous, with $\Delta^{17}O$ values of -0.24 ± 0.01 (2σ) and -0.07 ± 0.01 (2σ) respectively (Table 2). Despite the fact that its oxygen isotope composition is somewhat removed from other members of the group (Fig. 4a and b), there appears to be little additional justification for excluding Brachina from the brachinites. The mineralogy and texture displayed by Brachina, with the possible exception of its relatively high plagioclase content ($\sim$10%), are essentially the same as other members of the group. In terms of both its major and trace elements, Brachina is close to being chondritic in composition, with other brachinites showing varying degrees of fractionation relative to Brachina (Mittlefehldt et al., 2003; Shearer et al., 2010; Goodrich et al., 2010; Day et al., 2011). Thus, Brachina is probably the most primitive brachinite sample available. On this basis, the oxygen isotope heterogeneity of the brachinite group as a whole is best represented by the larger of the two boxes shown in Figs 4a and b, with a $\Delta^{17}O$ value of -0.25 ± 0.18 (2σ) (Table 2). This level of heterogeneity is greater than that of the winonaites and supports the classification of brachinites as primitive achondrites.

In contrast to the reduced mineralogy displayed by the acapulcoite–lodranite clan and the winonaites, brachinites are characterised by high modal content of relatively fayalitic olivine (Mittlefehldt et al., 1998, 2003; Goodrich et al., 2010). This may indicate that, prior to the onset of partial melting, brachinite precursor material experienced a period of thermal metamorphism under relatively oxidising conditions, similar to that which produced the CK chondrites (Greenwood et al., 2010). This possibility is consistent with the results of experimental work (Gardner-Vandy and Lauretta, 2011), which demonstrates that it is possible to reproduce the silicate mineralogy of brachinites by partial melting under oxidising conditions ($fO_2 = IW \pm 1$) of a CK-like precursor. However, as there are no known chondrites with an oxygen isotope composition that matches the brachinites, the CK chondrites could not be parental to the group.

The recognition that the unique, paired, sodic plagioclase-rich achondrites GRA 06128 and GRA 06129 (= GRA 06128/9) may be related to the brachinites, provides important constraints on the origin of the group as a whole (Day et al., 2009, 2011; Shearer et al., 2010). The oxygen isotope composition of GRA 06128/9 (Zeigler et al., 2008; Day et al., 2009) is plotted in Fig. 4b and falls well within the inner brachinite field. Experimental and petrological studies indicate that melts with a composition similar to GRA 06128/9 are produced at temperatures between Fe,Ni sulphide melting (950–980 °C) and the onset of basaltic melting (>1050 °C) (Shearer et al., 2010). In this temperature interval, partial melting of between 13–30% of an oxidised chondritic source, followed by inefficient removal of the felsic melt, will leave a residue with a brachinite composition (Shearer et al., 2010; Day et al., 2011).

A number of ungrouped olivine-rich achondrites analysed in this study show affinities to the brachinites

(NWA 1500, Divnoe and NWA 4042). As discussed in Section 3.4, NWA 1500 was originally classified as a basaltic ureilite (Bartoschewitz et al., 2003), but has an oxygen isotope composition that plots in the main brachinite field (Fig. 4b). Recent studies of the mineralogy and geochemistry of NWA 1500 have concluded that it should be reclassified as a brachinite (Kita et al., 2009; Goodrich et al., 2010). Divnoe is an ungrouped olivine-rich primitive achondrite, with an oxygen isotope composition that plots within the main cluster of brachinites in Fig. 4b. The composition of olivine in Divnoe (Fa_{20-28}) overlaps the brachinite range (Fa_{27-36}) (Petaev et al., 1994; Goodrich et al., 2010). It has been suggested by Delaney et al. (2000) that Divnoe may be related to the brachinites by a process involving reduction of iron-rich olivine of the type:

$$Fe_2SiO_4 + CO \rightarrow FeSiO_3 + Fe + CO_2$$

However, Divnoe plots off the redox trend defined by other brachinites (Goodrich et al., 2010) and consequently, despite showing mineralogical similarities to the brachinites, is probably derived from a distinct parent body. The olivine-rich achondrite NWA 4042 shows textural similarities to the brachinites and has an oxygen isotope composition that plots only slightly outside the inner brachinite field in Fig. 4b. However, like Divnoe, the composition of olivine in NWA 4042 ($Fa_{20.3}$) (Connolly, 2006) is less Fe-rich than that of the brachinites. Further work is required before NWA 4042 can be reclassified as a brachinite (Rumble et al., 2008).

A number of additional oxygen isotope analyses by laser fluorination of olivine-rich achondrites taken from the literature are plotted in Fig. 4b. As pointed out by Rumble et al. (2008), Zag (b) (Delaney et al., 2000) has an oxygen isotope composition indistinguishable from the brachinites (Fig. 4b). Despite the relatively magnesian composition of olivine in Zag (b) (Fa_{22}), the meteorite displays textures which suggest a link to the brachinites via a redox process similar to that outlined for Divnoe (Delaney et al., 2000). Further evidence that such redox reactions may be an important factor in the genesis of olivine-rich achondrites is given by the olivine-rich ultramafic breccia NWA 4518 (Lorenz et al., 2007, 2011). The oxygen isotope composition of this meteorite plots somewhat outside the inner brachinite field on Fig. 4b. NWA 4518 contains two generations of olivine: the equigranular groundmass has a composition of Fa_{32}, whereas olivine inclusions in pyroxene megacrysts have a more Mg-rich composition of $Fa_{19.4}$ (Lorenz et al., 2007). The nature of the relationship between NWA 4518 and the brachinites is the subject of ongoing studies. Two recently classified meteorites NWA 4363 and NWA 5400 have a brachinite-like mineralogy and oxygen isotope compositions that appear to extend the main brachinite field towards and slightly across the terrestrial fractionation line (Fig. 4b) (Irving et al., 2009; Weisberg, 2009).

LEW 88763 is still currently classified as a brachinite; however, a variety of evidence, including its oxygen and noble gas isotopic compositions, suggests that it is not a member of this group (Clayton and Mayeda, 1996; Swindle et al., 1998). LEW 88763 plots in the acapulcoite–lodranite field (Fig. 5), but has a mineralogy and geochemistry indicating that it is a unique, ungrouped achondrite (Swindle et al., 1998). LEW 88763 may be related to the metal-rich achondrite Tafassasset (Nehru et al., 2003, 2010; Gardner-Vandy et al., 2012).

4.3. How many parent bodies – The missing mantle problem

Recent estimates suggest that iron meteorites are samples of approximately 65 separate asteroidal cores (Haack and McCoy, 2005). The lack of meteorites and asteroids that might represent the mantle material of these disrupted differentiated bodies remains an outstanding issue (Burbine et al., 1996; Mittlefehldt et al., 1998; Scott et al., 2010). The most widely accepted explanation for this discrepancy is that, following their catastrophic disruption early in solar system history, core material has preferentially survived due to the intrinsic strength of iron meteorites, whereas silicate-rich mantle material has been lost by an extended process of fragmentation and collisional grinding (Burbine et al., 1996; Mittlefehldt et al., 1998; Scott et al., 2010).

The primitive achondrites may provide a new perspective on this question. As previously discussed, these lithologies formed at temperatures above initial Fe,Ni metal-sulphide melting (950–980 °C), but below that at which large scale basaltic melting took place. This suggests that most, if not all, primitive achondrite parent bodies had the potential to form metallic cores. Rapid breakup and reassembly of the winonaite–IAB–IIICD parent body during incipient core formation is further evidence of this fact (Benedix et al., 2000). Thus, the primitive achondrites could represent mantle material derived from asteroids with metal cores. Assessing the number of parent bodies represented by primitive achondrites may therefore throw some light on the missing mantle problem, even though there may not be a simple match (i.e. same parent body) between the irons in our meteorite collections and currently classified achondrite groups.

The smallest number of parent bodies that could have supplied the meteorites examined in this study is four. This assumes that all the brachinites and brachinite-like meteorites (excluding LEW 88763, but including GRA 06128/9) are samples from a single differentiated, heterogeneous asteroid (Rumble et al., 2008; Day et al., 2011). This minimum set of parent bodies would be: (1) heterogeneous brachinite body (including Brachina and other brachinites: Divnoe, GRA 06128/9, NWA 1500, NWA 4042, NWA 5363, NWA 5400, Zag (b)); (2) winonaite–IAB–IIICD body (including Dho 732); (3) acapulcoite–lodranite parent body; (4) LEW 88763 parent body. If the ureilites are included as coming from one heterogeneous parent body (Rumble et al., 2010), and pallasites as samples of three parent bodies (Clayton and Mayeda, 1996), this would bring the total number of bodies from which we have asteroidal mantle-like material to only eight.

However, as discussed in Section 4.2.3, many of the brachinite-like achondrites, such as Divnoe and Zag (b), may not be from the same parent body as the brachinites *sensu stricto*. In fact, a case can be made for Brachina and NWA 595 having a separate origin to the other brachinites (Mittlefehldt et al., 2003; Irving et al., 2005). Taking

an extreme position, in which each ungrouped olivine-rich achondrite is from a unique source, the number of possible parent bodies would be approximately 18 (including ureilites and pallasites). If the differentiated achondrites are also included (aubrites, HEDs, angrites, mesosiderites), the number of asteroidal sources would increase to just over twenty, roughly a third of that required for the iron meteorites (Haack and McCoy, 2005). This discrepancy is probably related to the greater survivability in space of irons compared to achondrites (Mittlefehldt et al., 1998). Iron meteorites have long, multi-stage, cosmic-ray exposure histories, sometimes in excess of one billion years, while achondrites generally have cosmic-ray exposure ages of less than 100 my (Eugster et al., 2006). Thus, early fragmentation of differentiated asteroids, followed by preferential destruction of their silicate-rich mantles, remains the most likely cause of the mismatch between the number of asteroidal sources indicated by irons compared to the achondrites (Burbine et al., 1996; Mittlefehldt et al., 1998; Scott et al., 2010).

4.4. Primitive achondrites – Evidence in favour of a primordial slope 1 line

The precise nature of the process that produced the non-mass dependent oxygen isotope variation seen in primitive meteorites and their constituents remains controversial. While self-shielding of CO, either in the early solar nebula (Clayton 2002; Lyons and Young, 2005) or precursor molecular cloud (Yurimoto and Kuramoto, 2004), is the currently favoured mechanism, alternative models have been proposed (Dominguez, 2010). The oxygen isotope composition of primitive achondrites provides additional constraints on the nature of the process involved, in particular whether a single slope 1 line can be used to define the primordial oxygen isotope variation in the early solar nebula.

An important aspect of this problem relates to the interpretation of various reference lines on oxygen three-isotope diagrams (Figs. 7 and 9). The Carbonaceous Chondrite Anhydrous Mineral (CCAM) line, derived from analyses of Allende (CV3) refractory inclusions, is the most widely used reference and has a slope of 0.94 (Clayton et al., 1977; Clayton and Mayeda, 1999). However, the fundamental significance of the CCAM line has been questioned by Young and Russell (1998). Based on the results of a UV laser ablation study of an Allende CAI, the authors suggested that a line of exactly slope 1 was of more fundamental significance. They pointed out that almost all solar system materials (with the exception of the R chondrites) plot either on or to the right of the slope 1 line. They went onto suggest that this variation could be explained if the primitive oxygen isotope composition of the solar system was represented by the slope 1 line, with subsequent mass fractionation or isotopic exchange shifting compositions away from this line to the right. Young (2010) suggested that igneous CAIs should display approximately 10‰ mass dependent variation with respect to $\delta^{18}O$, as a result of evaporation processes that took place when the inclusions were molten. If a reference line of exactly slope 1 is used, low-^{16}O minerals in such inclusions show a deviation of

~8 ‰, consistent with these predictions. In contrast, using the CCAM line as a reference removes the evidence for evaporation in molten CAIs. The fact that a highly $^{17,18}O$-enriched phase ($\delta^{18}O$ and $\delta^{17}O = \sim+180‰$) within the matrix of the primitive chondrite Acfer 094 plots on the extension of the slope 1 line may lend further support to the primordial significance of this reference line (Sakamoto et al., 2007).

The slope 1 (Y&R line) and CCAM lines are shown in Fig. 7, along with oxygen isotope analyses for the winonaites, acapulcoites and lodranites (this study), and CR chondrites (Clayton and Mayeda, 1999; Schrader et al., 2011). It is important to note that the Y&R and CCAM lines converge at a value of approximately $\delta^{18}O$ and $\delta^{17}O = -50‰$, a point more or less coincident with the values measured on ^{16}O-rich phases in pristine CAIs (Krot et al., 2010). It has been suggested that the ^{16}O-rich composition measured in such CAIs may be close to that of the primordial solar system (Clayton, 2002). This proposal is broadly consistent with recent measurements of captured solar wind from Genesis concentrator samples, which indicate that the Sun has a composition of $\delta^{18}O = -58.5‰$ and $\delta^{17}O = -59.1‰$ (McKeegan et al., 2011).

Both the acapulcoite–lodranite clan and the winonaites form distinct arrays that plot between the slope 1 line and the CCAM on Fig. 7. As noted in Section 4.2.2. (Fig. 9), chondrule-bearing winonaites, which may have a composition similar to that of the group's precursor material, plot closer to the slope 1 line than other more evolved winonaite samples. The CR chondrites display a similar relationship, with the least aqueously altered samples plotting close to the slope 1 line and the progressively more altered ones further away from it (Schrader et al., 2011). In particular, the Antarctic CR chondrite QUE 99177 (Fig. 7) contains abundant amorphous material and appears to have suffered relatively low levels of aqueous alteration (Abreu and Brearley, 2006). Recent oxygen isotope analysis of QUE 99177 appears to confirm its status as the least aqueously altered CR chondrite (Schrader et al., 2011). The fact that QUE 99177 shows some evidence of aqueous alteration (Abreu and Brearley, 2006) suggests that completely pristine CR precursor material would plot further along the CR line, towards even more ^{16}O-rich compositions. One possibility is that the composition of pristine CR precursor material is given by the point at which the CR mixing line intersects the slope 1 line.

As discussed in Section 4.2.1, the acapulcoites and lodranites may have experienced aqueous alteration. One possible interpretation of the data is that the precursor material to the acapulcoite–lodranite clan originally had a composition closer to the slope 1 line and this was then shifted to the right during the aqueous alteration and subsequent dehydration (Section 4.2.1). Alternatively, the present bulk composition of the acapulcoite–lodranite clan, which lies between the slope 1 and CCAM lines, suggests that primordial oxygen isotope variation may have fluctuated somewhat between the two reference lines. However, the fact that the precursor material to the winonaites and CR chondrites lies close to the slope 1 line provides strong evidence of its underlying significance with respect to the primordial oxygen isotope variation in the early solar system.

Recent CO photodissociation experiments (Chakraborty et al., 2008) and modelling studies (Lyons, 2011) yield slope values that diverge significantly from 1. Chakraborty et al. (2008) reported slope values that ranged from ~0.6 to 1.8 depending on the wavelength of radiation used. An alternative model to CO self-shielding proposed by Dominguez (2010) is that the $^{17,18}O$-enrichment took place by low temperature heterogeneous chemical processes, which form water ice around grains in the parent molecular cloud. Dominguez (2010) discounts the importance of CO self-shielding, but instead invokes a process analogous to the slope 1 ozone formation experiments of Thiemens and Heidenreich (1983). The mechanism proposed by Dominguez (2010) has yet to be experimentally verified.

Whatever model is used to explain the primordial oxygen isotope variation in the nebula, the evidence from primitive achondrites and CR chondrites supports the view that the initial conditions were essentially those described by a line of slope 1 on an oxygen three-isotope diagram (Young and Russell, 1998).

5. CONCLUSIONS

We have undertaken a detailed oxygen isotope study of the acapulcoites, lodranites, winonaites, brachinites and various related achondrites with the aims of understanding the earliest stages of asteroidal differentiation and the nature of their precursor materials. One major issue in undertaking this work has been the extensively weathered nature of the majority of samples comprising these groups. This has been mitigated by leaching samples in ethanolamine thioglycollate (EATG) solution. Due to their high metal and sulphide content, acapulcoite, lodranite and winonaite samples show much greater isotopic shifts during weathering than brachinites. In keeping with the results of previous studies, Antarctic finds are systematically shifted to lighter oxygen isotope compositions during terrestrial weathering, and non-Antarctic finds to heavier values. Contrary to the findings of previous studies, our results indicate that even low levels of terrestrial weathering produce detectable shifts in primary oxygen isotope compositions.

Even when the influence of weathering has largely been removed, primitive achondrites display much greater levels of oxygen isotope heterogeneity than those found in differentiated achondrite groups. This variation is reflected in the 2σ error on group mean $\Delta^{17}O$ values, which decrease in the following order: acapulcoite–lodranite clan > brachinites > winonaites. These levels of heterogeneity were most probably inherited from each group's precursor material. On an oxygen three-isotope diagram, the acapulcoite–lodranite clan define a limited trend with a slope of 0.61 ± 0.08 and an intercept of -1.43 ± 0.27 ($R^2 = 0.78$). A broad positive correlation between $\Delta^{17}O$ and olivine fayalite contents displayed by both acapulcoite and lodranite samples may be the result of early aqueous alteration and subsequent dehydration during thermal metamorphism.

Winonaites define a distinct mass fractionation line, with a slope of 0.53 ± 0.01 and an intercept of -0.53 ± 0.04 ($R^2 = 1$) on an oxygen three-isotope diagram. A number of samples currently classified as acapulcoites (NWA 725,

NWA 1052 and Dho 1222) have oxygen isotope compositions indicating that they are winonaites. Brachinites are a diverse group of olivine-rich achondrites that formed from an oxidised chondritic precursor. The relatively high level of oxygen isotope heterogeneity displayed by the brachinites supports their designation as primitive achondrites. A number of ungrouped olivine-rich achondrites (Divnoe, NWA 4042, NWA 4363, NWA 4518, NWA 5400, Zag (b)) as well as the unique plagioclase-rich achondrites GRA 06128 and GRA 06129 have similar oxygen isotope compositions to the brachinites. Brachinites and related achondrites could be derived either from a single heterogeneous parent body, or represent samples from multiple parent bodies. The primitive achondrites and related samples, together with the ureilites and pallasites, represent material from at most only 18 parent bodies, compared to an estimated 65 for the iron meteorites.

On an oxygen three-isotope diagram, primitive chondrule-bearing winonaites (Dho 1222, NWA 725, NWA 1052, NWA 1463, Mt. Morris (Wisconsin)) plot close to the slope 1 (Y&R) line, with more evolved samples extending away from it towards the CCAM line. A similar relationship is shown by the CR chondrites. The acapulcoite–lodranite clan plots between the slope 1 (Y&R) and CCAM lines. However, the precursor material to the clan may have had a composition closer to the slope 1 (Y&R) line prior to parent body alteration, if the processes involved included early aqueous alteration and subsequent dehydration. Taken in conjunction, the evidence from the primitive achondrites and CR chondrites, provides strong support for the proposal that primordial oxygen isotope variation in the early solar system is best represented by a line of exactly slope 1 on an oxygen three-isotope diagram.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2012.06.025.

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