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Alteration and metamorphism of CO3 chondrites: Evidence from oxygen and carbon isotopes

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Abstract–Carbonaceous chondrites of the Ornans-type (CO3) form a well-documented metamorphic series. To investigate the conditions under which metamorphism took place, whole rock oxygen and carbon isotope analysis has been carried out on 10 CO3 chondrites (ALH A77307 [3.0], Colony [3.0], Kainsaz* [3.1], Felix* [3.2], Ornans* [3.3], ALH 82101 [3.3], Lancé* [3.4], ALH A77003 [3.5], Warrenton* [3.6], and Isna [3.7] [*denotes a fall]). Whole rock oxygen isotope analysis was carried out by laser-assisted fluorination, whole rock carbon isotope analysis by continuous flow mass spectrometry.

The results of this study indicate that the oxygen and carbon isotopes in CO3 finds have been significantly disturbed by terrestrial weathering processes. Conclusions based on the isotopic composition of such weathered finds may be significantly flawed. In particular, the Antarctic meteorite ALH A77307 (3.0), suggested as being close in composition to CO-CM chondrite precursor material, has experienced significant terrestrial contamination. Oxygen isotope data for CO3 falls indicates that there is a subtle increase in $\Delta^{17}O$ values with increasing metamorphic grade for sub-types 3.1 to 3.4. This increase does not persist to higher sub-types, i.e., Warrenton (3.6). These relationships are explicable in terms of the progressive formation of phyllosilicates, coupled with loss of primary phases such as melilite, and suggest that an aqueous fluid phase was present during metamorphism. Carbon abundance and $\delta^{13}C$ values of CO3 falls decrease with increasing metamorphic grade. These trends reflect progressive changes in the nature of the organic macromolecular component during metamorphic heating and lend additional support to the evidence that CO3 chondrites are part of a metamorphic series.

The most likely setting for metamorphism was on the CO3 parent body. The "Ornans paradox," whereby Ornans (3.3) should belong to a higher sub-type based on chemical compared to petrographic evidence, may result from local-scale redox differences on the CO3 parent body. A wide variety of classification schemes have been proposed for CO3 chondrites. In view of its simplicity and applicability, the scheme of Scott and Jones (1990) is regarded as the most useful in assigning sub-types to new CO3 samples.

INTRODUCTION

Carbonaceous chondrites are among the oldest and most primitive materials available for study and provide critical information about the processes that operated in the early solar system. They are conventionally divided into six groups (CI, CO, CV, CM, CR, CK) on the basis of their composition, mineralogy, and oxygen isotope systematics. Two further proposed groupings (CB, CH) have yet to receive unanimous acceptance. Ornans-type chondrites (CO) arguably form the most coherent of these groups, having a particularly well-defined texture comprising of small chondrules (0.2–0.5 mm in diameter), clasts, and inclusions enclosed within a dark, fine-grained matrix (McSween 1977). Since all members of the group are of petrographic type 3, they are generally referred to as CO3 chondrites.

On the basis of increasing textural recrystallization and decreasing compositional heterogeneity, McSween (1977) was the first to suggest that CO3 chondrites form a metamorphic series analogous to that seen in ordinary chondrites. This conclusion has been substantially corroborated by subsequent studies that demonstrate that a wide range of features in CO3 chondrites show progressive changes with increasing metamorphic grade (Table 1).

Table 1. Features indicating that CO3 chondrites form a metamorphic series.

	With increasing grade:[a]
1	Silicate compositions homogenize (1, 2)
2	Textural recrystallization increases (1)
3	Thermoluminescence sensitivity increases (120 °C TL Peak) (3)
4	Ni and Co in kamacite increase, Cr decreases (1, 2)
5	Trapped rare gases decrease (1)
6	Presolar grain contents decrease (6)
7	Fe and Mn in amoeboid olivine inclusions increase (1, 9)
8	Amoeboid olivine inclusions show systematic textural changes (4, 9)
9	Refractory inclusions become progressively altered (5, 8)
10	Apparent mean chondrule diameter increases (4)
11	Bulk carbon contents decrease (1)
12	O isotopes become progressively ^{16}O-poor (7)

[a] 1) McSween 1977; 2) Scott and Jones 1990; 3) Keck and Sears 1987; 4) Rubin 1998; 5) Russell et al. 1998; 6) Newton 1994; 7) Clayton and Mayeda 1999; 8) Wasson et al. 2001; 9) Chizmadia et al. 2002.

McSween (1977) proposed a three-fold division of the group, from I–III, representing increasing degrees of metamorphic alteration. Subsequently, a number of different schemes to divide up the CO3 chondrites have been proposed (Table 2). Throughout this paper, we use the sub-types proposed by Scott and Jones (1990). The relative merits and applicability of these metamorphic schemes are dealt with in the Discussion section.

Phyllosilicates have been reported in various CO3 chondrites (Kerridge 1964; Christophe Michel-Levy 1969; Kurat 1973, 1975; Keller and Buseck 1990; Brearley 1993; Itoh and Tomeoka 2001), and this has led to the suggestion that hydrothermal fluids were involved in the alteration of the CO3 chondrites (Rubin 1998; Chizmadia et al. 2002). It has been reported that a general correlation exists between the oxygen isotopic composition of CO3 chondrites and metamorphic grade, such that the least metamorphosed members of the group have the most ^{16}O-rich oxygen isotope values (Rubin 1998; Clayton and Mayeda 1999). If valid, this correlation would appear to confirm the important role played by hyrdrothermal fluids during alteration. To improve our understanding of the conditions that prevailed during the metamorphism of this important meteorite group, we have undertaken a detailed investigation of the whole rock oxygen and carbon systematics of CO3 chondrites.

EXPERIMENTAL TECHNIQUES

Oxygen isotope analysis was carried out using an infrared laser fluorination system (Miller et al. 1999). Violent ejection of powders from sample wells can occur when dealing with volatile-rich material such as carbonaceous chondrites. To avoid this problem, all analyses were obtained on whole rock samples (0.5–2 mg) that were heated progressively in the presence of BrF_5 for periods lasting up to 1 hr. 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 analyzed using a Micromass Prism III dual inlet mass spectrometer. Analytical precision (1σ) based on replicate analyses of international (NBS-28 quartz, UWG-2 garnet) and internal standards is approximately ±0.04‰ for δ^{17}O, ±0.08‰ for δ^{18}O, and ±0.024‰ for Δ^{17}O (Miller et al. 1999). Carbonaceous chondrites are a heterogeneous mixture of high and low temperature components; consequently, the precision is less than that obtained on international standards. The precision (1σ) quoted for individual meteorite samples analyzed in this study is based on replicate analysis. For ease of comparison with previous oxygen isotope studies of CO3 chondrites (Clayton and Mayeda 1999), Δ^{17}O has been calculated as: $\Delta^{17}O = \delta 17O - 0.52\ \delta^{18}O$ rather than the alternative formulation proposed by Miller (2002).

Carbon isotopes were determined on homogenized whole rock samples from which aliquots of 10–30 mg were taken and loaded into tin buckets. The samples were combusted in an ANCA elemental analyzer (PDZ Europa), and the liberated gas was purified and then analyzed by continuous flow mass spectrometry using a Geo 20-20 mass spectrometer. The analytical precision (1σ) is typically ±0.1‰ for δ^{13}C.

RESULTS

Oxygen Isotopes

The results of oxygen isotope analyses for all the samples studied are given in Table 3 and plotted on Figs. 1, 2, 3a, and 3b. With the exception of Colony (3.0) and ALH A77307 (3.0), the samples fall within an extremely restricted area of the oxygen three isotope diagram, being even more limited in range than reported by previous studies (Clayton and Mayeda 1999). In particular, our analyses do not seem to corroborate the ^{18}O-enriched values for Lancé (3.4) and Warrenton (3.6) found by Clayton and Mayeda (1999). One explanation for these apparent discrepancies is the issue of sample heterogeneity. Whole rock samples represent a mixture of CAIs, ferromagnesium silicates, and matrix components, all with potentially very large isotopic variations. Therefore, it is possible that these differences are due to real variations between the various sub-samples used in the two studies. To examine this possibility, sub-samples of both Warrenton and Lancé obtained from different sources were analyzed (Table 3). Sub-samples of Lancé demonstrate small but significant levels of sample heterogeneity (up to approximately 0.5‰ for both δ^{17}O and δ^{18}O). Sample heterogeneity is also present in the case of Warrenton, although to a lesser extent than seen in Lancé. However, the level of heterogeneity observed in Lancé and Warrenton is still insufficient to explain the difference between our measurements and those of Clayton and Mayeda (1999).

Table 2. Metamorphic classification schemes for CO3 chondrites.

	Chizmadia et al. (2002)	Scott and Jones (1990)	Sears et al. (1991)	McSween (1977)
ALH A77307	3.0	3.0	3.1	–
Colony	3.0	3.0	3.0	–
Kainsaz[a]	3.2	3.1	3.2	I
Felix[a]	3.3	3.2	3.4	II
Ornans[a]	3.4	3.3	3.4	II
ALH 82101	–	3.3	3.4	–
Lancé	3.5	3.4	3.4	II
ALH A77003	3.6	3.5	3.4	–
Warrenton[a]	3.7	3.6	3.6	III
Isna	3.8	3.7	3.7	III

[a] Denotes a fall.

Table 3. Oxygen isotope composition of CO3 chondrites.[a]

Sample	Grade	n	δ^{17}O‰	±1σ	δ^{18}O‰	±1σ	Δ^{17}O‰	±1σ
ALH A77307	3.0	2	–6.51	0.06	–4.61	0.14	–4.12	0.02
Colony	3.0	2	–3.62	0.34	–1.64	0.22	–2.76	0.23
Kainsaz[b]	3.1	3	–5.89	0.28	–2.26	0.15	–4.71	0.21
Felix[b]	3.2	2	–6.09	0.01	–2.75	0.04	–4.67	0.01
Ornans[b]	3.3	3	–5.65	0.27	–2.31	0.23	–4.45	0.16
ALH 82101	3.3	1	–5.98	–	–2.97	–	–4.43	–
Lancé[b]	3.4	6	–5.63	0.25	–2.44	0.31	–4.36	0.12
ALH A77003	3.5	2	–6.17	0.25	–3.13	0.20	–4.54	0.14
Warrenton[b]	3.6	6	–5.97	0.45	–2.84	0.59	–4.49	0.20
Isna	3.7	2	–5.23	0.10	–2.16	0.11	–4.11	0.04
Sub-samples								
Lancé (11/7/85)		3	–5.83	0.07	–2.66	0.26	–4.45	0.08
Lancé (NHM900)		2	–5.35	0.12	–2.16	0.04	–4.23	0.10
Lancé (Wiik)		1	–5.56	–	–2.32	–	–4.36	–
Warrenton (Yale)		2	–5.98	0.06	–2.72	0.03	–4.56	0.05
Warrenton (Wiik)		2	–6.08	0.22	–2.92	0.01	–4.56	0.23
Warrenton (BM53290)		2	–5.84	0.95	–2.87	1.31	–4.35	0.27

[a] The precision quoted for individual measurements is ±1σ on the mean of replicate analyses.

[b] Denotes a fall.

The limited range of oxygen isotope compositions displayed by CO3 chondrites is even more pronounced if data from falls alone are considered (Fig. 1, squares). These plot in an extremely restricted area, with finds (circles) plotting on either side. CO3 finds show a distinct bimodal distribution (Fig 1) with Antarctic samples ALH A77307 (3.0), ALH 82101 (3.3), and ALH A77003 (3.5) being isotopically light compared to falls, while Isna (3.7) and Colony (3.0), both collected in temperate latitudes, are isotopically heavier. This relationship is even more clearly demonstrated when the data are plotted in terms of Δ^{17}O against δ^{18}O (Fig. 2) ($\Delta^{17}O = \delta^{17}O - 0.52\ \delta^{18}O$). In view of the well-established "latitude effect" (Faure 1986), whereby precipitation has an increasingly negative δ^{18}O value at progressively higher latitudes, one explanation for this relationship is that it reflects the influence of terrestrial weathering processes. This topic is examined in more detail in the Discussion section.

Fig. 3a shows a plot of Δ^{17}O against metamorphic subtype for all the CO3 chondrites analyzed in this study. The data of Clayton and Mayeda (1999) are shown for comparison. The plot shows no clear evidence in support of the reported increase in Δ^{17}O whole rock values with increasing metamorphic grade (Rubin 1998; Clayton and Mayeda 1999). As discussed, there is strong evidence that CO3 finds have undergone isotopic exchange during terrestrial weathering. This is particularly noticeable in the case of Colony (3.0), which has a much heavier Δ^{17}O value than the other CO3 samples (Fig. 3a). To eliminate the influence of terrestrial contamination only, data for CO3 falls have been plotted on Fig. 3b. On this plot, the data of Clayton and Mayeda (1999) appear to show a clearly defined trend of progressively increasing Δ^{17}O values with increasing metamorphic grade. However, it should be noted that the value for Lancé given by Clayton and Mayeda (1984) is different from that quoted by Clayton and Mayeda (1999). If the earlier value is used, the trend becomes less obvious.

The data collected during this study do not support the simple relationship between Δ^{17}O and metamorphic grade

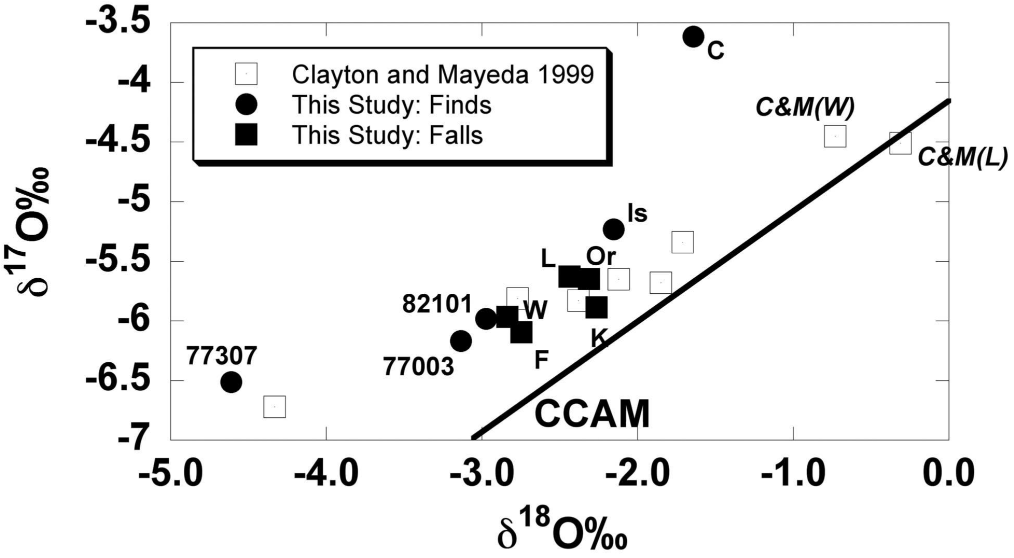

Fig. 1. Oxygen isotopic compositions of CO3 chondrite whole rock samples. The carbonaceous chondrite anhydrous mineral line (CCAM) of Clayton and Mayeda (1999) is shown for reference. Symbols: C = Colony (3.0); 77307 = ALH A77307 (3.0); K = Kainsaz (3.1); F = Felix (3.2); Or = Ornans (3.3); 82101 = ALH 82101 (3.3), L = Lancé (3.4); 77003 = ALH A77003 (3.5); W = Warrenton (3.6); Is = Isna (3.7); C&M(W) = Warrenton (Clayton and Mayeda 1999); C&M(L) = Lancé (Clayton and Mayeda 1999).

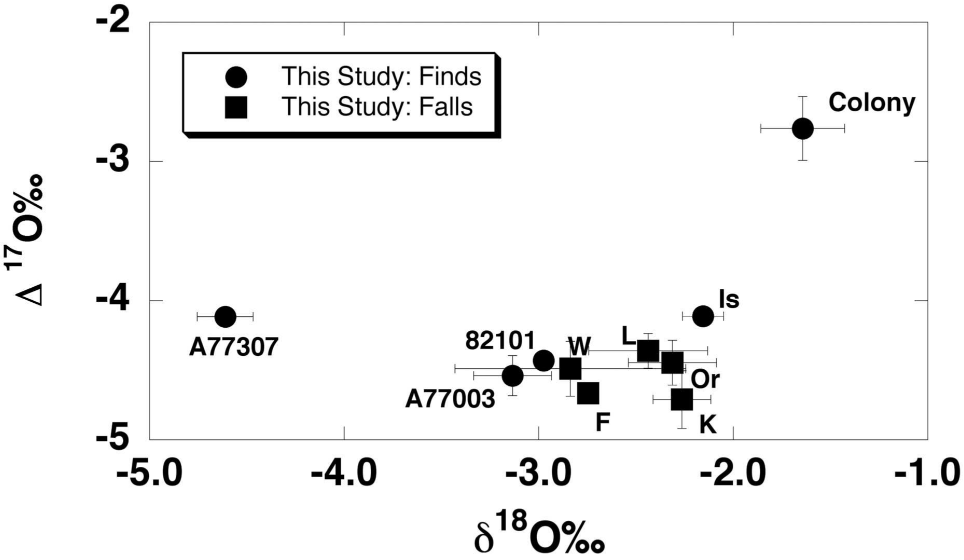

Fig. 2. Plot of $\Delta^{17}O$ versus $\delta^{18}O$ for CO3 chondrite finds and falls. The symbols are as in Fig. 1. The error bars are ±1σ on the mean of replicate analysis.

that is implied by the results of Clayton and Mayeda (1999). In particular, our analysis of Warrenton (3.6) differs significantly from that obtained in this previous study. In view of this discrepancy, we have analyzed three distinct sub-samples of Warrenton (Table 3), all of which have significantly more negative $\Delta^{17}O$ values than that reported by Clayton and Mayeda (1999). For sub-types 3.1 to 3.4, there is good agreement between our data and that of Clayton and Mayeda (1999), with both data sets showing a slight increase in $\Delta^{17}O$ with increasing metamorphic grade (Fig. 3b). However, this increase is fairly subtle so that Kainsaz (3.1) has a $\Delta^{17}O$ value of −4.71‰ and Lancé (3.4) has a value of −4.36‰, giving an overall difference of 0.35‰, only marginally greater than the 1σ error on the $\Delta^{17}O$ value for Kainsaz (±0.21). The significance of these relationships is examined in the Discussion section.

Carbon Isotopes

The results of carbon abundance (wt%) and carbon isotope measurements are given in Table 4a and plotted on Figs. 4a, 4b, 5a, and 5b. As first noted by McSween (1977),

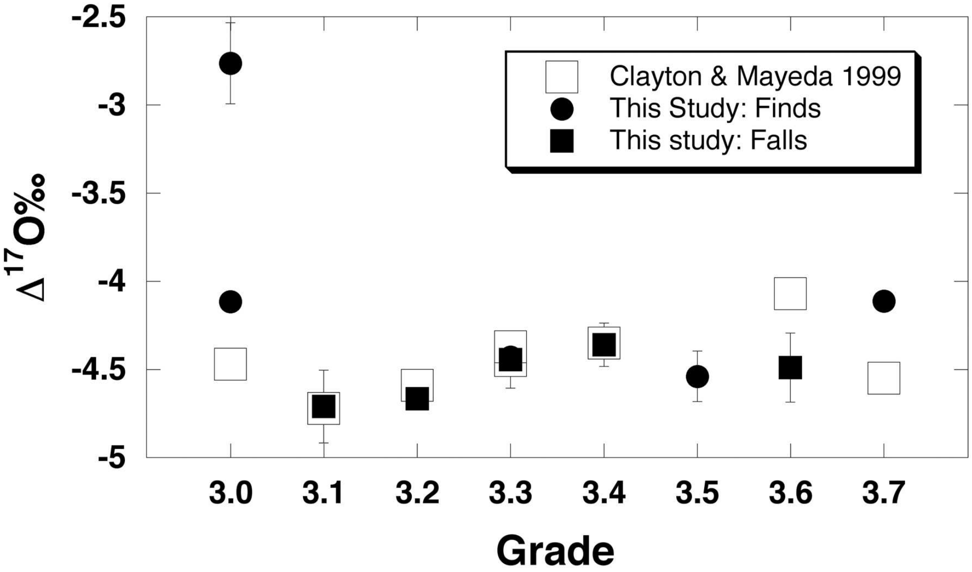

Fig. 3a. Plot of $\Delta^{17}O$ versus metamorphic grade (sub-types of Scott and Jones [1990]) for CO3 chondrite finds and falls. The error bars are ±1σ on the mean of replicate analysis.

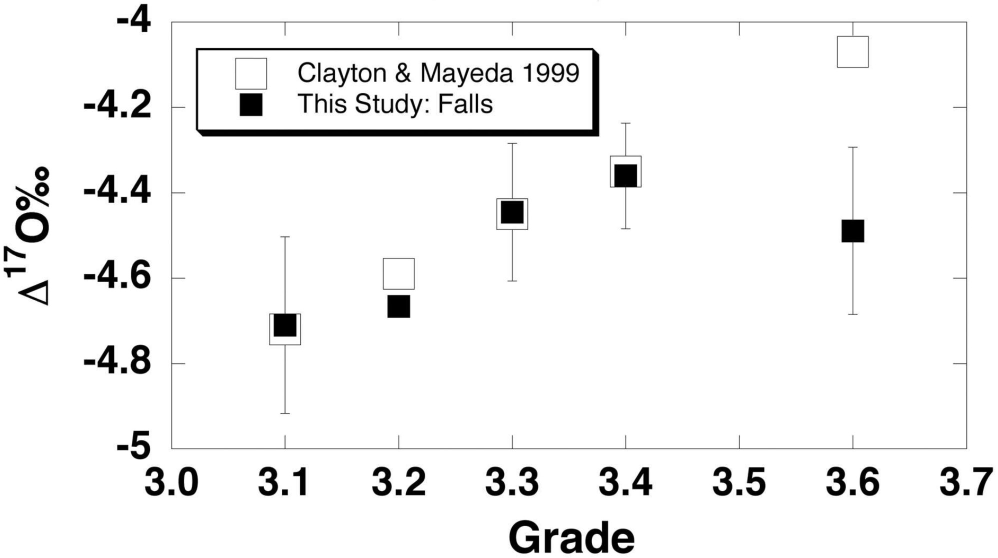

Fig. 3b. Plot of $\Delta^{17}O$ versus metamorphic grade (sub-types of Scott and Jones [1990]) for CO3 chondrite falls only. The error bars are ±1σ on the mean of replicate analysis.

carbon abundance decreases systematically with increasing metamorphic grade (Fig 4a), such that Colony (3.0) and ALH A77307 (3.0) have C contents of 0.98 and 0.78 wt% respectively, while Isna (3.7) has only 0.28 wt%. However, it is now well-established that both total carbon abundance and carbon isotope systematics are disturbed by both Antarctic and non-Antarctic weathering processes (Grady et al. 1991; Ash and Pillinger 1995). If falls alone are considered (Fig. 4b), the trend of decreasing carbon abundance with increasing metamorphic grade is far less obvious. In particular, Ornans (3.3) has a much lower carbon content than might be predicted from its sub-type. This is perhaps an example of what McSween (1977) termed the "Ornans paradox," meaning that Ornans should belong to a higher metamorphic sub-type on the basis of its chemical properties than it does on the basis of petrographic criteria alone.

When carbon isotopic compositions are plotted against metamorphic sub-type (Fig 5a), for all samples, there is a slight suggestion that $\delta^{13}C$ values become increasingly negative with increasing metamorphic grade. However, again there is a significant difference between finds and falls, with three finds, namely, ALH A77307 (3.0), Colony (3.0), and ALH A77003 (3.5), having significantly heavier $\delta^{13}C$ values than the other samples. If finds are excluded (Fig. 5b), the

Table 4a. Carbon abundance and carbon isotope composition of CO3 chondrites.

Sample	Grade	n	C (wt%)	±1σ	δ^{13}C‰	±1σ
ALH A77307	3.0	2	0.78	0.04	–4.9	0.0
Colony	3.0	2	0.98	0.08	–11.7	0.3
Kainsaz[a]	3.1	3	0.69	0.07	–17.8	0.6
Felix[a]	3.2	2	0.51	0.15	–18.6	0.9
Ornans[a]	3.3	2	0.18	0.04	–21.9	2.2
ALH 82101	3.3	1	0.19	–	–19.3	–
Lance[a]	3.4	2	0.62	0.11	–20.7	0.3
ALH A77003	3.5	2	0.28	0.01	–11.0	1.3
Warrenton[a]	3.6	2	0.38	0.06	–23.2	1.9
Isna	3.7	1	0.28	–	–18.4	–

[a]Denotes a fall.

Table 4b. Comparison of carbon abundance and isotope analyses of CO3 chondrites obtained in this and previous studies.

Sample	Grade	C (wt%) This study	C (wt%) Kerridge (1985)	C (wt%) Newton (1984)	C (wt%) Mean	δ^{13}C‰ This study	δ^{13}C‰ Kerridge (1985)	δ^{13}C‰ Newton (1984)	δ^{13}C‰ Mean
ALH A77307	3.0	0.78	–	0.78	0.78	–4.9	–	–9.0	–7.0
Colony	3.0	0.98	–	0.41	0.70	–11.7	–	–8.2	–10.0
Kainsaz[a]	3.1	0.69	0.39	0.60	0.56	–17.8	–18.5	–16.4	–17.6
Felix[a]	3.2	0.51	0.64	0.42	0.52	–18.6	–14.2	–15.4	–16.1
Ornans[a]	3.3	0.18	0.12	0.13	0.14	–21.9	–16.0	–12.9	–16.9
ALH 82101	3.3	0.19	–	0.05	0.12	–19.3	–	–15.2	–17.3
Lance[a]	3.4	0.62	0.46	0.52	0.53	–20.7	–17.0	–19.0	–18.9
ALH A77003	3.5	0.28	–	0.18	0.23	–11.0	–	–7.5	–9.2
Warrenton[a]	3.6	0.38	0.25	0.29	0.31	–23.2	–19.3	–19.9	–20.8
Isna	3.7	0.28	–	–	–	–18.4	–	–	–

[a]Denotes a fall.

data displays a clear trend of decreasing δ^{13}C values with increasing metamorphic grade. The "Ornans paradox" is again evident. On the basis of the trend displayed by Fig. 5b, the δ^{13}C value of –21.93‰ for Ornans is more consistent with a sub-type of 3.5 rather than the 3.3 assigned using petrographic evidence (Scott and Jones 1990).

Our measurements are not the first bulk carbon isotopic analyses for CO3 chondrites. Table 4b compares the results obtained in this study with those of Kerridge (1985) and Newton (1994). In terms of carbon abundance, there is fairly reasonable agreement between all three sets of results. The value of 0.39 wt% carbon obtained by Kerridge (1985) for Kainsaz (3.1) appears anomalously low, as does the value of 0.41 wt% carbon for Colony (3.0) obtained by Newton (1994). However, the results of all three studies show the general trend of decreasing carbon abundance with increasing metamorphic grade discussed above.

There is significantly more variation between the three studies in terms of δ^{13}C values, so that, for example, the spread of values for Ornans (3.3) ranges from –12.9‰ to –21.9‰. This variability in the carbon isotopic measurements for common meteoritic samples obtained by different studies has been discussed by Kerridge (1985). He discounted the possibility of contamination, there being no obvious correlation with carbon content, and concluded that the spread of results most likely reflects intrinsic sample inhomogeneity. A mean δ^{13}C value for each sample has been calculated based on the results of this and previous studies (Table 4b). With the exception of Kainsaz (3.1.), these mean values still show a clear trend of decreasing δ^{13}C values with increasing grade (Fig. 5b). Further, although the mean value for Kainsaz (3.1) is slightly more negative than either Felix (3.2) or Ornans (3.3), there is still a significant decrease in δ^{13}C values with increasing grade when Kainsaz (3.1) is compared to Warrenton (3.6). Therefore, we conclude that, despite the strong evidence for sample inhomogeneity, the trend of decreasing whole rock δ^{13}C values with increasing metamorphic grade is a real and significant feature of the CO3 group.

DISCUSSION

How Useful Are CO3 Finds?

The weathering processes taking place in hot and cold deserts are markedly different (Lee and Bland 1999; Bland et al. 2000) and result in distinctive shifts in the primary oxygen isotope composition of meteorite finds (Clayton et al. 1984; Clayton and Mayeda 1990; Franchi et al. 1994; Bland et al. 1996; Stelzner et al. 1999). Weathering in the Antarctic environment will displace oxygen isotope ratios toward lighter values, while hot desert weathering will move ratios toward heavier values. ALH A77307 and Colony have both been assigned to metamorphic sub-type 3.0 but have very distinct oxygen isotope compositions (Figs. 1 and 2). Figure 6

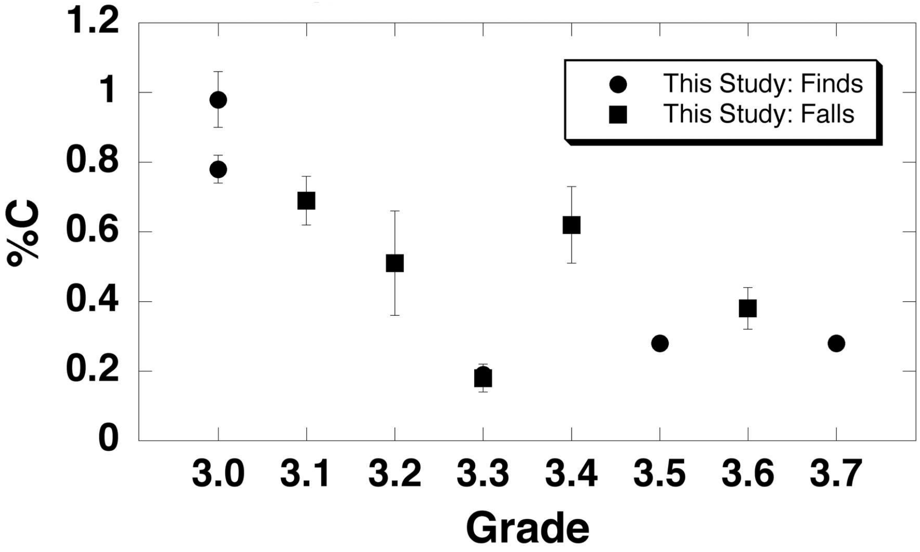

Fig. 4a. Plot of carbon abundance (wt%) versus metamorphic grade (sub-types of Scott and Jones [1990]) for CO3 chondrite finds and falls. The error bars are ±1σ on the mean of replicate analysis.

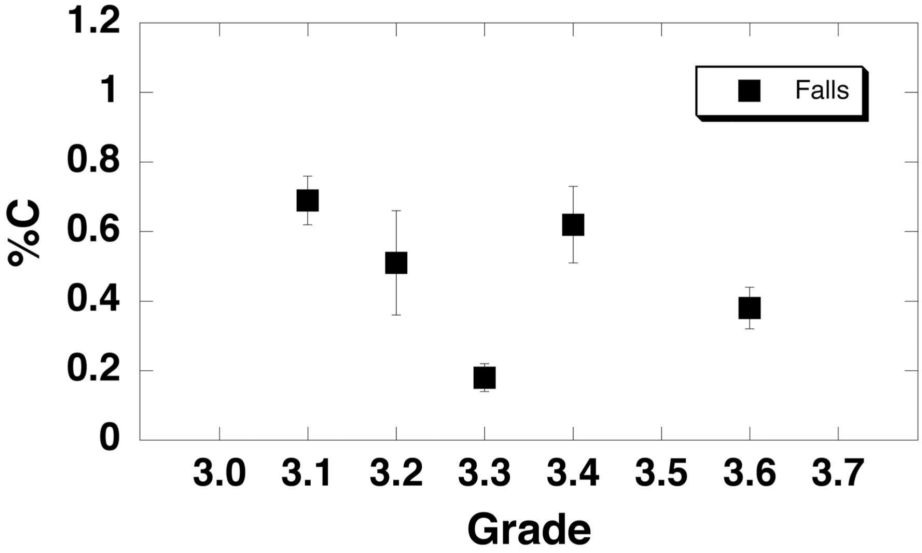

Fig. 4b. Plot of carbon abundance (wt%) versus metamorphic grade (sub-types of Scott and Jones [1990]) for CO3 falls only. The error bars are ±1σ on the mean of replicate analysis.

shows the oxygen isotope data for CO3 chondrites in relation to the terrestrial fractionation line (TFL). If a line is extrapolated from Kainsaz (3.1) (the CO3 fall with the lowest metamorphic sub-type) through ALH A77307, it would intersect the terrestrial fractionation line at a $\delta^{18}O$ value of about −20‰, which is reasonably consistent with Antarctic weathering products (Fig. 6). Using the same method, a line from Kainsaz through Colony intersects the terrestrial fractionation line at a value of about −0.8‰, consistent with weathering products formed in more temperate climatic conditions. A similar relationship was observed by Grossman et al. (2000) in relation to the heavily weathered CO (3.1–3.2) Rainbow, which was found in a semi-arid region of Australia. They noted that analysis of Rainbow yielded a $\delta^{18}O$ value significantly heavier than other CO3 falls of similar sub-type (Fig. 6). Grossman et al. (2000) point out that the oxygen isotope data of Clayton and Mayeda (1999) display similar hot versus cold desert weathering isotopic shifts, so all of their non-Antarctic finds are isotopically heavy compared to falls, while the Antarctic finds are isotopically light.

It is well-established that both the carbon abundance and carbon isotope composition of meteorites can be significantly altered by terrestrial weathering processes (Gooding et al. 1988; Grady et al. 1988, 1991; Jull et al. 1988, 1993; Ash and Pillinger 1993, 1995). This is most clearly demonstrated by the results of a study of the Holbrook (L6) chondrite, which

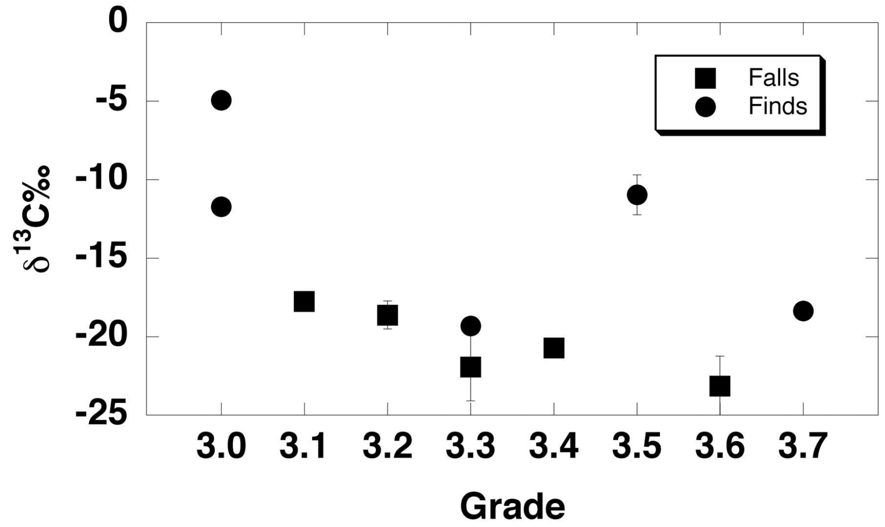

Fig. 5a. Plot of δ^{13}C versus metamorphic grade (sub-types of Scott and Jones [1990]) for CO3 finds and falls. The error bars are ±1σ on the mean of replicate analysis.

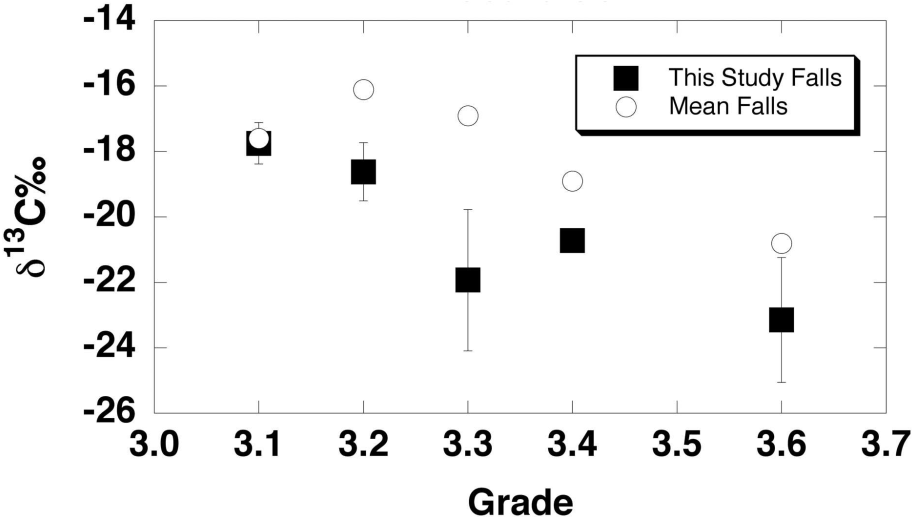

Fig. 5b. Plot of δ^{13}C versus metamorphic grade (sub-types of Scott and Jones [1990]) for CO3 falls only. The error bars are ±1σ on the mean of replicate analysis.

fell in 1912 (Gibson and Bogard 1978). Compared to samples recovered immediately after the fall, material collected up to 56 yr later showed a greater than two fold increase in carbon abundance. Gibson and Bogard (1978) ascribe this to terrestrial weathering processes, in particular, the effects of a carbon-rich terrestrial component on a relatively carbon-poor meteorite. In contrast, a study of 17 Saharan carbonaceous chondrites by Ash and Pillinger (1995) found that most showed a significant reduction in carbon content compared to non-Saharan meteorites of similar composition. Ash and Pillinger (1995) suggest that the reduction in carbon content was mainly due to partial loss of the initially abundant macromolecular organic fraction during hot desert weathering. They estimate that peak temperatures may have reached 100 °C, resulting in pyrolysis and oxidation reactions that liberated volatile organics and CO_2. In comparison, carbonaceous chondrites collected in Antarctica show no significant decrease in carbon content (Grady et al. 1991). In terms of their δ^{13}C values, carbonaceous chondrites recovered from hot and cold deserts display considerably more variation than falls of equivalent composition (Grady et al. 1991; Ash and Pillinger 1995). The reasons for this increased variation are complex and involve both the loss of various indigenous components of differing isotopic composition and the formation of various terrestrial weathering products such as carbonates (Grady et al. 1991; Ash and Pillinger 1995).

Colony (3.0) and Isna (3.7), the two non-Antarctic finds analyzed in this study, show no evidence of significant carbon depletion, as documented for Saharan specimens (Ash and

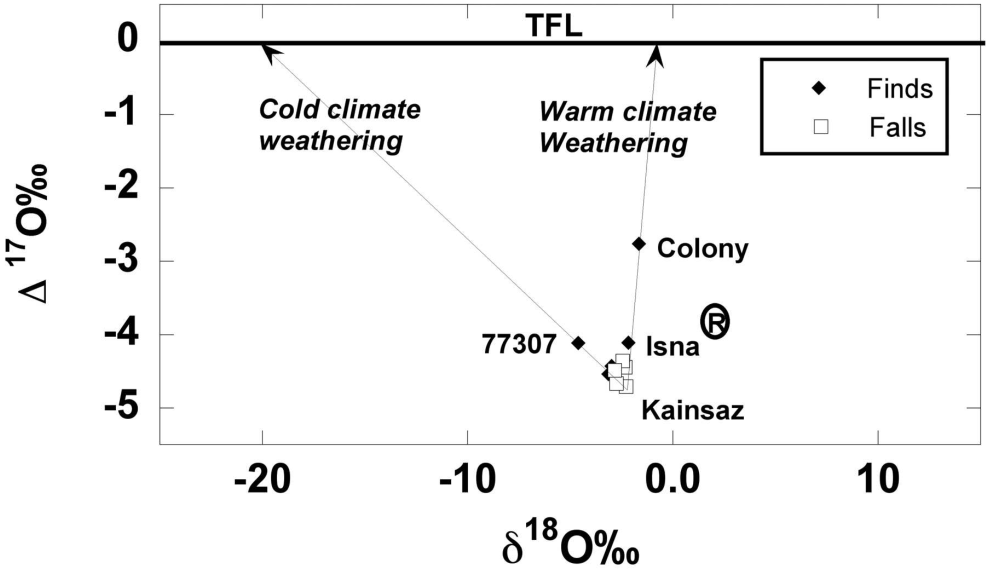

Fig. 6. Plot of $\Delta^{17}O$ versus $\delta^{18}O$ for CO3 chondrite finds and falls. R = Rainbow CO3 chondrite (Grossman et al. 2000).

Pillinger 1995). On the contrary, Colony has the largest carbon content (0.98 wt%) of any sample examined in this study. In the case of Isna, this seems to be because it has suffered minimal weathering, fusion crust still being present, and the metal appears to be relatively fresh (Methot et al. 1975). In contrast, Colony is heavily weathered, containing 22.7 wt% Fe_2O_3 and 5.7 wt% H_2O (Rubin et al. 1985). In a suite of ordinary chondrites from Roosevelt County, Ash and Pillinger (1993) found that the oldest, most weathered samples with terrestrial ages in excess of 44,000 yr had gained a significant carbon component from the enclosing soil material. Ash and Pillinger (1993) concluded that organic contamination of meteorite finds is a complex process that depends both on local conditions and the length of time involved. In the case of Colony, weathering appears to have taken place under conditions similar to those experienced by the Roosevelt County specimens rather than the Saharan samples studied by Ash and Pillinger (1995). In keeping with the results of Grady et al. (1991), CO3 Antarctic finds do not show significantly greater variation in carbon content than that displayed by CO3 falls (Fig.4a).

Antarctic and non-Antarctic finds are significantly heavier in terms of their $\delta^{13}C$ values than CO3 falls (Fig. 5a). The only exception is ALH 82101 (3.3), which has a $\delta^{13}C$ value only slightly heavier than Ornans (3.3) (Fig. 5a). Terrestrial weathering products found in meteorites generally have $\delta^{13}C$ values of −10 to +10‰ (Jull et al. 1995). Thus, while it is likely that weathering will involve the loss of various indigenous components of differing isotopic composition (Grady et al 1991; Ash and Pillinger 1995), the most likely reason for the consistently heavy $\delta^{13}C$ values seen in finds compared to falls is the formation of terrestrial weathering products (Grady et al. 1988; Gooding et al. 1988; Jull et al. 1995).

Clayton and Mayeda (1999) noted that their oxygen isotope analysis for ALH A77307 (3.0) lies close to the mean value of Murchison anhydrous silicates, which Clayton and Mayeda (1984) took to represent the precursors for Murchison phyllosilicates. On this basis, they suggested that a composition close to ALH A77307 might represent the precursor material to both the CO and CM groups. While our oxygen isotope analysis of ALH A77307 is in good agreement with the results obtained by Clayton and Mayeda (1999), it is clear from the previous discussion that this sample has experienced a significant level of terrestrial contamination (Figs. 5a and 6). The oxygen and carbon isotopic composition of ALH A77307 should be used with caution when constructing models about the interrelationship of CO and CM chondrites. More generally, the oxygen and carbon isotopic compositions of all the finds examined in this study, with the possible exception of ALH 82101, indicate that they have experienced significant levels of terrestrial contamination. In trying to use oxygen and carbon isotope analysis to understand metamorphic alteration processes on the CO3 parent body, it is important to treat the data from finds with great caution.

CO3 Metamorphic Sequences

Following McSween's (1977) initial proposal to divide CO3 chondrites into a three stage metamorphic sequence, a number of alternative schemes have been advanced (Table 2). Before discussing their relative merits, it is important to note that all these schemes are in broad agreement; thus, Colony and ALH A77307 are invariably assigned to the lowest sub-types and Isna the highest.

Based on analysis of olivine and low-Ca pyroxene in type IA and II chondrules, Scott and Jones (1990) divided the CO3 chondrites into a sequence of sub-types ranging from 3.0 to

3.7. One major reason for Scott and Jones (1990) adopting this nomenclature was to draw a comparison with the subdivision of the ordinary chondrites into sub-types 3.0–3.9 (Sears et al. 1980). In particular, Scott and Jones (1990) assigned Colony and ALH A77307 to sub-type 3.0 because of their similarity to Semarkona (LL3.0), and they designated Warrenton as a sub-type 3.6 on the basis of its resemblance to Parnallee (LL3.6). However, as pointed out by Sears et al. (1991), there are important differences between the metamorphic histories of CO3 and ordinary chondrites. In particular, peak temperatures for the highest sub-type CO3s were in the range of 450–500 °C (cooling rate 0.1 °C/Ma) (Jones and Rubie 1990), while for type 3.6–3.8 ordinary chondrites, they were in the range of 600–700 °C (Sears et al. 1991). Although Scott and Jones (1990) reject the possibility that their sub-type nomenclature invites invalid comparison between CO3 and ordinary chondrites, this is clearly a potential drawback to their scheme.

Sears et al. (1991) used a variety of evidence, particularly thermoluminescence and cathodoluminescence properties, to formulate a metamorphic sequence that again ranged from sub-type 3.0 to 3.7 (Table 2). One significant problem with this scheme is that Felix, Ornans, and Lancé are all assigned to sub-type 3.4, while Scott and Jones (1990) assign them to 3.2, 3.3, and 3.4, respectively. Carbon isotope data (Fig. 5b) also suggests a separate sub-type for each of these samples, although Ornans might be better classed as a 3.5 rather than a 3.3.

Chizmadia et al. (2002) have recently proposed a metamorphic sequence of sub-types ranging from 3.0 to 3.8. Their scheme is primarily based on the progressive changes in amoeboid olivine inclusions with increasing metamorphic grade. The only significant difference between this scheme and that of Scott and Jones (1990) is that a gap has been left at 3.1 for an as yet unfound sample. The effect of this is that all the sub-types of Scott and Jones (1990) above 3.0 are increased by 0.1; thus, Isna, in this scheme, moves from 3.7 to 3.8. In view of the fact that the sub-types are arbitrary divisions, leaving a vacancy for a presently undiscovered sample would appear to unnecessarily complicate matters.

The evidence presented in this paper is broadly in agreement with the scheme proposed by Scott and Jones (1990). As discussed, Ornans displays ambiguous behavior and has a higher grade based on chemical properties compared to petrographic characteristics (McSween 1977). However, moving it from 3.3 to 3.5 would not solve this problem. Another important advantage of the Scott and Jones scheme (1990) is its applicability to features other than those for which it was formulated. Thus, the scheme was devised on the basis of the increasing extent of silicate homogenization but can equally be applied to changes in amoeboid olivine inclusions (Chizmadia et al. 2002), or CAIs (Russell et al. 1998). In view of these advantages, it is recommended that the Scott and Jones (1990) scheme be adopted as the main classification tool when attempting to assign sub-types to new CO3 samples.

Alteration and Metamorphism of CO3 Chondrites

While it is now established that CO3 chondrites represent a well-defined metamorphic series, what is less clear is where and under what conditions this metamorphism took place. There are two possibilities. Metamorphism occured either: i) in the nebular; or ii) during parent body alteration.

It has been proposed that alteration of some CO3 refractory inclusions (Tomeoka et al. 1992) and plagioclase-rich chondrules (Jones 1997) took place in the nebular before accretion. While such processes may have occurred on a limited scale, studies of refractory inclusions (Russell et al. 1998) and chondrule suites (Scott and Jones 1990) demonstrate that the main period of metamorphism post-dated parent body formation. Although a nebular model involving interaction between ^{16}O-rich solids and ^{16}O-poor gas (Clayton 1993; Cassen 2001) could be invoked to explain the oxygen isotope systematics of CO3 chondrites (Fig. 1), it is less clear why such variation should appear to correlate with metamorphic sub-type (Fig. 3b). One mechanism that might overcome this problem and, therefore, avoid the need to invoke later parent body processes is if sorting occurred during accretion. The constituents of CO3 chondrites (matrix, CAIs, and chondrules) have widely varying isotopic compositions. Thus, the C and O isotopic systematics discussed earlier may simply reflect slight changes in the proportion of these constituents. If the CO3 parent body accreted heterogeneously, component proportions might have varied radially, so for example, the interior might have been CAI-poor while the exterior was CAI-rich. If some metamorphic reheating took place after accretion, one might then have a thermally and compositionally zoned body with a hotter CAI-poor interior (i.e., sub-types 3.4–3.7) and a cooler CAI-rich exterior (i.e., sub-types 3.0–3.3). The main problem with such a model is that there is no evidence for either modal changes, or layering, within or between CO3 chondrites. In the absence of such evidence, the correlation between metamorphic grade and oxygen isotope variation (Fig. 3b), carbon content (Figs. 4a and 4b), and carbon isotope variation (Fig. 5b) indicates that metamorphism took place after parent body formation.

The suggestion that parent body metamorphism can take place by accretion of still hot components (chondrules, CAIs, etc.), so-called autometamorphism, has largely been discredited (Haack et al. 1992; Rubin and Brearley 1996). As a starting point, we assume that the CO3 parent body was initially cold, relatively homogeneous and composed of unequilibrated type 3.0 material and that after formation internal heating took place driven by a short-lived thermal event such as the decay of ^{26}Al (Rubin and Brearley 1996; Scott et al. 1997). This scenario is supported by the results of diffusion modeling (Jones and Rubie 1990), which demonstrate that olivine Fe-Mg zoning profiles in CO3 chondrules from sub-types 3.4–3.7 can be derived by in situ equilibration of type 3.0 material, with matrix material as the source of Fe. Using cooling rates derived from metallographic studies (Wood 1967; Willis and Goldstein 1981), the calculations of Jones and Rubie (1990) indicate extremely narrow ranges of peak metamorphic temperatures for sub-types 3.4–3.7, which vary between 450–500 °C (0.1 °C/Ma) and 510–570 °C (10 °C/Ma). The uncertainty in peak temperature is ±50 °C. Major and minor element distributions in isolated olivines are also consistent with in situ, closed-system metamorphism on the CO3 parent body (Jones 1993). Thermoluminescence studies (Keck and Sears 1987; Sears et al. 1991) suggest that CO3 chondrites have not experienced temperatures higher than the order/disorder transformation for sodic feldspar (500–600 °C) and cooled more slowly than type 3 ordinary chondites, which give rates of (~1 °C/Ma). This lends support to the values of 0.3 °C/Ma and 0.1 °C/Ma obtained for Felix and Lancé by Wood (1967).

The results of a wide range of studies indicate that CO3 chondrites experienced aqueous alteration, most probably within a parent body environment. Phyllosilicates have been identified in ALH A77307 (3.0) (Brearley 1993; Itoh and Tomeoka 2001), Ornans (3.3) (Kerridge 1964), and Lancé (3.4) (Christophe Michel-Levy 1969; Kurat 1973, 1975; Keller and Buseck 1990). In contrast, phyllosilicates appear to be absent from the matrices of Kainsaz (3.1) and Warrenton (3.6), although both do show the development of Fe^{3+} oxides (Keller and Buseck 1990).

Although relatively pristine in comparison with CIs or CMs, Lancé (3.4) appears to have experienced more extensive aqueous alteration than other CO3 chondrites (Keller and Buseck 1990). Matrix olivines (Fo_{40-50}) in Lancé are partially altered to Fe-bearing serpentine and Fe^{3+} oxides (Keller and Buseck 1990). Kamacite is absent from the matrix of Lancé, which contains only Ni-rich taenite and minor chromite. Based on the relatively Fe-rich composition of serpentine compared to the matrix olivines, Keller and Buseck (1990) argue that the formation of phyllosilicate also required the oxidation of metal. These processes resulted in the preferential removal of kamacite with respect to taenite, as well as enrichment of Ni in the residual metal grains (Keller and Buseck 1990). Oxidation of metal during aqueous alteration appears to have been an important process in CO3 chondrites, and Brearley (1993) reports that metal in the matrix of ALH A77307 (3.0) is relatively pristine and consists predominantly of kamacite (Ni 4–5 element %). In Kainsaz (3.1), fine-grained metal comprises a mixture of kamacite (Fe94, Ni6) and taenite (Fe55, Ni45), while in Ornans (3.3) and Warrenton (3.6), like Lancé (3.4), only Ni-rich taenite is present (McSween 1977; Keller and Buseck 1990). This evidence suggests that oxidation of metal increases progressively with increasing metamorphic grade.

Serpentine in Lancé (3.4) occurs chaotically mixed with Fe^{3+} oxides filling channels in matrix olivines and as discrete packets along olivine grain boundaries. Keller and Buseck (1990) argue that, although aqueous alteration was pervasive in Lancé (3.4), it was far from complete, being limited by the paucity of available fluid. Support for this view comes from hydrothermal alteration studies of olivine (Fo_{85}) that indicate that, under the conditions that prevailed on the CO3 parent body (temperature 200–500 °C, alkali-bearing fluids, low pressure), complete serpentinization would have been extremely rapid, i.e., within 30 days (Korytkova and Makarova [1971], as reported by Deer et al. [1997]). Thus, as suggested by Keller and Buseck (1990), the main reason for the low level of alteration in CO3 chondrites would appear to be the relatively dry conditions involved.

One major and as yet unresolved problem is the relative timing of aqueous alteration and thermal metamorphism. On the basis that the matrix of Lancé (3.4) contains serpentine rather than the lower temperature phyllosilicate smectite common in CV3s, Keller and Buseck (1990) conclude that both processes took place more or less simultaneously. However, smectite is the dominant phase in ALH A77307 (3.0) (Itoh and Tomeoka 2001), where it occurs in both angular clasts and replacing mesostasis in chondrules. Since the degree of alteration varies from clast to clast and chondrule to chondrule, Itoh and Tomeoka (2001) conclude that the CO parent body was heterogeneous with respect to aqueous alteration and that ALH A77307 comprises material from many different locations within the parent body. The relative abundance of low temperature smectite in ALH A77307 (3.0) and higher temperature serpentine in Lancé (3.4) would appear to support the view of Keller and Buseck (1990) that there is a general correlation between thermal metamorphism and aqueous alteration.

From observations of dark inclusions in various CO3 chondrites, Itoh and Tomeoka (2003) propose a much more complex scenario for the relative timing of aqueous alteration and metamorphism. As a starting point, they suggest that the CO parent body consisted of a heterogeneous conglomerate with both water-bearing and water-free regions. During asteroidal heating, the water-bearing regions were first aqueously altered and then dehydrated to form the dark inclusions. Subsequent brecciation then mixed the dark inclusions with unaltered material. Itoh and Tomeoka (2003) regard the main phase of thermal metamorphism as having taken place after incorporation of the aqueously altered-dehydrated dark inclusions into their present location.

Oxygen Isotope Evidence for Aqueous Alteration

The oxygen isotope data for CO3 falls (Fig. 3b) indicate that there is a subtle increase in whole rock $\Delta^{17}O$ values with increasing metamorphic grade for sub-types 3.1 to 3.4. This increase does not appear to persist to higher sub-types, as our $\Delta^{17}O$ value for Warrenton (3.6) is less than that of either Lancé (3.4) or Ornans (3.3) (Table 3). As suggested by Rubin (1998) and Clayton and Mayeda (1999), this trend indicates that metamorphism also involved interaction with an external oxygen-bearing reservoir. In view of the evidence that water in the early solar system had a significantly higher $\Delta^{17}O$ value than coexisting solids (Baker et al. 1998, 2002; Young et al. 1999; Franchi et al. 2001), the most likely explanation for the trend in Δ^{17}O for sub-types 3.1 to 3.4 is that it is due to increasing degrees of aqueous alteration. As discussed earlier, the magnitude of this increase is small, and the difference between the Δ^{17}O value of Lancé (3.4) and Kainsaz (3.1) is only 0.35‰. On a mineralogical scale the increase in Δ^{17}O whole rock values with alteration may be due to three related processes: 1) removal of primary phases with Δ^{17}O values more negative than the whole rock value, such as those found in CAIs (Clayton 1993); 2) oxygen exchange with high Δ^{17}O fluids, which then increases the Δ^{17}O value of primary phases such as melilite in CAIs (Wasson et al. 2001); and 3) formation of secondary phases with Δ^{17}O values higher than that of the unaltered whole rock value, i.e., phyllosilicates (Clayton and Mayeda 1999). The first two processes are well-displayed by the behavior of melilite in CO3 CAIs (Russell et al. 1998; Wasson et al. 2001). Melilite is present in CO3 CAIs from sub-types 3.0 to 3.4, where it shows progressive replacement by a fine-grained mixture of nepheline, pyroxene, and FeS (Russell et al. 1998). Melilite is absent from CO3 CAIs above sub-type 3.4. Coupled with this progressive dissolution, melilite also undergoes isotopic exchange, and in the lowest sub-type CO3s, it has primitive Δ^{17}O values of less than −20‰, while in Ornans (3.3), they may be as high as −2.4‰ (Wasson et al. 2001). The CAI abundance data of Russell et al. (1998) indicate that Kainsaz contains no more than 0.5% melilite. Using a value of −28.2‰ for the Δ^{17}O value of melilite (the most negative value for Kainsaz measured by Wasson et al. [2001]), complete removal of all the melilite in Kainsaz would only increase the Δ^{17}O whole rock value by 0.12‰, i.e., insufficient to account for the difference between Kainsaz (3.1) and Lancé (3.4).

Lancé (3.4) has the highest phyllosilicate content of any CO3, while in Kainsaz (3.1), hydrated phases are absent (Keller and Buseck 1990). Clayton and Mayeda (1999) argue that, although less extensive in scale, the alteration processes in CO3s were similar to those seen in CM2s, such as Murchison. Thus, although the oxygen isotope composition of CO3 phyllosilicates has not yet been directly determined, the isotopic composition of Murchison matrix Δ^{17}O = −2.08‰ (Clayton and Mayeda 1999) can be employed as an analogue. This value can then be used to estimate the maximum percentage of phyllosilicate required to change the whole rock Δ^{17}O value of Kainsaz to that of Lancé. Such a calculation suggests that, compared to Kainsaz, Lancé would need to have a phyllosilicate content of 12%. Given that phyllosilcates form principally by replacement of matrix olivine (Keller and Buseck 1990) and that Lancé comprises 33% matrix (McSween 1977), this estimate does not appear unreasonable. Additionally, phyllosilicates and other hydrous phases are probably present in CAIs and replacing chondrule mesostasis. Given the uncertainties in such a calculation, the development of secondary phyllosilicates in response to aqueous alteration would seem to represent a realistic means of explaining the increase in Δ^{17}O whole rock values with increasing metamorphic grade. However, interaction with aqueous fluids may have been a complex process and would also have involved both removal and isotopic exchange of primary phases such as melilite.

Our Δ^{17}O value for Warrenton (3.6) falls well below any possible trend of increasing Δ^{17}O with increasing metamorphic grade. It is possible that this is a reflection of the apparent absence of phyllosilicates in Warrenton (Keller and Buseck 1990). However, in view of the differences between our analysis of Warrenton and that of Clayton and Mayeda (1999), attempting to draw significant implications from this relationship appears premature. Recent studies indicate that dehydration of phyllosilicates was an important process during parent body alteration (Akai 1988; Mayeda and Clayton 1998; Itoh and Tomeoka 2003). The lack of phyllosilicates in Warrenton may have been the result of dehydration reactions that occurred at peak metamorphic temperatures. A detailed TEM study of Warrenton would help to assess the importance of dehydration both on the CO3 parent body and, more generally, on other thermally and aqueously altered asteroids.

Carbon Isotopes: Further Evidence for a Metamorphic Series

Like other carbonaceous chondrites, carbon in CO3 chondrites is present both as organic matter and various inorganic phases, such as carbonate, diamond, graphite, and silicon carbide (Newton et al. 1992a, b; Newton 1994; Alexander et al. 1998; Sephton 2002; Sephton et al. 2003). Organic matter is by far the most important of these phases, representing approximately 90% of the carbon-bearing inventory present in carbonaceous chondrites (Sephton et al. 2003). Due to this high abundance, the bulk δ^{13}C of a whole rock sample should be dominated by the contribution from the organic matter present. The only potential exception to this is where a minor carbon-bearing phase carries a large isotopic anomaly and is sufficiently abundant to overprint the contribution from the organic component. The only likely candidate phases are silicon carbide (δ^{13}C +1200‰) and graphite (δ^{13}C −50 to +340‰) (Sephton 2002; Sephton et al. 2003). However, silicon carbide is only present in type 3.0 CO3 chondrites and then only at the level of 1 ppm (Newton et al. 1992b; Huss et al. 2002), and presolar graphite is absent from all CO3s (Huss et al. 2002). Although presolar diamonds are present in CO3 chondrites the amounts involved (Colony, 135 ppm; Kainsaz, 61 ppm; Lancé, 59 ppm) and the magnitude of the δ^{13}C anomaly they carry (δ^{13}C −34.3‰ to −40.3‰) (Newton et al. 1992b) are again insufficient to significantly perturb the overwhelming contribution of organic matter to the whole rock δ^{13}C value. To summarize, the variation in whole rock δ^{13}C values displayed by CO3 chondrites essentially reflects changes in the composition of the organic fraction present.

Based on a relatively constant ratio of presolar nanodiamonds to organic macromolecular material, Alexander et al. (1998) suggest that all carbonaceous chondrites initially had a relatively similar component of organic material, both in terms of chemical and isotopic composition. These authors go on to suggest that differences between the organic material of one carbonaceous chondrite compared to another are primarily due to secondary parent body processes, in particular, thermal metamorphism and aqueous alteration. Therefore, to assess the composition of the organic component initially present in CO3 chondrites, we need to look at other less processed carbonaceous chondrites.

Using data from step combustion and hydrous pyrolysis of Murchison (CM2) and Orgueil (CI1) whole rock and HF/HCl residues, Sephton et al. (2003) divide carbonaceous chondrite organic matter into three components: 1) free organic matter (FOM) extractable with common solvents; 2) labile organic matter (LOM), which is macromolecular material that can be liberated by hydrous pyrolysis; and 3) refractory organic matter (ROM), which is unaffected by solvents, HF/HCl treatment, or hydrous pyrolysis. These three fractions differ in terms of their step combustion temperatures and $\delta^{13}C$ isotopic compositions. During step combustion, FOM is released at the lowest temperature <250 °C and has a $\delta^{13}C$ value of ~+5‰, LOM is released from HF/HCl residues at between 250 to 350 °C and has an average $\delta^{13}C$ value of −5‰, and ROM is released at between 350 and 500 °C and has a $\delta^{13}C$ value of ~−20‰.

The organic matter originally incorporated into carbonaceous chondrites was enriched in the heavy isotopes of carbon, nitrogen, and hydrogen (Alexander et al. 1998: Sephton et al. 2003). Sephton et al. (2003) argue that increasing degrees of both aqueous and thermal alteration result in progressive loss of the FOM and LOM fractions. The $\delta^{13}C$ value of the remaining residue, therefore, decreases progressively until all that is left is the isotopically light ROM fraction. The results of step combustion of Murchison HF/HCl residues (Kerridge et al. 1987) appear to corroborate these ideas and display a progressive decrease in $\delta^{13}C$ values from −12.4‰ to −18.5‰ during the temperature interval 250–360 °C, with this latter $\delta^{13}C$ value maintained until a temperature of 420 °C is attained. Hydrous pyrolysis experiments (Sephton et al. 2003) on Murchison HF/HCl residues remove carbon that combusts in the 200 to 300 °C interval ($\delta^{13}C$ −10‰) and leave a residue that contains carbon that combusts in the range of 350–500 °C ($\delta^{13}C$ ~−20‰).

The carbon isotopic composition of CO3 falls (Fig. 5b) shows significant similarities to the data obtained from Murchison HF/HCl residues (Kerridge et al. 1987; Sephton et al. 2003). With increasing metamorphic grade, whole rock $\delta^{13}C$ values decrease progressively from −17.75‰ in Kainsaz (3.1) to −23.15‰ in Warrenton (3.6). As discussed earlier for sub-types 3.4 to 3.7, peak metamorphic temperatures would have been in the range of 450–500 °C (cooling rate 0.1 °C/Ma) (Jones and Rubie 1990). Peak temperatures for sub-types 3.0–3.3 would have been somewhat lower. Under such conditions FOM ($\delta^{13}C$ +5‰) and most of the LOM fraction ($\delta^{13}C$ ~−5‰) would have been completely removed during initial heating so that, particularly in the case of sub-types 3.4–3.7, only the ROM fraction ($\delta^{13}C$ ~−20‰) would remain. However, because labile material liberated during alteration is always isotopically heavy compared to the residue, even when only ROM is present, the $\delta^{13}C$ value of this remaining organic material continues to decline (Sephton et al. 2003).

Direct measurements of the intrinsic oxygen fugacity (fO_2) of Felix (3.2) demonstrate that it is a relatively oxidized meteorite lying just above the iron-wüstite buffer (Brett and Sato 1984). The evidence from TEM studies also indicates that metamorphism on the CO3 parent body took place under relatively oxidizing conditions (Keller and Buseck 1990). The presence of carbonate in Warrenton (3.6), as detected in step combustion studies (Newton 1994), provides evidence of high CO_2 levels during alteration and, again, indicates relatively oxidizing conditions. In such an oxidizing environment, if loss of organic material was only due to combustion reactions, the results of step combustion experiments imply that all of the organic material should have been completely removed from the highest sub-type samples (i.e., Lancé and Warrenton), which is not the case. The most likely reason for this discrepancy is the presence of an aqueous fluid phase during metamorphism, which would have significantly modified the chemical processes occurring at high temperature. Thus, in addition to simple combustion resulting in release of CO/CO_2 gases, hydrolysis reactions would also have been involved. In consequence, the nature of the remaining organic fraction would have been significantly different to that which is present during step combustion experiments.

Inherent uncertainties in the method used to calculate peak metamorphic temperatures in CO3 chondrites also pose significant problems in any attempt to compare our isotopic results with those obtained by step combustion. The calculations of Jones and Rubie (1990) involve extrapolation of Fe-Mg interdiffusion rates from the high temperatures where they were determined (>900 °C) to the lower temperatures relevant to parent body metamorphism (~500 °C). Even at these higher temperatures, recent work indicates that there are significant discrepancies between olivine Fe-Mg interdiffusion rates measured in different studies (Chakrobarty 1997). In addition, olivine Fe-Mg interdiffusion rates show strong fO_2 dependence, being more rapid under oxidizing conditions compared to reducing conditions (Jurewicz and Watson 1988). These uncertainties pose a challenge when defining peak metamorphic temperatures in CO3 chondrites using Fe-Mg zoning profiles in olivine (Jones and Rubie 1990).

Finally, and briefly, it is worth re-examining the "Ornans paradox" (McSween 1977) in light of the carbon isotope data. Ornans (3.3) has a lower carbon abundance and more negative δ^{13}C value than Lancé (3.4) (Table 4a), which is at a higher metamorphic grade based on petrographic criteria, hence, the paradox. This relationship might be explained if local conditions were dryer and, hence, more reducing for Ornans than was the case for Lancé and if, in fact, Ornans experienced somewhat higher temperatures than Lancé. Under such conditions, Ornans would have lost more carbon and, thus, would have a more refractory organic component, i.e., more negative δ^{13}C value compared to Lancé. At the same time, locally more oxidizing conditions for Lancé would have promoted more rapid Fe-Mg diffusion in olivine, giving the appearance that Lancé is of higher petrographic sub-type than Ornans.

CONCLUSIONS

The principal conclusions of this study are:

1. The trend of decreasing δ^{13}C whole rock values with increasing sub-type displayed by CO3 chondrites is best explained in terms of progressive changes in the nature of the organic macromolecular component during metamorphic heating. This relationship lends further support to the evidence that CO3 chondrites are part of a single metamorphic series and, hence, originally derived from the same asteroidal parent body.
2. The oxygen isotope data for CO3 falls indicate that there is a subtle increase in whole rock Δ^{17}O values with increasing metamorphic grade for sub-types 3.1 to 3.4. However, this increase does not appear to persist to higher sub-types, i.e., Warrenton (3.6). The increase in Δ^{17}O values for sub-types 3.1 to 3.4 suggests that an aqueous fluid phase was present during metamorphism.
3. Both the carbon and oxygen isotopic composition of CO3 finds have been significantly modified by terrestrial weathering processes. Conclusions based on the isotopic composition of such weathered finds may be seriously flawed.
4. A wide variety of classification schemes have now been proposed for CO3 chondrites. In view of its relative simplicity and general applicability, we would recommend that the scheme of Scott and Jones (1990) is adopted as the main classification tool when attempting to assign sub-types to new CO3 samples.
5. The so-called "Ornans paradox" may be the result of local scale differences in redox conditions.

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REFERENCES

Akai J. 1988. Incompletely transformed serpentine-type phyllosilicates in the matrix of Antarctic CM chondrites. *Geochimica et Cosmochimica Acta* 52:1593–1599.

Alexander C. M. O'D., Russell S. S., Arden J. W., Ash R. D., Grady M. M., and Pillinger C. T. 1998. The origin of chondritic macromolecular organic matter: A carbon and nitrogen isotope study. *Meteoritics & Planetary Science* 33:603–622.

Ash R. D. and Pillinger C. T. 1993. Carbon in weathered ordinary chondrites from Roosevelt county. Proceedings, 24th Lunar and Planetary Science Conference. pp. 43–44.

Ash R. D. and Pillinger C. T. 1995. Carbon, nitrogen, and hydrogen in Saharan chondrites: The importance of weathering. *Meteoritics* 30:85–92.

Baker L., Franchi I. A., Maynard J. M., Wright I. P., and Pillinger C. T. 1998. Measurement of Oxygen isotopes in water from CI and CM chondrites (abstract #1740). 29th Lunar and Planetary Science Conference. CD-ROM.

Baker L., Franchi I. A., Wright I. P., and Pillinger C. T. 2002. The oxygen isotopic composition of water from Tagish Lake: Its relationship to low-temperature phases and to other carbonaceous chondrites. *Meteoritics & Planetary Science* 37: 977–985.

Bland P. A., Franchi. A., Sexton A. S., Berry F. J., and Pillinger C. T. 1996. The O isotopic composition of weathered ordinary chondrites from the Nullarbor region (abstract). *Meteoritics & Planetary Science* 31:A16.

Bland P. A., Lee M. R., Sexton A. S., Franchi I. A., Fallick A. E. T., Miller M. F., Cadogan J. M., Berry F. J., and Pillinger C. T. 2000. Aqueous alteration without a pronounced oxygen-isotopic shift: Implications for the asteroidal processing of chondritic materials. *Meteoritics & Planetary Science* 35:1387–1395.

Brearley A. J. 1993 Matrix and fine-grained rims in the equilibrated CO3 chondrite ALH A77307: Origins and evidence for diverse, primitive nebular dust components. *Geochimica et Cosmochimica Acta* 57:1521–1550.

Brett R. and Sato M. 1984. Intrinsic oxygen fugacity measurements on seven chondrites, a pallasite, and a tektite and the redox state of meteorite parent bodies. *Geochimica et Cosmochimica Acta* 48:111–120.

Cassen P. 2001. Nebular thermal evolution and the properties of primitive planetary materials. *Meteoritics & Planetary Science* 36:671–700.

Chakraborty S. 1997. Rates and mechanisms of Fe-Mg interdiffusion in olivine at 900 °C–1300 °C. *Journal of Geophysical Research* 102:12317–12331.

Chizmadia L. J., Rubin A. E., and Wasson J. T. 2002. Mineralogy and petrology of olivine inclusions in CO3 chondrites: Relationship to parent-body aqueous alteration. *Meteoriics & Planetary Science* 37:1781–1796.

Christophe Michel-Levy M. 1969. Etude minéralogique de la chondrite CIII de Lancé. In *Meteorite research,* edited by Millman P. Dordrecht: D. Reidel. pp. 492–499.

Clayton R. N. 1993. Oxygen isotopes in meteorites. *Annual Review of Earth and Planetary Sciences* 21:115–149.

Clayton R. N. and Mayeda T. K. 1984. The oxygen isotope record in Murchison and other carbonaceous chondrites. *Earth and Planetary Science Letters* 67:151–161.

Clayton R. N. and Mayeda T. K. 1990. Oxygen isotopic composition of Antarctic meteorites (abstract). In *Workshop on differences between Antarctic and non-Antarctic meteorites,* edited by

Koeberl C. and Cassidy W. A. Technical Report 90-01. Houston: Lunar and Planetary Institute.

Clayton R. N. and Mayeda T. K. 1999. Oxygen isotope studies of carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 63: 2089–2104.

Clayton R. N., Mayeda T. K., and Yanai K. 1984. Oxygen isotopic compositions of some Yamato meteorites. *Proceedings of the 9th Symposium on Antarctic Meteorites* 35:267–271.

Deer W. A., Howie R. A., and Zussman J. 1997. *Rock-forming minerals, vol. 1A, Orthosilicates*. London: Longman Scientific & Technical.

Faure G. 1986. *Principles of isotope geology,* 2nd ed. New York: John Wiley & Sons, Inc.

Franchi I. A., Bland P., Berry F. J., Speck A., and Pillinger C. T. 1994. The influence of weathering on the measured oxygen isotopic composition of ordinary chondrites (abstract). *Meteoritics* 29: 467–468.

Franchi I. A., Baker L., Bridges J. C., Wright I. P., and Pillinger C. T. 2001. Oxygen isotopes in the early solar system. *Philosophical Transactions of the Royal Society of London A* 359:2019–2035.

Gibson E. K. and Bogard D. D. 1978. Chemical alterations of the Holbrook chondrite resulting from terrestrial weathering. *Meteoritics* 13:277–289.

Gooding J. L., Jull A. J. T., Cheng S., and Velbel M. A. 1988. Mg-carbonate weathering products in Antarctic meteorites: Isotopic composition and origin of nesquehonite from LEW 85320. Proceedings, 19th Lunar and Planetary Science Conference. pp. 397–398.

Grady M. M., Gibson E. K., Wright I. P., and Pillinger C.T. 1988. Alteration products on the LEW 85320 H5 chondrite. Proceedings, 19th Lunar and Planetary Science Conference. pp. 409–411.

Grady M. M., Wright I. P., and Pillinger C. T. 1991. Comparisons between Antarctic and non-Antarctic meteorites based on carbon isotope geochemistry. *Geochimica et Cosmochimica Acta* 55:49–58.

Grossman J. N., Birch B., Benoit P. H., Sears D. W. G., Clayton R. N., Rubin A. E., and Chizmadia L. J. 2000. Rainbow: A new CO3 chondrite from Australia (abstract #1355). 31st Lunar and Planetary Science Conference. CD-ROM.

Haack H., Taylor G. J., Scott E. R. D., and Keil K. 1992. Thermal history of chondrites: Hot accretion versus metamorphic reheating. *Geophysical Research Letters* 19:2235–2238.

Huss G. R., Meshik A. P., Hohenberg C. M., and Smith J. B. 2002. Relationships among chondrite groups inferred from presolar-grain abundances (abstract #1910). 33rd Lunar and Planetary Science Conference. CD-ROM.

Itoh D. and Tomeoka K. 2001. Phyllosilicate-bearing chondrules and clasts in the ALH A77307 CO3 chondrite: Evidence for parent body processes (abstract). *Proceedings of the NIPR Symposium on Antarctic Meteorites* 14:47–49.

Itoh D. and Tomeoka K. 2003. Dark inclusions in CO3 chondrites: New indicators of parent-body processes. *Geochimica et Cosmochimica Acta* 67:153–169.

Jones R. H. 1993. Effect of metamorphism on isolated olivine grains in CO3 chondrites. *Geochimica et Cosmochimica Acta* 57:2853–2867.

Jones R. H. 1997. Alteration of plagioclase-rich chondrules in CO3 chondrites: Evidence for late-stage sodium and iron metasomatism in a nebular environment (abstract). In *Workshop on parent body and nebular modification of chondritic materials,* edited by Zolensky M. E., Krot A. N., and Scott E. R. D. LPI Technical Report 97-02. Houston: Lunar and Planetary Insitute. pp. 30–31.

Jones R. H. and Rubie D. C. 1990. Thermal metamorphism in CO3 chondrites: Application of olivine diffusion modeling to post-accretionary metamorphism (abstract). Proceedings, 21st Lunar and Planetary Science Conference. pp. 583–584.

Jull A. J. T., Cheng S., Gooding J. L., and Velbel M. A. 1988. Rapid growth of magnesium-carbonate weathering products in a stony meteorite from Antarctica. *Science* 242:417–419.

Jull A. J. T., Donahue D. J., Cielaszyk E., and Wlotzka F. 1993. Carbon-14 terrestrial ages and weathering of 27 meteorites from the southern high plains and adjacent areas (USA). *Meteoritics* 28:188–195.

Jull A. J. T., Eastoe C. J., Xue S., and Herzog G. F. 1995. Isotopic composition of carbonates in the SNC meteorites Allan Hills 84001 and Nakhla. *Meteoritics* 30:311–318.

Jurewicz A. J. G. and Watson E. B. 1988. Cations in olivine, part 2: Diffusion in olivine xenocrysts, with applications to petrology and mineral physics. *Contributions to Mineralogy and. Petrology* 99:186–201.

Keck B. D. and Sears D. W. G. 1987. Chemical and physical studies of type 3 chondrites, VIII: The CO chondrites. *Geochimica et Cosmochimica Acta* 51:3013–3022.

Keller L. P. and Buseck P. R. 1990. Matrix mineralogy of the Lancé CO3 carbonaceous chondrite: A transmission electron microscope study. *Geochimica et Cosmochimica Acta* 54:1155–1163.

Kerridge J. F. 1964. Low-temperature minerals from fine-grained matrix of some carbonaceous meteorites. *Annuls of the New York Academy of Science* 119:41–53.

Kerridge J. F. 1985. Carbon, hydrogen, and nitrogen in carbonaceous chondrites: Abundances and isotopic compositions in bulk samples. *Geochimica et Cosmochimica Acta* 49:1707–1714.

Kerridge J. F., Chang S., and Shipp R. 1987. Isotopic characterization of kerogen-like material in the Murchison carbonaceous chondrite. *Geochimica et Cosmochimica Acta* 51:2527–2540.

Kurat G. 1973. The Lancé chondrite: Further evidence for the complex development of chondrites. *Meteoritics* 8:51–52.

Kurat G. 1975. Der köhlige chondrit Lancé: Eine petrologische Analtse der komplexen Genese eines Chondriten. *Tschermaks Mineralogische und Petrographische Mitteilungen* 22:38–78.

Lee M. R. and Bland P. A. 1999. SEM and TEM characterisation of terrestrial weathering products in equilibrated ordinary chondrite finds from hot and cold deserts (abstract). *Meteoritecs* 34:A73.

Mayeda T. K. and Clayton R. N. 1998 Oxygen isotope effects in serpentine dehydration (abstract #1405). 29th Lunar and Planetary Science Conference. CD-ROM.

McSween H. Y. 1977 Carbonaceous chondrites of the Ornans type: A metamorphic sequence. *Geochimica et Cosmochimica Acta* 41:477–491.

Methot R. L., Noonan A. F., Jaroseewich E., Degasparis A. A., and Al-Far D. M. 1975. Mineralogy, petrology, and chemistry of the Isna (C3) meteorite. *Mineralogy* 10:121–131.

Miller M. F. 2002 Isotopic fractionation and the quantification of ^{17}O amomalies in the oxygen three-isotope system: An appraisal and geochemical sugnificance. *Geochimica et Cosmochimica Acta* 66:1881–1889.

Miller M. F., Franchi I. A., Sexton A. S., and Pillinger C. T. 1999. High precision δ^{17}O measurements of oxygen from silicates and other oxides: Method and applications. *Rapid Communications in Mass Spectrometry* 13:1211–1217.

Newton J. 1994. A carbon and nitrogen isotope study of CO3 chondrites. Ph.D. thesis, Open University, Milton Keynes, U.K.

Newton J., Arden J. W., and Pillinger C. T. 1992a. Carbon and nitrogen isotope studies of a suite of type CO3 carbonaceous chondrites (abstract). Proceedings, 23rd Lunar and Planetary Science Conference. pp. 985–986.

Newton J., Arden J. W., and Pillinger C. T. 1992b. Metamorphism of CO3 chondrites: A carbon and nitrogen isotope study (abstract). *Meteoritics* 27:267–268.

Rubin A. E. 1998. Correlated petrologic and geochemical characteristics of CO3 chondrites. *Meteoritics & Planetary Science* 33:385–391.

Rubin A. E. and Brearley A. J. 1996. A critical evaluation of the evidence for hot accretion. *Icarus* 124:86–96.

Rubin A. E., James J. A., Keck B. D., Weeks K. S., Sears D. W. G., and Jarosewich E. 1985.The Colony meteorite and variations in CO3 chondrite properties. *Meteoritics* 20:175–195.

Russell S. S., Huss G. R., Fahey A. J., Greenwood R. C., Hutchison R., and Wasserburg G. J. 1998. An isotopic and petrologic study of calcium-aluminum-rich inclusions from CO3 meteorites. *Geochimica et Cosmochimica Acta* 62:689–714.

Scott E. R. D. and Jones R. H. 1990. Disentangling nebular and asteroidal features of CO3 carbonaceous chondrite meteorites. *Geochimica et Cosmochimica Acta* 54:2485–2502.

Scott E. R. D., Krot A. N., and Browning L. B. 1997. Asteroidal modifications of C and O chondrites: Myths and models (abstract). In *Workshop on parent body and nebular modification of chondritic materials,* edited by Zolensky M. E., Krot A. N., and Scott E. R. D. LPI Technical Report 97-02. Houston: Lunar and Planetary Institute. pp. 56–57.

Sears D. W., Grossman J. N., Melcher C. L., Ross L. M., and Mills A. A. 1980. Measuring metamorphic history of unequilibrated ordinary chondrites. *Nature* 287:791–795.

Sears D. W. G., Batchelor J. D., Lu J., and Keck B. D. 1991. Metamorphism of CO and CO-like chondrites and comparisons with type 3 ordinary chondrites. *Proceedings of the NIPR Symposium on Antarctic Meteorites* 4:319–343.

Sephton M. A. 2002. Organic compounds in carbonaceous meteorites. *Natural Product Reports* 19:292–311.

Sephton M. A., Verchovsky A. B., Bland P. A., Gilmour I., Grady M. M., and Wright I. P. 2003. Investigating the variations in carbon and nitrogen isotopes in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 67:2093–2108.

Stelzner T., Heide K., Bischoff A., Weber D., Scherer P., Schultz L., Happel M., Schrön W., Neupert U., Michel R., Clayton R. N., Mayeda T. K., Bonani G., Haidas I., Ivy-Ochs S., and Suter M. 1999. An interdisciplinary study of weathering effect in ordinary chondrites from the ACFER region, Algeria. *Meteoritics & Planetary Science* 34:787–794.

Tomeoka K., Nomura K., and Takeda H. 1992. Na-bearing Ca-Al-rich inclusions in the Yamato-791717 CO carbonaceous chondrite. *Meteoritics* 27:136–143.

Wasson J. T., Yurimoto H., and Russell S. S. 2001. ^{16}O-rich melilite in CO3.0 chondrites: Possible formation of common, ^{16}O-poor melilite by aqueous alteration. *Geochimica et Cosmochimica Acta* 65:4539–4549.

Wood J. A. 1967. Chondrites: Their metallic minerals, thermal histories, and parent planets. *Icarus* 6:1–49.

Willis J. and Goldstein J. I. 1981. The revision of metallographic cooling rate curves for chondrites (abstract). Proceedings, 12th Lunar and Planetary Science Conference. pp. 1188–1190.

Young E. D., Ash R. D., England P., and Rumble D. 1999. Fluid flow in chondritic parent bodies: Deciphering the compositions of planetesimals. *Science* 286:1331–1335.