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Planetesimal sulfate and aqueous alteration in CM and CI carbonaceous chondrites

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Abstract—Water-soluble sulfate salts extracted from six CM chondrites have oxygen isotope compositions that are consistent with an extraterrestrial origin. The $\Delta^{17}\text{O}$ of sulfate are correlated with previously reported whole rock $\delta^{18}\text{O}$ and with an index of meteorite alteration, and may display a correlation with the date of the fall. The enrichments and depletions for $\Delta^{17}\text{O}$ of water-soluble sulfate from the CM chondrites relative to the terrestrial mass dependent fractionation line are consistent with sulfate formation in a rock dominated asteroidal environment, and from aqueous fluids that had undergone relatively low amounts of oxygen isotope exchange and little reaction with anhydrous components of the meteorites. It is unresolved how the oxidation of sulfide to sulfate can be reconciled with the inferred low oxidation state during the extraterrestrial alteration process. Oxygen isotope data for two CI chondrites, Orgueil and Ivuna, as well as the ungrouped C2 chondrite Essebi are indistinguishable from sulfate of terrestrial origin and may be terrestrial weathering products, consistent with previous assertions. Our oxygen isotope data, however, can not rule out a preterrestrial origin either. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

Primitive meteorites preserve information about the gas and dust that accreted to form planetesimals during the first few million years of the solar system, as well as about the aqueous processes in these planetesimals. The presence of salts, hydrous minerals and carbonates in CI and CM chondrites are generally believed to result from alteration of solar nebula primary minerals by liquid water (Fuchs et al., 1973; Bunch and Reid, 1975; Clayton and Mayeda, 1984; Johnson and Prinz, 1973; Browning et al., 1996; Brearley and Prinz, 1992); however, there are arguments that suggest that some salts may have formed on Earth during the time that some meteorites were curated (Gounelle and Zolensky, 2001).

The oxygen isotopic compositions and oxygen isotopic evolution of the aqueous fluids that produced the alteration have been deduced using models that incorporate oxygen isotopic data for bulk meteorite samples, mineral separates, and matrix concentrates. Analyses of bulk meteorites (Rowe et al., 1994; Clayton and Mayeda, 1999) indicate that the CI chondrites have higher $\delta^{18}\text{O}$ values ($\delta^{18}\text{O} = [(^{18}\text{O}_{\text{sample}}/^{16}\text{O}_{\text{sample}})/(^{18}\text{O}_{\text{SMOW}}/^{16}\text{O}_{\text{SMOW}})] - 1$) than other chondrites and are slightly enriched in ^{17}O relative to the terrestrial fractionation line (TFL) while CM chondrites typically have oxygen isotopic compositions below the TFL. The oxygen isotopic evolution of the aqueous fluid phase may have progressed from a composition enriched in ^{17}O to a composition depleted in ^{17}O relative to the TFL (Clayton and Mayeda, 1984, 1999). The $\delta^{18}\text{O}$ of the fluid phase is inferred to evolve from more to less ^{18}O enriched compositions.

In this study we examine the oxygen isotopic composition of

water-soluble sulfate from a collection of CM chondrites falls, two CI chondrites, and one ungrouped C2 chondrite to assess whether it has a terrestrial or preterrestrial origin, and its potential to preserve information about the fluids that were present at the time of sulfate formation. Sulfate is likely to have formed by oxidation reactions of sulfides in the presence of water, and once formed, the sulfate ion is slow to exchange oxygen with water and other oxygen-bearing species (Gamsjager and Murmann, 1983). The important distinction here between sulfate minerals and other oxygen-bearing species such as carbonate, is that they do not readily exchange oxygen with water at low to neutral pH and low temperature, even when this water causes the sulfate minerals to dissolve and reprecipitate. As a consequence, when sulfide oxidizes to form sulfate, this sulfate has a good potential to preserve an isotopic record of the oxidation process. Sulfate thus formed can precipitate as secondary minerals that can be later dissolved, remobilizing the sulfate, and ultimately precipitated as new minerals or mineral overgrowths. In contrast, minerals like calcite have the potential to preserve their oxygen isotopic compositions only until the point they are dissolved. The dissolution-reprecipitation process resets the oxygen isotopic compositions of carbonates, but does not affect the isotopic composition of the sulfate ions, unless the pH is very acidic (<2), or the temperatures are high $>100^\circ\text{C}$ (Van Stempvoort and Krouse, 1994). In this study, we advance the hypothesis that sulfate preserves information about the oxygen isotopic composition of the fluids at the time of sulfide oxidation. We also argue that the sulfate preserves information about aqueous alteration processes that occurred on the CM parent body and that this information is distinct and complementary to existing information obtained by analysis of bulk meteorite data, silicate and oxide mineral separates, matrix concentrates, and carbonates. Sulfate has the potential to be soluble and therefore more

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mobile in the fluid phase than other oxygen-bearing phases, and the timing of sulfate formation from sulfide is not necessarily synchronous with that of the silicates, carbonates, and other oxygen-bearing phases. This combination of characteristics makes sulfate a carrier of the signature of water, a potentially mobile species that carries the oxygen isotopic imprint of the fluids from the time at which it formed.

2. METHODS

Sulfate was extracted from 1 g of crushed meteorite samples in three consecutive rinses in 50 mL polypropylene centrifuge tubes with 10 mL of Millipore water. Each rinse was sonicated and left for three days at room temperature for sulfate to dissolve. After centrifugation and filtration with a 0.22 micron nylon filter, the three solutions were combined and the volume was reduced to 5 mL by heating in a beaker at 80°C overnight in a laminar flow hood. The solutions were acidified by addition of 5 drops of 0.2 M HCl. Three milliliters of 0.2 M BaCl₂ solution were added to precipitate BaSO₄. Each sample was centrifuged and washed several times with Millipore water, then dried overnight in a 80°C oven. The BaSO₄ was fluorinated with BrF₅ using a 25-watt CO₂ laser (Bao et al., 2000). The molecular oxygen was purified cryogenically and analyzed using a Finnigan MAT 251 mass spectrometer at the University of California, San Diego. Oxygen isotope data are reported using $\delta^{18}\text{O}$, and $\delta^{17}\text{O}$. The reference is Standard Mean Ocean Water (SMOW), and is expressed in parts per thousand (‰). The TFL is empirically defined by measurements of terrestrial silicate minerals and waters (Miller, 1999, 2002). We also report

$$[\Delta^{17}\text{O} = \delta^{17}\text{O} - 1000 \times ((1 + \delta^{18}\text{O}/1000)^{0.5247} - 1)]$$

which is the deviation from the TFL defined above. Measurements of $\delta^{18}\text{O}$ were also undertaken using an elemental analyzer at 1450°C (TCEA) coupled to a Finnigan MAT 253 at Louisiana State University. Our measurement uncertainties (1σ) are approximately $\pm 0.5\text{‰}$ for $\delta^{18}\text{O}$ undertaken using the TCEA, and $\pm 0.1\text{‰}$ for $\Delta^{17}\text{O}$ using the laser fluorination techniques. The uncertainties for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ associated with the laser fluorination procedure are larger, estimated to be $\pm 0.8\text{‰}$, and $\pm 0.4\text{‰}$, respectively.

3. RESULTS

We present the results of our oxygen isotope analyses of water-soluble sulfate in Table 1. The $\delta^{18}\text{O}$ values of sulfate range from 4.5‰ to 9.7‰, and the $\Delta^{17}\text{O}$ values range from -0.23‰ to $+1.18\text{‰}$. The $\Delta^{17}\text{O}$ values we measure for sulfate from CM chondrites are more positive than those reported for both whole rock analyses and analyses of other minerals from these CM chondrites (-0.67‰ to -3.07‰) (Clayton and Mayeda, 1984, 1999; Rowe et al., 1994; Benedix et al., 2003). The $\Delta^{17}\text{O}$ values of sulfate from CI chondrites are generally less positive than observed for bulk samples of CI chondrites (0.39‰ to 0.47‰) (Clayton, 1999).

The $\Delta^{17}\text{O}$ of water-soluble sulfates from CM chondrites are inversely proportional to whole rock $\delta^{18}\text{O}$ values (Fig. 1), and are linearly correlated with the mineralogic alteration index (MAI) (Browning et al., 1996) (Fig. 2). It has also been sug-

Table 1. Results of oxygen isotope analyses.^a

Meteorite	Sulfate	
	$\delta^{18}\text{O}$	$\Delta^{17}\text{O}$
CM		
Murchison USNM 5453	9.5	0.78
Murray USNM 1769	9.7	0.56
Mighei USNM 2917	6.3	0.19
Nogoya ASU	(5.5)	-0.04
Cold Bokkeveld ASU	4.5	-0.23
Banten USNM 6017	(10.1)	1.18
CI		
Orgueil USNM 1104	(5.4)	-0.12
Ivuna USNM 2478	(4.8)	-0.08
Ungrouped C2		
Essebi USNM 3200	9.3	-0.07

^a All units are ‰ relative to SMOW. $\delta^{18}\text{O}$ values determined by TCEA. Values in parentheses were determined by laser fluorination. $\Delta^{17}\text{O} = \delta^{17}\text{O} - 1000 \times ((1 + \delta^{18}\text{O}/1000)^{0.5247} - 1)$.

gested that there may be a relationship between $\Delta^{17}\text{O}_{\text{sulfate}}$ and residence time on Earth, but a similar correlation is also observed between whole rock $\delta^{18}\text{O}$ values for the same meteorites and fall date (Fig. 3). Banten does not fall on the array and it is also noted that Cold Bokkeveld, has a negative $\Delta^{17}\text{O}$ (-0.23‰) that lies more than 4σ below the terrestrial fractionation line.

4. DISCUSSION

4.1. Origin of Sulfate

The CM chondrites preserve evidence of ancient aqueous alteration in the form of an abundant phyllosilicate-rich matrix with sulfates (mostly gypsum), carbonates (calcite, aragonite, and dolomite), sulfides (troilite, pentlandite, pyrrhotite), minor tochilinite, and oxides (magnetite) (McSween, 1977). The CI

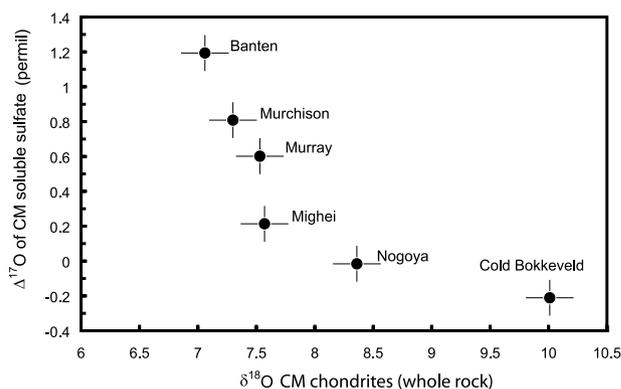


Fig. 1. Plot of $\Delta^{17}\text{O}$ of sulfate vs. $\delta^{18}\text{O}$ values for whole rock analyses of Clayton and Mayeda. The $\Delta^{17}\text{O}$ of sulfate is inversely proportional to the $\delta^{18}\text{O}$ whole rock values, being most positive for meteorites with the lowest $\delta^{18}\text{O}$. Clayton and Mayeda (1999) suggest that CM chondrites with higher $\delta^{18}\text{O}$ have interacted with greater amounts of high $\delta^{18}\text{O}$ water. The inverse relationship between $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ suggests that samples that contain sulfate with higher $\Delta^{17}\text{O}$ have interacted with less water. ^{17}O -enrichments and depletions are defined by $\Delta^{17}\text{O}$, which is the deviation from the TFL in $\delta^{17}\text{O}$ expressed in permil (‰) at a given value of $\delta^{18}\text{O}$.

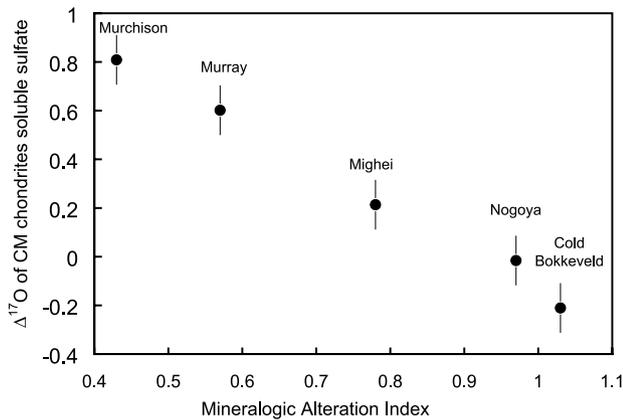


Fig. 2. Plot of $\Delta^{17}\text{O}$ vs. MAI (mineralogic alteration index) of Browning et al. (1996). This plot illustrates the relationship between sulfate oxygen isotope composition and previously published indicators of aqueous alteration for the CM chondrites. $\Delta^{17}\text{O}$ is positive for meteorites with the lowest MAI. The sulfate with higher $\Delta^{17}\text{O}$ is observed for meteorites that have undergone lesser amounts of aqueous alteration.

chondrites also preserve abundant evidence for aqueous alteration in the form of a phyllosilicate matrix with secondary oxides, carbonates, sulfate, and isolated grains of olivine and

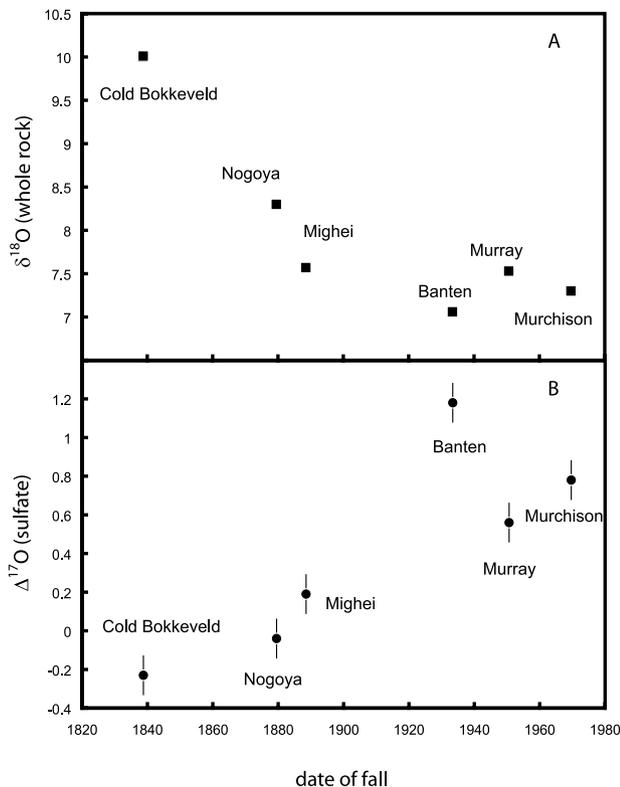


Fig. 3. (A) Plot of $\delta^{18}\text{O}$ whole rock vs. date of fall and (B) plot of $\Delta^{17}\text{O}$ for sulfate vs. date of fall. The plots are presented to examine the possibility of a correlation between date of fall and sulfate $\Delta^{17}\text{O}$ as suggested by Benedix and Bland (2004). We do not think a correlation is significant despite an R^2 of 0.7 because similar relationships are also observed for $\delta^{18}\text{O}$ whole rock vs. date of fall.

pyroxene (Dufresne and Anders, 1962; Richardson, 1978; Kerridge and Bunch, 1979; Fredriksson and Kerridge, 1988; Tomooka and Buseck, 1988; Brearley and Prinz, 1992; Brearley and Jones, 1998; Johnson and Prinz, 1993; Zolensky et al., 1993; Endress et al., 1996).

The question of whether sulfate could have a preterrestrial origin is not a trivial one. The nonzero $\Delta^{17}\text{O}$ in these samples suggests a preterrestrial origin for sulfate, but studies of closed system aqueous alteration of likely meteoritic precursor lithologies such as those of Rosenberg et al. (2001) and Zolensky et al. (1989) do not suggest Eh-pH conditions conducive for oxidation of sulfide to sulfate. Moreover, petrographic observations support the formation of sulfide during the alteration process (Zolensky et al., 1997; Chokai et al., 2004). Rosenberg et al. (2001) did note however that higher oxidation states could be attained in an open system with hydrogen loss, but their focus was on magnetite stability which begins at slightly lower Eh than sulfate stability. It is not known whether photochemically produced radicals or other oxidized species were present in water ice that accreted during formation of the CM parent and whether these species would have been present during oxidation of sulfide. It has been documented on the basis of sulfur isotopic analyses however, that sulfonic acids of preterrestrial origin are present in Murchison (Cooper et al., 1997). Such sulfonic acids suggest the presence of sulfur in oxidation states higher than that in monosulfide and if similar processes also produced sulfate, it is hypothesized that once formed, sulfate could persist in the presence of H_2S and during the low Eh, high pH conditions inferred for the alteration process because its reduction to sulfide is kinetically inhibited.

Oxidation of sulfide since delivery to Earth and during curation is a possibility. Gounelle and Zolensky (2001) have discussed in detail the possibility of terrestrial sulfate formation and mobilization for Orgueil. Evidence has also been observed for the oxidation of sulfide to sulfate for the Noblesville ordinary chondrite that occurred within a few days of falling in 1991.

Interpretation of our oxygen isotope data bears on the question of when the sulfate in these meteorites was formed. It is well established that sulfate, even in aqueous ionic form, is kinetically inhibited from oxygen isotope exchange with water unless temperature significantly exceed 100°C or the pH falls below a value of 2 (Gamsjager and Murmann, 1983; Van Stempvoort and Krouse, 1994). This is a significant difference in the behavior of sulfate relative to carbonate, because it means that the oxygen isotopic composition of sulfate will be preserved even if the sulfate minerals are dissolved, the sulfate ions are mobilized in aqueous phase, and reprecipitated as other sulfate minerals. This approach forms the foundation for our extraction chemistry, and for the interpretations that we make below.

The positive and negative $\Delta^{17}\text{O}$ values that we observe for sulfate are inconsistent with oxidation of indigenous sulfide by terrestrial waters. On earth, oxidation of sulfide occurs predominantly by a variety of biologic and physical processes that occur in aqueous phase (Aller and Rude, 1988; Schippers and Jorgensen, 2002), and produce sulfate with $\Delta^{17}\text{O}$ values of ~ 0 (Bao et al., 2000). Some terrestrial sulfate of atmospheric origin has been observed however with small positive $\Delta^{17}\text{O}$ values, but this sulfate is thought to be formed by transfer of a mass-

independent signal from ozone and hydrogen peroxide during the aqueous phase oxidation of SO_2 in rainwater droplets (Savarino et al., 2000). The experimental studies of Savarino et al. (2000) also indicate that the presence of even minor amounts of iron in the aqueous solutions destabilizes aqueous phase ozone and hydrogen peroxide, causing any product sulfate to be mass-dependent with respect to the water. The possibility that the sulfate in the meteorite fragments contain sulfate that was deposited from aerosol sources is ruled out on the basis of the amount of sulfate ($>10 \mu\text{mol}$) extracted from the $\sim 1 \text{ g}$ samples of meteorite. We suggest that these considerations make it highly unlikely that there is a path for production with nonzero (positive and negative) $\Delta^{17}\text{O}$ values by atmospheric oxidation of sulfide during meteorite curation.

We interpret the positive and negative nonzero $\Delta^{17}\text{O}$ values of Banten, Murray, Murchison, Mighei, and Cold Bokkeveld to indicate that a significant proportion of the sulfate in these meteorites has an extraterrestrial origin, lending support to the hypothesis that salt-rich fluids were responsible for alteration of the CM parent body (McSween, 1977; Riciputi et al., 1994). On the basis of nonzero $\Delta^{17}\text{O}$ values we do not rule out the possibility that this sulfate contains a terrestrial component. For the remainder of the discussion we will explore the implications of our data for preterrestrial alteration conditions.

4.2. Relationship between Sulfate $\Delta^{17}\text{O}$ and Alteration

We have argued that the occurrence of nonzero $\Delta^{17}\text{O}$ of sulfate requires a parent body source of sulfate and that its most likely formation is via sulfide oxidation processes involving the same aqueous fluids that are responsible for the meteoritic alteration. The relationship between $\Delta^{17}\text{O}$ values of water-soluble sulfate and whole rock $\delta^{18}\text{O}$ values (Fig. 1) suggests a link between the sulfate formation and the meteorite alteration processes. This link may be reinforced by a similar relationship between $\Delta^{17}\text{O}$ of CM chondrites and the MAI (Fig. 2), but recent studies have suggested that this measure of alteration may reflect in part terrestrial processes (Benedix and Bland, 2004), raising questions about the origin of the correlations that we see. The ultimate answer to this puzzle may come only after the occurrence of new falls of CM2 chondrites with varying degrees of aqueous alteration.

The $\Delta^{17}\text{O}$ value of $+1.18 \text{ ‰}$ in Banten is the highest yet measured for a component of CM chondrites and places a new limit on the lowest possible $\Delta^{17}\text{O}$ of water on the CM parent asteroid. The more extensively altered samples have lower sulfate $\Delta^{17}\text{O}$ values. A similar trend exists for water-soluble or bulk carbonates in many of the same CM chondrites (Benedix et al., 2003), however the sulfates systematically exhibit higher $\Delta^{17}\text{O}$ values by $\sim 1.5 \text{ ‰}$, and we infer that this indicates that sulfide oxidation occurred with more primitive fluids than were responsible for the ultimate meteorite alteration.

Two basic models for aqueous alteration on carbonaceous chondrite parent bodies exist. The closed alteration model (Clayton and Mayeda, 1984, 1999) infers that water and rock possess different initial $\Delta^{17}\text{O}$ values and interact without significant fluid transport. The $\Delta^{17}\text{O}$ of minerals produced by the aqueous alteration reflects the reaction progress for a given water-rock ratio. The open system model (Young et al., 1999, 2003; Young and Ash, 2000) incorporates fluid flow which

occurs through capillaries on the parent body. The isotopic composition of minerals produced during alteration depend on the degree of equilibration between the water and the rocks it encounters throughout the entire alteration process. The interpretation of our data are model-dependent, and the implications differ in each case.

In the closed model, the isotopic variation observed for the CM chondrites and for other carbonaceous chondrite groups reflects low temperature interactions between aqueous phases, either ice or water and anhydrous phases in the meteorite parent bodies. The model features an aqueous phase evolving along a straight line from a high $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ composition towards a low $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ composition. The lower composition is inferred to be related to the phyllosilicate matrix presently found in the meteorites by a mass-dependent isotopic fractionation of $\sim 12.0 \text{ ‰}$ for $\delta^{18}\text{O}$ and $\sim 6.2 \text{ ‰}$ for $\delta^{17}\text{O}$.

Our measured $\Delta^{17}\text{O}$ values of CM chondrite sulfate (-0.23 to $+1.18 \text{ ‰}$) fall between the $\Delta^{17}\text{O}$ values of CM chondrite matrix (-1.61 and -2.30 ‰) and the $\Delta^{17}\text{O}$ values inferred for the initial water ($+2.7$ and $+3.1 \text{ ‰}$) of Clayton and Mayeda (1999). In the context of the Clayton and Mayeda (1999) model, we interpret the CM chondrite sulfate $\Delta^{17}\text{O}$ values to indicate that aqueous oxidation of sulfide occurred before the full extent of water-rock reaction (i.e., before the $\Delta^{17}\text{O}_{\text{water}}$ evolved to its final composition— $\Delta^{17}\text{O}_{\text{matrix-final}}$). Our oxygen isotope data for Banten, Murray, Murchison, Mighei, and Cold Bokkeveld are consistent with the preferred trajectory proposed by Clayton and Mayeda (1999) for the oxygen isotopic evolution of water for the CM chondrites, but we note that this does not take into the mass-dependent fractionation that may occur between sulfate and water when sulfate is formed by oxidation of sulfide and if this fractionation were large, it would disrupt the apparent agreement of our data with this model isotopic evolution of the aqueous phase. On Earth the kinetics of sulfate formation are known to produce sulfate-water fractionations of varying magnitude, ranging from values near 0 to greater than 15 ‰ (Van Stempvoort and Krouse, 1994), making it difficult to use the $\delta^{18}\text{O}_{\text{sulfate}}$ to constrain the evolution of $\delta^{18}\text{O}_{\text{water}}$.

Our interpretation in the context of the open model (Young et al., 1999, 2003; Young and Ash, 2000) is different. Here, the oxygen isotopic data for CM chondrites, and other carbonaceous chondrites could be produced in a system where fluids migrated through the parent body. The high $\Delta^{17}\text{O}$ values of sulfate relative to other phases in the rock, and the negative correlation between $\Delta^{17}\text{O}$ sulfate and MAI are indicators of sulfate growth in liquid water in physical regions of the flow system where the oxygen of the water was exchanged with rock containing enough original oxygen to control the oxygen isotope ratios of the fluid. Such regions in a flow system, called rock dominated regions, are characterized by decreases in $\Delta^{17}\text{O}$ of water with progressive alteration. This is in contrast to “water dominated” regions where the rock has been so altered as to lose its capacity to influence the isotopic composition of the pore fluid. In this model, the negative correlation between $\Delta^{17}\text{O}$ of water, reflected in secondary minerals like sulfates, and progress of alteration reactions can therefore be interpreted to mean that CM rocks represent the rock-dominated portions of hydrothermal systems in parent bodies. In this interpretation, the CI sulfates should record water in water-dominated portions

of parent body hydrothermal systems (Young et al., 1999, 2003; Young and Ash, 2000). The fluid flow interpretation predicts that the water $\Delta^{17}\text{O}$ values recorded by the sulfates represent waters that have evolved significantly from the original ices from which they ultimately were derived, but does not carry the same implications for the timing of sulfate formation. This is because any given packet of water representing ice melt on the parent body will pass through, and exchange oxygen with, a large column of rock before significant progress of mineralogical alteration reactions (Young et al., 2003). The model allows inhomogeneous isotopic compositions, so that late packets of fluid may have a higher $\Delta^{17}\text{O}$ than early fluids.

In the case of CI chondrites, the sulfate $\Delta^{17}\text{O}$ from Ivuna (0.05‰) and Orgueil (−0.1‰), are indistinguishable from the TFL within measurement uncertainties, and are lower than the $\Delta^{17}\text{O}$ of the matrix, whole rock, magnetite, and carbonates of the CI chondrite group (Clayton, 1999; Leshin, 2001; Rowe, 1994). This makes interpretations about the origin of CI chondrite sulfate problematic. It is possible that the formation of sulfate in the CI chondrites studied here occurred since they fell to Earth. Clear evidence and compelling arguments indicate that the formation of sulfate veins in one of the meteorites we examined (Orgueil) occurred during curation (Gounelle, 2001). This does not rule out the oxidation of sulfide to sulfate ions and salts before delivery to Earth. However it implies that these salts, if present, were remobilized during the time the meteorite was in curation. We note that both $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of sulfate in Orgueil and Ivuna also continue the array formed by the CM chondrite sulfate and could be explained by extraterrestrial fluid evolution related to aqueous processes on the CI parent body, possibly another C-type asteroid. The data are allowed by the open system models because these models predict that different parts of the parent body and the water that they contain evolve to different oxygen isotopic compositions ($\delta^{17}\text{O}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$) (Young et al., 1999, 2003). Our data are consistent with a case where fluids with low $\Delta^{17}\text{O}$ migrated to regions of higher $\Delta^{17}\text{O}$. The data cannot be explained in the context of the closed model because it does not predict waters with more negative $\Delta^{17}\text{O}$ than that of the final rock. We do not however consider our two CI chondrite sulfate data to be sufficient to distinguish between a preterrestrial origin in an open system or a secondary (terrestrial) source of sulfate.

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