Mass independent sulfur isotope signatures in CMs: implications for sulfur chemistry in the early solar system

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Abstract

We have investigated the quadruple sulfur isotopic composition of inorganic sulfur-bearing phases from 13 carbonaceous chondrites of CM type. Our samples include 4 falls and 9 Antarctic finds. We extracted sulfur from sulfides, sulfates, and elemental sulfur (S^0) from all samples. On average, we recover a bulk sulfur (S) content of 2.11 ± 0.39 wt.% S (1σ). The recovered sulfate, S^0 and sulfide contents represent $25 \pm 12\%$, $10 \pm 7\%$ and $65 \pm 15\%$ of the bulk S, respectively (all 1σ). There is no evidence for differences in the bulk S content between falls and finds, and there is no correlation between the S speciation and the extent of aqueous alteration. We report ranges of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values in CMs that are significantly larger than previously observed. The largest variations are exhibited by S^0 , with $\Delta^{33}\text{S}$ values ranging between $-0.104 \pm 0.012\text{‰}$ and $+0.256 \pm 0.018\text{‰}$ (2σ). The $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios of S^0 are on average -3.1 ± 1.0 (2σ). Two CMs show distinct $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios, of $+1.3 \pm 0.1$ and $+0.9 \pm 0.1$. We suggest that these mass independent S isotopic compositions record H_2S photodissociation in the nebula. The varying $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios are interpreted to reflect photodissociation that occurred at different UV wavelengths. The preservation of these isotopic features requires that the S-bearing phases were heterogeneously accreted to the CM parent body. Non-zero $\Delta^{33}\text{S}$ values are also preserved in sulfide and sulfate, and are positively correlated with S^0 values. This indicates a genetic relationship between the S-bearing phases: We argue that sulfates were produced by the direct oxidation of S^0 (not sulfide) in the parent body. We describe two types of models that, although imperfect, can explain the major features of the CM S isotope compositions, and can be tested in future studies. Sulfide and S^0 could both be condensates from the nebula, as the residue and product, respectively, of incomplete H_2S photodissociation by UV light (wavelength < 150 nm). This idea requires that FeS formation and the S^0 condensation co-occur. As an alternative, ice accretion to the CM parent body could allow the delivery of S-MIF in CMs. In that case, sulfides would have been the only S-bearing condensate in CM precursors, and S^0 would have been derived from the oxidation of H_2S trapped in ices, after its photodissociation at low temperature (< 500 K) in the nebula. In our models, the observations of H_2S UV photodissociation is required to occur at the disk surface, and allowed in nebular environments with canonical C/O ratios. Vertical motions in the disk would redistribute phases that condensed at high altitude to the midplane, where they accreted in the phases that make up the chondritic matrix.

1. Introduction

The sulfur (S) isotopic compositions of meteorites reflect a complex collection of nucleosynthetic, physical, and chemical processes that occurred both in nebular and asteroidal environments. The magnitude of mass-independent S isotope signatures in meteorites is typically sub-permil, nowhere near as large as those seen for oxygen. However, a growing body of evidence suggests that they are widespread, and these signatures have largely been interpreted to reflect photochemical reactions (Cooper et al., 1997, Farquhar et al., 2000a; Rai et al., 2005; Chakraborty et al., 2013; Antonelli et al., 2014).

Subtle but widespread $\Delta^{33}\text{S}$ variations have been reported in achondrites and iron meteorites, with $\Delta^{33}\text{S}$ variations extending up to 0.050‰ for bulk S (Farquhar et al. 2000a, Rai et al. 2005, Antonelli et al. 2014, DeFouilloy et al. 2016). Aubrites carry only small ^{33}S enrichments relative to Canyon Diablo Troilite (CDT) for their bulk S, with a mean $\Delta^{33}\text{S}$ value of $+0.015 \pm 0.006$ ‰ (n=6, Rai et al., 2005, 2σ), but an oldhamite (CaS) mineral separate from the Norton County aubrite was reported to have a $\Delta^{33}\text{S}$ value of $+0.161 \pm 0.012$ ‰ (2σ , Rai et al., 2005). DeFouilloy et al. (2016) reported near zero to significantly negative $\Delta^{33}\text{S}$ values in oldhamites (CaS) from aubrites, down to -0.085 ± 0.020 ‰ (2σ) for Norton County. Because the Rai et al. (2005) result constitutes the highest $\Delta^{33}\text{S}$ value in the meteorite inorganic S record, oldhamite was suggested as a carrier for S-MIF in aubrites and other meteorites (Rai et al. 2005). Oldhamite being a relatively refractory mineral would have acquired its S-MIF signatures in the inner, hotter and reducing parts of the nebula (Rai et al., 2005). After condensation, a heterogeneous distribution of CaS grains in the precursors of achondrites could account for their variable $\Delta^{33}\text{S}$ values (Rai et al., 2005). Antonelli et al. (2014) also suggested that refractory sulfides, such as oldhamite, would have acted as carriers of S-MIF to iron meteorite precursors.

In contrast to the achondrites, the chondrites have been considered to preserve evidence for predominantly mass dependent sulfur. Gao and Thiemens (1993a) reported mass dependent S isotope ratios in seven carbonaceous chondrites, three of which were CM chondrites (Mighei, Allan Hills (ALH) 84029, and Murchison), and observations of S-MIF signature have been considered to be isolated occurrences. One of these observations includes S-MIF identified in a minor component of the CV chondrite

Allende (Rees and Thode, 1977: $\Delta^{33}\text{S}=+1.1\pm0.1\text{‰}$ 2σ). A second observation is for the sulfonic organic acids from the Murchison CM chondrite that carry $\Delta^{33}\text{S}$ values between $-0.40\pm0.05\text{‰}$ and $+2.00\pm0.05\text{‰}$ (Cooper et al., 1997, 2σ). Smaller magnitude S-MIFs were also observed in chondrules of the Djahala ordinary chondrite (Rai and Thiemens, 2007: $\Delta^{33}\text{S}=+0.10\pm0.03\text{‰}$, 2σ). Rees and Thode (1977) considered their observation as a possible nucleosynthetic anomaly, whereas Cooper et al., (1997) suggested that the organic acids S isotopic compositions reflected the composition of photo-processed interstellar S. Rai and Thiemens (2007) envisioned a very different scenario that tied anomalies in chondrules to those in achondrites. The X-wind astrophysical model (Shu et al., 1997) was suggested as a way to redistribute CaS grains from a region close to the Sun where they formed (and captured S-MIF) to other parts of the early solar nebula where the precursors to achondrites formed (Rai et al. 2005). This model was favoured to account for the $\Delta^{33}\text{S}$ value in sulfides extracted from Djahala (H3.8) chondrules ($+0.10\pm0.03\text{‰}$, 2σ), because it provides a “mechanism for chondrule precursors to be irradiated with high energy UV light from the early Sun” (Rai and Thiemens, 2007).

The X-wind model is, however, hard to reconcile with several major features of chondrites. For example, it predicts highly oxidizing formation conditions for CAIs in the X-region, due to the removal of H_2 (Shu et al., 2001). However, oxygen barometers of CAI formation indicate a gas of solar composition (Simon et al., 2007). In addition, the X-wind model does not allow chondrules to form from material containing primary S, as the starting temperatures experienced by the precursors of chondrules would be too high (~ 1100 K in Shu et al., 2001, which is ~ 400 K above the FeS condensation temperature). Primary and secondary Fe sulfides are, however, common phases in chondrules (i.e., Tachibana and Huss, 2005; Marrocchi and Libourel, 2013). For more details, the reader is referred to review contributions (Krot et al., 2009; Desch et al., 2010).

Carbonaceous chondrites of CM type are often considered as among the most primitive chondrites (e.g., Huss et al., 2003), although they have clearly experienced varying degree of aqueous alteration (e.g., Rubin et al., 2007; Alexander et al., 2013; Howard et al., 2015 and references therein). The CMs have amongst the highest bulk S contents of any chondrite group (Dreibus et al., 1995; Burgess et al., 1991), and host various S-bearing phases, including Ni-Fe sulfides and tochilinite, elemental S (S^0), and sulfates (Airieau et al. 2005,

Bullock et al. 2010, Gao and Thiemens, 1993, Rubin et al. 2007). These meteorites may thus have recorded and preserved the complex S chemistry that occurred in the nebula and during parent body processes. Here, we report S isotope data for 13 CM carbonaceous chondrites that preserve anomalous $\Delta^{33}\text{S}$ values. We show that a photolytic origin in the hotter, inner parts of the solar nebula, combined with a mixing process such as that provided by the X-wind does not explain the occurrence of S-MIF in CMs, and may not be required to account for S-MIF in achondrite parent bodies. Our data support the idea that S-MIF was produced by H_2S photolysis under low temperature conditions near the surface of the disk, and imply that S-MIF can potentially be produced at various heliocentric distances. We discuss whether it could constitute a viable alternative to the idea of a refractory high-temperature sulfide condensate such as oldhamite as the origin of the signature in the parent bodies of achondrites and iron meteorites as well as in chondrules.

2. Samples

Thirteen meteorites were studied here, including four observed falls and nine Antarctic finds (Table 1). Samples were chips from the interiors of the meteorites taken well away from the fusion crust to minimize the effects of terrestrial contamination and modification during atmospheric entry. Other than the Antarctic samples allocated by the Johnson Space Center that were stored under N_2 atmosphere for curation and subsequently in desiccators, no special precautions were taken with regard to sample storage history. The samples were selected to cover the full range of CM aqueous alteration (Table 1). These CMs were previously divided into unheated and heated meteorites based on their water contents and hydrogen isotopic composition (Alexander et al., 2013). Here, 12 unheated CMs and one heated CM were investigated.

Samples of meteorite falls include Murchison and Cold Bokkeveld (allocated by the British Natural History Museum), as well as Banten and Nogoya (allocated by the Smithsonian Institution). With the exception of Murchison and Cold Bokkeveld, all the processed powders were previously investigated for their bulk hydrogen, nitrogen and carbon isotope compositions (Alexander et al., 2012, 2013). The H, N and C isotope compositions of their insoluble organic matter (IOM) (Alexander et al., 2007, 2010), as well as their carbonate C and O isotope composition (Alexander et al., 2015) have also been reported for most of the samples. The H contents and isotope compositions (Alexander et al., 2013) and bulk mineralogies

(Howard et al., 2015) of the samples have been used to place the samples on an alteration sequence. Murchison and Cold Bokkeveld were also investigated by Alexander et al. (2007, 2012, 2013, 2015), but on different samples.

The samples were crushed in a steel percussion mortar and then ground in an agate mortar to pass through 100-150 μm sieves. About 200 mg aliquots were taken from the ~ 1000 mg powdered samples that had been previously studied by Alexander et al. (2012, 2013, 2015).

3. Methods

3.1 Extraction

Various authors have reported the occurrence of S^0 in CIs and CMs, in addition to ubiquitous sulfides. Monster et al. (1965), Kaplan and Thode (1966) and Gao and Thiemens (1993) used wet chemistry techniques to recover S^0 . The main strategy these studies employed was to process the samples in organic solvents to selectively dissolve S^0 . Burgess et al. (1991) used a stepped combustion technique to survey the relative and absolute abundances of S^0 in various carbonaceous chondrites (CI, CM and CR). Sulfates have also been previously observed in carbonaceous chondrites, especially in CMs. Fuchs et al. (1973) observed gypsum plates in both Murchison and Cold Bokkeveld. Although petrographic studies of CMs report sulfides to be the dominant (if not the exclusive) observed S-bearing phase (e.g., Bullock et al., 2005, 2010), Gao and Thiemens (1993) report sulfate as being the dominant S-bearing pool in CMs. Hence, we developed an extraction protocol in anticipation of the complex S speciation in CMs. We present here a technique for redox-specific S extraction out of CMs that allows for determination of the S speciation, abundances and isotopic compositions for three recovered S-pools: S^0 , sulfate, and sulfide.

We used sequential extraction techniques to extract S from these three pools. Organic S was not the target of this study, and will not be further discussed. The protocol is summarized in Fig. 1 and is described below. Samples were first processed in N_2 -flushed Milli-Q water for 24 hours at room temperature to dissolve sulfate and soluble organic compounds. After centrifugation and extraction of the water, we added BaCl_2 to the water solutions leading to the precipitation of BaSO_4 from dissolved sulfate. This step yielded the equivalent of from 1100 ± 100 ppm S (MacKay Glacier (MCY) 05230) to 12900 ± 100 ppm S (Pecora Escarpment (PCA) 91084). For 10 of the 13 samples, the sulfate contents were more tightly constrained to

164 4500-6000 ppm S. After rinsing with Milli-Q water, this extraction was repeated and yielded non-
165 detectable (< 50 ppm) sulfate in the repeat, indicating that the first extraction was quantitative. It also
166 indicates that our protocol does not lead to sulfate formation via sulfide oxidation, as it would otherwise
167 yield significant SO_4^{2-} amounts in the repeat as well. The S in our BaSO_4 precipitates was then reduced to
168 H_2S and recovered as silver sulfide (Ag_2S) using the standard technique described by Thode et al. (1961).

169 Elemental sulfur is insoluble in water at room temperature (19 ± 6 nM; Boulegue, 1978). After rinsing,
170 the rock samples were processed in N_2 -flushed ethanol (reagent grade, anhydrous 200 proof) for 72 hours
171 at room temperature to extract S^0 . The ethanol solutions then underwent reaction with a sub-boiling
172 ($\sim 80^\circ\text{C}$) 5N HCl solution for 1 hour. At this step, any hypothetical ethanol-soluble, acid-volatile sulfide
173 phases would be converted into H_2S and recovered as Ag_2S . This step, however, only yielded blank level
174 amounts of S for all samples (< 1 ppm S), ruling out the occurrence of any such phases. The solutions were
175 then processed in sub-boiling $\text{CrCl}_2 + \text{HCl}$ solutions for 3 hours using the standard technique described by
176 Canfield et al. (1986), which quantitatively reduces S^0 to H_2S via the oxidation of Cr^{2+} to Cr^{3+} and allows for
177 the recovery of H_2S as Ag_2S . Between 400 ± 100 ppm and 5500 ± 100 ppm S was extracted during this step,
178 with most samples yielding < 2500 ppm S. Aliquots of these ethanol extracts were also processed for
179 independent S^0 analysis via High Performance Liquid Chromatography (HPLC) with UV-detection
180 (Kamyshny et al., 2009). An Agilent 1200 HPLC system with an Agilent Eclipse XDB-C18 column (4.6 x 150
181 mm; 5 μm particle size) was utilized with an isocratic 100% HPLC-grade methanol mobile phase.
182 Calibrations for the quantification of S^0 were prepared from stock solutions of S^0 (reagent grade refined S
183 powder, 100 mesh; Sigma Aldrich) dissolved in ethanol (reagent grade, anhydrous 200 proof) over a
184 concentration range of 1-1000 μM (retention times of ca. 5.5 min with our method). The HPLC
185 determinations of S^0 matched our wet chemistry extractions across the large range of observed S
186 abundances within $\pm 10\%$ (supplementary Fig. 1 and Table 2). The convergence of these two independent
187 approaches strongly indicates that the S extracted with ethanol is predominately in the form of S^0 . We
188 further argue below that this S-bearing pool is naturally occurring S^0 in the CMs. As for the water
189 extractions, this step was repeated and did not yield any significant additional S extraction (i.e., always <
190 2% of what was extracted in the first step), indicating that the first extraction was quantitative. It also

indicates that the protocol did not lead to the formation of S^0 from sulfide oxidation, as it would otherwise lead to significant S^0 amounts in the repeat.

After rinsing with Milli-Q water, the rock samples were digested in a sub-boiling 5N HCl solution for 3 hours. H_2S was evolved from all samples (recovered as Ag_2S) and is referred to as the acid-volatile S (AVS) fraction. Such fractions are usually considered to be the products of monosulfide digestion (e.g., FeS, NiS, but not pyrite, see Canfield et al., 1986). Between 100 and 3100 ppm S were extracted at this step. For three samples, AVS extractions yielded ~ 100 ppm, which was insufficient to analyze their isotopic compositions.

Solid residues and acid solutions from the HCl treatments were then transferred to Falcon™ tubes for centrifugation. The acid solution was subsequently transferred back to the distillation apparatus, and underwent reaction with a sub-boiling $CrCl_2$ solution (after Canfield et al., 1986). H_2S was evolved for all samples and recovered as Ag_2S . This fraction is referred to as step 12. Between 200 ppm S and 1000 ppm S were extracted at this step. The solid residue of the AVS extraction was processed in N_2 -flushed ethanol (reagent grade, anhydrous 200 proof) for 72 hours at room temperature. The ethanol extracts were then processed in a sub-boiling 5N HCl solution for 1 hour. As for the first ethanol extraction steps (step 2), this never yielded detectable AVS, ruling out the occurrence of any acid volatile sulfide phases in the ethanol solutions. The solutions were then processed in sub-boiling $CrCl_2$ solution for 3 hours. Again, evolved H_2S was recovered as Ag_2S . Between 5400 ppm and 19000 ppm S was extracted, which represent roughly an order of magnitude more than in step 12. This fraction is referred to as step 13. The AVS, step 12 and step 13 extracts were analyzed separately for their S isotopic compositions, and the results are given in Table 2. These three extractions (AVS, step 12 and step 13) were pooled by mass balance and considered to represent the bulk sulfide (see below).

3.2 Isotopic Analysis

Weighed silver sulfide samples were wrapped in Al-foil and placed in Ni-reaction vessels for fluorination with at least 10 times excess of pure F_2 at 250 °C overnight. The produced SF_6 was isolated from impurities with cryogenic and chromatographic techniques, as described in Bains-Sahota and Thiemens (1988), Rumble et al. (1993) and modified by Ono et al. (2006). The volume of purified SF_6 was

then measured with a manometer, and transferred to the dual inlet of a ThermoFinnigan MAT 253 isotope ratio gas-source mass spectrometer that was used to measure ion beams at $m/z = 127+$, $128+$, $129+$ and $131+$. Once δ^nS are determined ($n = 33, 34, 36$), $\Delta^{33}S$ and $\Delta^{36}S$ are calculated ($\Delta^{33}S = \delta^{33}S - 1000[(\delta^{34}S/1000 + 1)^{0.515} - 1]$ and $\Delta^{36}S = \delta^{36}S - 1000[(\delta^{34}S/1000 + 1)^{1.90} - 1]$). The results are given in Table 3. IAEA S1 values are used to evaluate our long-term accuracy and precision on standards, and to anchor our $\delta^{34}S$ to the V-CDT scale. Analyses of the S1 standard performed along with the CM analyses yield average $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ values of $-5.28 \pm 0.09\text{‰}$, $+0.083 \pm 0.008\text{‰}$ and $-0.78 \pm 0.26\text{‰}$ ($n=13$, all 2s.d.) relative to our reference gas. Relative to the same reference gas, our CDT yield $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ values at $-4.88 \pm 0.15\text{‰}$, $-0.035 \pm 0.008\text{‰}$ and $-0.08 \pm 0.08\text{‰}$ ($n=6$, all 2 s.d.). The S isotope shift for $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ between CDT and S1 is comparable to what was obtained elsewhere (Ono et al., 2006; Labidi et al., 2012).

We use the CDT scale to anchor our $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ values. We additionally report our $\delta^{34}S$ values on the V-CDT scale to allow comparisons with other datasets also reported relative to V-CDT (e.g., terrestrial mantle-derived rocks, Labidi et al. 2013). We obtained 2σ uncertainties of 0.10, 0.012 and 0.25‰ for $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ values, respectively, for all measurements with a SF_6 amount $> 1 \mu\text{mol}$. When the SF_6 amount was $< 1 \mu\text{mol}$ ($n=4$), we obtained 2σ uncertainties of 0.10, 0.018 and 0.35‰ for $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ values, respectively (Table 3). The whole procedure of S extraction and isotope analysis was repeated once on Murchison, and twice on Cold Bokkeveld, to address sample heterogeneity at the scale of the studied powders (Table 4).

4. Results

4.1. Bulk S content

The S abundances in the five extracted S reservoirs of each sample are reported in Table 1, and shown in Fig. 2. Bulk S contents range between $1.72 \pm 0.2 \text{ wt.\% S}$ (Graves Nunataks (GRA) 98074) and $3.01 \pm 0.2 \text{ wt.\% S}$ (Dominion Range (DOM) 08013), and averages at $2.11 \pm 0.39 \text{ wt.\% S}$ (1σ). There is no evidence for differences in the bulk S content between falls and finds. We find Antarctic finds to have an average bulk S content of $2.18 \pm 0.43 \text{ wt.\%}$ ($n=9$, 1σ), whereas the finds have an average of $1.95 \pm 0.29 \text{ wt.\%}$ ($n=4$, 1σ).

4.2 Sulfur speciation

For all the studied CMs, three S pools were systematically recovered and analyzed: Sulfide, sulfate, and S^0 . The absolute abundances of each pool are given in Table 2 and shown in Fig. 2. The average sulfate content of our samples is 5400 ± 3000 ppm S (n=13), but the contents range between 1100 ± 100 ppm S (MCY 05230) to 12900 ± 100 ppm S (PCA 91084). Exclusion of these two extreme samples significantly decreases the standard deviation, leading to an average value of 5100 ± 1700 ppm S (n=11, 1σ). Fall and find sulfate contents average at 5400 ± 1200 ppm S (n=4, 1σ) and 5400 ± 3500 ppm S (n=9, 1σ), respectively. The recovered sulfate contents represent $25 \pm 12\%$ of the bulk S of the studied CM chondrites (n=13, 1σ , 6% for MCY 05230, 47% for PCA 91084).

Elemental S abundances recovered from the ethanol extractions average at 1900 ± 1400 ppm S, and range between 400 ± 100 ppm S (Lewis Cliffs (LEW) 85312) and 5500 ± 100 ppm S (Allan Hills (ALH) 84029). Fall and find S^0 contents average at 1300 ± 300 ppm S (n=4, 1σ) and 2222 ± 1600 ppm S (n=9, 1σ), respectively. These S^0 contents represent $10 \pm 7\%$ of the bulk S (n=13, 1σ , 2% for LEW 85312, 28% for ALH 84029).

Sulfides are the dominant pool in every chondrite studied here, with the exception of PCA 91084. Sulfide contents average at 13700 ± 3600 ppm S, and ranges between 9500 ± 100 ppm S (ALH 84029) and 20800 ± 100 ppm S (DOM 08013). These values represent $65 \pm 15\%$ of the bulk S (n=13, 1σ , 48% for ALH 84029, 69% for DOM 08013). Note that PCA 91084 is the only CM where sulfide is not the dominant pool – sulfide and sulfate represent 41% and 47% of its bulk S, respectively. Fall and find sulfide contents average at 12900 ± 3900 ppm S (n=4, 1σ) and 14100 ± 3700 ppm S (n=9, 1σ), respectively.

4.3 Bulk S isotope compositions

The average bulk S $\delta^{34}S$ for all CMs is $-0.08 \pm 0.44\text{‰}$ (1σ , n=13) versus our CDT estimate. The average $\Delta^{33}S$ and $\Delta^{36}S$ are $+0.021 \pm 0.071\text{‰}$ and $0.00 \pm 0.09\text{‰}$, respectively (1σ , n=13), relative to CDT. The standard deviations for $\Delta^{33}S$ indicate a much greater level of variability than reported by Gao and Thieme (1993a). Bulk S isotope compositions are plotted in Fig. 3: $\delta^{34}S$ values range from $-1.11 \pm 0.30\text{‰}$ (LEW 85312) to $+0.60 \pm 0.30\text{‰}$ (PCA 91084) relative to CDT (Fig. 3a). For $\Delta^{33}S$, bulk S values range from $-0.058 \pm 0.008\text{‰}$

(LEW 85312) and $+0.207 \pm 0.008\text{‰}$ (Murchison) relative to CDT (Fig. 3). Bulk S $\Delta^{36}\text{S}$ values range from $-0.11 \pm 0.25\text{‰}$ (PCA 91084) and $+0.22 \pm 0.25\text{‰}$ (MCY 05230) relative to CDT (Fig. 3b). Although the two CMs with significantly positive $\Delta^{33}\text{S}$ both display positive $\delta^{34}\text{S}$, there is no systematic trend between $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$. $\Delta^{36}\text{S}$ values remain within uncertainties indistinguishable from CDT, and no trends appear in a $\Delta^{33}\text{S}$ vs $\Delta^{36}\text{S}$ plot. Additionally, no systematic S isotope difference was observed between falls and finds.

4.4 S isotopic compositions of sulfide, sulfate and elemental sulfur

The S isotope compositions of the sulfide pools in the meteorites were estimated by combining the AVS, step 12 and step 13 results (section 5.1.3). The calculated CM average sulfide $\delta^{34}\text{S}$ is $-0.15 \pm 0.33\text{‰}$ (1σ , $n=13$) relative to CDT, with values for individual meteorites ranging between $-0.70 \pm 0.15\text{‰}$ (DOM 08003) and $+0.18 \pm 0.15\text{‰}$ (MCY 05230). The average CM sulfide $\Delta^{33}\text{S}$ is $+0.015 \pm 0.061\text{‰}$ (1σ , $n=13$), with values ranging between $-0.070 \pm 0.008\text{‰}$ (LEW 85312) and $+0.177 \pm 0.008\text{‰}$ (split 2, Murchison – table 4). For $\Delta^{36}\text{S}$, average CM value is $+0.04 \pm 0.11\text{‰}$ (1σ , $n=13$), with values ranging between $-0.10 \pm 0.09\text{‰}$ (LEW 87022) and $+0.22 \pm 0.23\text{‰}$ (DOM 08003). The variability in the sulfide S isotopic compositions is comparable to the variability observed for bulk S, as illustrated by the comparable (or lower) standard deviations of the average values (Table 3).

Sulfate and S^0 have S isotope compositions that are more variable than those of the sulfide. The average CM $\delta^{34}\text{S}$ for sulfate is $-1.15 \pm 1.48\text{‰}$ (1σ , $n=13$) relative to CDT, with values ranging over $\sim 6\text{‰}$ between $-4.54 \pm 0.50\text{‰}$ (LEW 85312) and $+1.65 \pm 0.50\text{‰}$ (PCA 91084). There is no systematic trend between sulfate $\delta^{34}\text{S}$ and abundance (Table 2 and 3), although PCA 91084 has both the highest $\delta^{34}\text{S}$ and the highest sulfate content ($1.75 \pm 0.50\text{‰}$ and 12900 ± 100 ppm S, respectively). PCA 91084 is the only heated CM in our suite (Alexander et al., 2012, 2013). If PCA 91084 is excluded, the CM sulfate $\delta^{34}\text{S}$ average becomes $-1.39 \pm 1.28\text{‰}$ (1σ , $n=12$), which is the lowest across the S pools in CMs. The CM average $\Delta^{33}\text{S}$ for sulfate is $+0.036 \pm 0.084\text{‰}$ (1σ , $n=13$), with values ranging between $-0.036 \pm 0.008\text{‰}$ (LEW 87022) and $+0.263 \pm 0.008\text{‰}$ (Murchison). For $\Delta^{36}\text{S}$, the CM sulfate average is -0.16 ± 0.15 (1σ , $n=13$), with values ranging between $-0.33 \pm 0.25\text{‰}$ (TIL 91722) and $+0.26 \pm 0.25\text{‰}$ (MCY 05230). Whereas the sulfate

component of PCA 91084 has an extreme $\delta^{34}\text{S}$ compared other CMs, its $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values are $+0.016 \pm 0.008\text{‰}$ and $-0.15 \pm 0.25\text{‰}$ respectively, i.e., within the range of the other CMs.

The average $\delta^{34}\text{S}$ for S^0 is $+3.06 \pm 1.63\text{‰}$ (1σ , $n=13$) relative to CDT, with values ranging between $-1.84 \pm 0.15\text{‰}$ (PCA 91084) and $+5.19 \pm 0.15\text{‰}$ (LEW 87022), representing a $\sim 7\text{‰}$ range. When all CMs are considered, no trend appears between the S^0 $\delta^{34}\text{S}$ values and contents. If PCA 91084 (the only heated CM) is excluded, the average becomes $+3.46 \pm 0.74\text{‰}$ (1σ , $n=12$), with the minimum value displayed by ALH 84029 at $+2.32 \pm 0.15\text{‰}$ ($\sim 3\text{‰}$ total range only). Elemental S is the S-bearing phase with the highest average $\delta^{34}\text{S}$. The average $\Delta^{33}\text{S}$ is $+0.016 \pm 0.113\text{‰}$, with values ranging between $-0.104 \pm 0.008\text{‰}$ (LEW 87022) and $+0.256 \pm 0.008\text{‰}$ (MCY 05230). While the S^0 pool is the least abundant S-bearing phase in our CMs, it is the pool with the highest $\Delta^{33}\text{S}$ variability. The $\Delta^{36}\text{S}$ average is $+0.159 \pm 0.172\text{‰}$ (1σ , $n=13$), with values ranging from $-0.23 \pm 0.25\text{‰}$ (PCA 91084) to $+0.39 \pm 0.42\text{‰}$ (Cold Bokkeveld, see table 4). As for sulfate, S^0 in PCA 91084 has an extreme $\delta^{34}\text{S}$ compared other CMs, but its $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values, of $+0.045 \pm 0.008\text{‰}$ and $-0.23 \pm 0.25\text{‰}$, respectively, are, within uncertainties in the range of the other CMs.

In comparison with Murchison and MCY 05230, all our meteorites lie relatively close to the origin in a $\Delta^{33}\text{S}$ vs. $\Delta^{36}\text{S}$ plot. In detail, they display $\Delta^{33}\text{S}$ values ranging between indistinguishable from CDT to significantly negative (Fig. 4 and 5). The data form a rough array with a slope of -3.9 ± 2.2 in the $\Delta^{33}\text{S}$ vs. $\Delta^{36}\text{S}$ plot (2σ , Fig. 5). Only Murchison and MCY 05230 are clearly outside of this main trend. This is also observed for their bulk S (Fig. 3b), and is a result of their sulfide, sulfate and S^0 extracts all showing large positive $\Delta^{33}\text{S}$ associated with near-zero $\Delta^{36}\text{S}$ (Fig. 5). Again, no systematic S isotope differences were observed between falls and finds.

4.5 Duplicates

The samples of Murchison and Cold Bokkeveld were of sufficient size to allow us to perform replicates of our whole S extraction protocol (Table 4). Two and three replicates were produced for Murchison and Cold Bokkeveld, respectively. Whereas the sulfate extractions yielded S contents that were consistent within 10% between replicates (and indistinguishable isotope compositions), the S^0 and sulfide extractions showed variations of up to roughly a factor of two. The $\delta^{34}\text{S}$ values of the sulfide duplicates for Murchison

remain close, $-0.02 \pm 0.30\text{‰}$ (5700 ppm S) and $+0.30 \pm 0.30\text{‰}$ (10800 ppm S), despite the factor of two difference in sulfide S contents. In contrast, $\Delta^{33}\text{S}$ variations for sulfide S are outside of four times the estimated analytical uncertainty, with values of $+0.136 \pm 0.010\text{‰}$ (5700 ppm S), and $+0.177 \pm 0.010\text{‰}$ (10800 ppm S). The $\delta^{34}\text{S}$ values of S^0 are resolvable across the two Murchison duplicates, being $+4.62 \pm 0.15\text{‰}$ (1100 ppm S) and $+2.59 \pm 0.15\text{‰}$ (2100 ppm S). In contrast, their $\Delta^{33}\text{S}$ values are indistinguishable from one another, being $+0.236 \pm 0.008\text{‰}$ (1100 ppm S) and $+0.247 \pm 0.008\text{‰}$ (2100 ppm S). These variations are significant but remain lower than the overall variations between Murchison and other CMs. In contrast with Murchison, no $\Delta^{33}\text{S}$ variability was resolved between Cold Bokkeveld duplicates (Table 4).

5. Discussion.

5.1 Evaluation of our S-extraction protocol

5.1.1 Sulfate

Gao and Thiemens (1993) report the sulfate contents of two pieces of Murchison (Field Museum, Chicago), one piece of ALH 84029, and one piece of Mighei. They extracted 6900 ppm S as sulfate from Mighei, which is similar to the range of sulfate concentrations observed in our CM extractions. The extractions by Gao and Thiemens (1993) of sulfate from two pieces of Murchison yielded 5600 and 6000 ppm S, which are indistinguishable from our extractions for this meteorite (Table 2). Their extraction of sulfate from ALH 84029 yielded 8000 ppm S, which is nearly twice the amount that we extracted (4800 ppm). Burgess et al. (1991) used combustion techniques to determine sulfate contents in Murchison, Mighei, Nogoya and Murray. They report 14100 ppm S as sulfate for Murchison, and 14500 ppm S as sulfate for Nogoya, both of which are much higher than we obtained from our samples (Table 1). These discrepancies could indicate sample heterogeneity in the sulfate distribution, as reported for carbonate abundances in these samples (e.g., Alexander et al., 2015). Alternatively, they could reflect the extraction of tochilinite (in which S is present as a sulfide) by Burgess et al. (1991) together with sulfate, as suggested by these authors. Tochilinite mineral could account for more than 50% of the S released at the temperature

assigned for sulfate (Burgess et al., 1991), possibly explaining the roughly factor of two of difference between our data and the combustion data.

5.1.2 Elemental S

Burgess et al. (1991) report S⁰ contents of 1500 ppm in Murchison, and 900 ppm for Nogoya using their stepped combustion approach. These values compare well with our extractions, being 1600±100 ppm and 1400±100 ppm S, respectively (Table 1). Note that Burgess et al. (1991) also reported 600 ppm S⁰ for both Mighei and Murray, in the range of our CM extractions that averaged 1900±1400 ppm S. Gao and Thiemens (1993) used CCl₄ as a solvent to extract S⁰, and they report S⁰ contents that were typically < 500 ppm S. We do not think that the higher S⁰ contents we obtained compared to Gao and Thiemens (1993) results from an oxidation reaction during the extraction process (for instance from sulfide, or from an organic polysulfur compound). Our extractions were performed under anoxic conditions in an N₂ atmosphere. We also note that water-soluble S-bearing organics would have been removed in the water traps before the S⁰ extraction (section 3.1). The discrepancy between our dataset and those of Gao and Thiemens (1993) therefore appears to be best explained by sample heterogeneity.

5.1.3. Sulfide

The extraction of sulfide was conducted with multiple steps. We first extracted the acid-volatile S fraction (AVS) by digesting the powdered samples in sub-boiling 6N HCl. After the extractions, all the solutions displayed a yellow coloration, suggesting the presence of dissolved Fe³⁺. Iron speciation is poorly characterized in CM, but Fe³⁺ is thought to be ubiquitous, hosted in magnetite and cronstedtite (e.g., Zolensky et al., 1997; Beck et al., 2012; Sutton et al., 2013; Howard et al., 2015). Reaction between reduced S and ferric iron can occur in acidic solution (Pruden and Bloomfield, 1968; Rice et al., 1993), producing S⁰ as follows:

S⁰ produced by reaction 1 can be recovered by the use of CrCl₂ solution (Canfield, 1986; Mayer and Krouse, 2004). We extracted the S⁰ in solution (step 12) and the S⁰ fraction that had precipitated (step 13). Because S⁰ is poorly soluble in acidic environments, S in step 13 is more abundant than in step 12. AVS

represents only ~7% of the extracted sulfide pool, whereas steps 12 and 13 represent ~4% and ~89%, respectively. If correct, most of the sulfide is oxidized to S^0 during the AVS extraction, presumably due to the large Fe^{3+} contents in the studied samples. AVS $\Delta^{33}S$ values are compared to those of step 12 and step 13 in Fig. S2, and compared with the naturally occurring S^0 (i.e., step 2) in Fig. S3. The AVS, step 12 and step 13 isotopic compositions have, to first order, indistinguishable $\Delta^{33}S$ for most CMs (see detailed discussion in Appendix A). When compared with step 2, the data show considerable scatter, and do not fall on a 1:1 slope. Despite the lack of a clear $\delta^{34}S$ relationship, this further supports the conclusion that AVS, step 12 and step 13 are linked through sulfide oxidation during the AVS extraction (reaction 1). The differences between the step 2 and sulfide pools (Fig. S3) indicate that our protocol results in minimal contamination of the sulfide-derived S by the naturally occurring S^0 .

5.1.4 Bulk S and sulfide contents of CMs: Comparison with previous work

Our observations suggest that most of the sulfide pool is oxidized during the AVS step and recovered in step 13. If not recovered properly, this might lead to an underestimation of both the sulfide content and the bulk S content of chondrites. We suggest that this accounts for the discrepancy between our study and Gao and Thiemens (1993) who reported bulk S contents for three CMs ≤ 1 wt.%, ~75% of which is in sulfate. This is in contrast to the bulk S contents in our 13 CMs that range from 1.7 wt.% to 3.0 wt.%, with sulfide making up at least half the bulk S in most of them (Table 1). Gao and Thiemens (1993) recovered sulfide by digesting their chondrites in HCl, and only considered their AVS extractions as sulfide-derived S. Using this approach, < 2000 ppm S from sulfide was extracted from each of their three CMs, compared to 8300-20800 ppm in our study.

Burgess et al. (1991) and Dreibus et al. (1995) also determined S abundances in several CM falls. Burgess et al. (1991) reported an average S content of 2.99 ± 0.31 wt.% S (1σ) for four CMs (Murchison, Mighei, Nogoya, and Murray) and ranging from 2.65 wt.% to 3.38 wt.% S. Dreibus et al. (1995) report a comparable average bulk content of 3.26 ± 0.68 wt.% (1σ) for eleven CMs, including three falls (Murchison, Cold Bokkeveld, and Nogoya) with individual bulk S contents varying between 2.20 wt.% and 4.90 wt.% S. Our bulk S contents for the same samples are lower by ~20-35%. Burgess et al. (1991) and Dreibus et al.

(1995) both used combustion techniques and, therefore, likely accessed organic S. This could at least partially explain the differences in reported bulk S contents as only inorganic S was extracted with our protocol. Sulfur in soluble organic matter is likely to be < 1% of the S budget (Cooper et al., 1997). The S content of insoluble organic matter is $\sim 10 \pm 5$ wt.% (Alexander et al., 2007), representing ~ 0.1 wt.% S in the bulk rock or $\sim 5\%$ of the S budget in CMs. Thus, organically bonded S is only a partial explanation for the differences in bulk S contents reported here and the two earlier studies. If there were any sulfates that were insoluble in water (e.g., BaSO_4 and/or jarosite), these would not have been extracted by our protocol (section 3.1). If so, the 20-30% lower S content associated with our technique relative to combustion studies (Burgess et al. 1991) would suggest that about half of the CMs sulfates would not be extracted by our technique. We cannot exclude this possibility, and systematic studies comparing bulk S data obtained by wet chemistry to combustion extractions on the same batches of powder are needed. Finally, sample heterogeneity is also a possible explanation, particularly when samples come from different stones of the same fall. Our replicate extractions on aliquots of the same Cold Bokkeveld and Murchison powdered samples yielded bulk S contents that varied by roughly a factor of 2 (Table 4). Bulk S contents reported by a number of other authors also show factors of two variations for a given chondrite (Mason 1963; Kaplan and Hulston, 1966; Fitzgerald and Jacques, 1982; Kinnunen and Saikkonen, 1983; Graham and Yanai, 1985; Jarosewitch, 1971). The only puzzle with this explanation is why, for the same meteorites, all our samples should have lower S contents than reported by Burgess et al. (1991) and Dreibus et al (1995).

5.1.5 Sulfur isotope heterogeneity in different pieces of the Murchison meteorite

The comparison of our isotopic measurements of S from the British Natural History Museum sample of Murchison (BM.1988,M23) and the measurements by Gao and Thiemens (1993) (ME 2641) reveals a striking difference in the $\Delta^{33}\text{S}$ and provides evidence for significant S isotope heterogeneity in the Murchison material. This heterogeneity may reflect the fact that Murchison is a breccia containing xenolithic fragments of several other meteorite types, which are millimeter-to-centimeter-sized (e.g., Fuchs et al., 1973; Benedix et al., 2015).

For the Murchison splits reported by Gao and Thiemens (1993), all the S components have near zero $\Delta^{33}\text{S}$ values. In contrast, we observe strongly positive $\Delta^{33}\text{S}$ values in the three components extracted from

our Murchison splits. It requires the redistribution of S-bearing phases along parent body processes (if any redistribution at all) to be limited to a scale below the meter scale (i.e. below what is sampled between Murchison rocks in different museums).

5.2 Exploring the genetic link between S⁰ and sulfate

Based on their S isotopic composition, we develop the idea that sulfates in CMs result from parent body processing. The thermodynamic modeling of Zolensky et al. (1989) suggested that the Eh-pH conditions prevailing during aqueous alteration on the CM parent body would not allow for oxidation of sulfide to sulfate. However, Airieau et al. (2005) reported the occurrence of non-terrestrial $\Delta^{17}\text{O}$ for sulfate in 6 CMs falls (including Murchison, Cold Bokkeveld, Nogoya and Banten). This observation demonstrates that the sulfate formation occurred on the parent body, with extraterrestrial water, as opposed to sulfates forming on Earth.

If the only heated CM, PCA 91084, is excluded, sulfate has an average $\delta^{34}\text{S}$ of $-1.38 \pm 1.28\text{‰}$ (1σ , $n=12$). This is systematically lower than the S⁰ average of $3.56 \pm 0.74\text{‰}$ (1σ , $n=12$ PCA 91084 excluded) or than the sulfide average of $-0.17 \pm 0.33\text{‰}$ (1σ , $n=12$). Despite some overlap, the $\delta^{34}\text{S}$ of sulfate is generally lower than for sulfide, and is systematically lower than for S⁰ in a given CM. Similar observations were made in the pioneering study of a single chip of Orgueil (CI) by Monster (1965), as well as on Cold Bokkeveld, Mighei and Murray (Kaplan and Hulston, 1966). Gao and Thiemens (1993) also report low $\delta^{34}\text{S}$ sulfate values relative to S⁰ or sulfide in their CMs. If sulfates were formed by oxidation of a more reduced precursor (sulfide or S⁰), these S isotope data would indicate an oxidation process that preferentially incorporates ³²S into the sulfate, producing isotopically light sulfate. This is consistent with a *normal* kinetic isotope effect associated with oxidation like those that have been observed in the oxidation of aqueous sulfide (principally HS⁻; e.g., Fry et al., 1988) and sulfide minerals (FeS; e.g., Lewis and Krouse, 1968).

Depending on the size of the studied reservoirs, resolvable ³⁴S enrichments are expected in the residual precursor. Sulfate represents on average $25 \pm 12\%$ of the bulk S whereas sulfide and S⁰ represent $65 \pm 15\%$ and $9 \pm 7\%$ respectively (section 4.2). Assuming closed system (Bland et al., 2009) and that the sulfate

precursor (sulfide or S⁰) had a $\delta^{34}\text{S}$ equal to CDT, the roughly 1‰ ³⁴S-depletion in sulfate relative to CDT should be compensated by a roughly 0.4 or 2.5‰ ³⁴S-enrichment in the sulfide or S⁰ pool, respectively. Sulfide and S⁰ have average $\delta^{34}\text{S}$ values of $-0.15 \pm 0.33\text{‰}$ and $+3.46 \pm 0.74\text{‰}$ (1 σ), respectively. Within uncertainty, both mechanisms could be reasonable explanations, and on the basis of this ³⁴S mass balance, sulfate could be formed by both oxidation of sulfide or S⁰.

Sulfates in chondrites could have been produced on Earth, by reaction of sulfides (and/or elemental S) with atmospheric oxygen. For example, Gounelle and Zolensky (2001) report clear evidence for sulfate veins formation in Orgueil (CI chondrite) during the storage history of the samples. This is consistent with the Orgueil sulfate $\Delta^{17}\text{O}$ value of $-0.12 \pm 0.20\text{‰}$ (2 σ , Airieau et al., 2005), i.e. indistinguishable from sulfates formed on Earth (with a $\Delta^{17}\text{O}$ value of 0.00‰, Airieau et al. 2005). This could indicate that mostly terrestrial oxygen was involved in the formation of these sulfates (Airieau et al., 2005). On the other hand, CMs have sulfate with variable $\Delta^{17}\text{O}$ values, between $+1.18 \pm 0.20\text{‰}$ and $-0.23 \pm 0.20\text{‰}$. These values are clearly not terrestrial, indicating that sulfates in CMs, in contrast to CIs, were mostly produced in their parent body during late stage aqueous alteration (Airieau et al., 2005). Interestingly, the bulk $\Delta^{17}\text{O}$ values for CMs is between -0.67‰ and -3.07‰ (Clayton and Mayeda, 1999), always significantly lower than the corresponding sulfate values (Airieau et al., 2005). In the canonical water/rock interaction model (Clayton and Mayeda, 1999), this would indicate that the sulfates were produced early in the aqueous alteration sequence, before substantial isotopic exchange between water (presumably carrying a high $\Delta^{17}\text{O}$ value) and the anhydrous silicates (presumably carrying a low $\Delta^{17}\text{O}$ value) had occurred (Clayton and Mayeda, 1999).

Independent of when and where the chondritic sulfates were produced, the question of their precursor (sulfide, S⁰, or another S-bearing phase) remains elusive, at best, in the literature. Petrographic analyses of CMs report alteration of sulfides (e.g., Zolensky et al., 1997; Rubin et al., 2007), suggesting that sulfide oxidation will contribute to the chondritic sulfate budget. However, sulfates always display $\Delta^{33}\text{S}$ anomalies that are significantly larger than sulfide (Fig. 7). Since sulfide oxidation would only transfer the sulfide $\Delta^{33}\text{S}$ to the sulfates, the mismatch between sulfates and sulfides $\Delta^{33}\text{S}$ values indicate that sulfides cannot be the main precursor of sulfate. On the other hand, sulfate and S⁰ have similar $\Delta^{33}\text{S}$ values (Fig. 7). The slope observed between $\Delta^{33}\text{S}$ values of S⁰ and sulfate is 0.86 ± 0.24 (2 σ) with an intercept of $0.028 \pm 0.018\text{‰}$. At

first order, this slope is statistically indistinguishable of a 1:1 slope, allowing sulfate to be produced by S^0 oxidation, not sulfide oxidation. This is not true for the sulfates from MCY 02530 that have a $\Delta^{33}S$ value that is indistinguishable from the sulfides of this CM, and significantly different from that of S^0 . This CM is excluded from the following discussion.

Although sulfates and S^0 have similar $\Delta^{33}S$ values, sulfates always seem to be biased toward slightly higher $\Delta^{33}S$ values than S^0 at the ~ 0.020 - 0.060‰ level (averaging at $+0.036 \pm 0.042\text{‰}$, 2σ , versus a total range of $\sim 0.300\text{‰}$). This is evident in Table 3, Fig. 7A and 9. This slightly higher $\Delta^{33}S$ value in sulfate, relative to S^0 , is correlated to the ^{34}S difference between sulfate and S^0 : The more sulfates are depleted in ^{34}S relative to S^0 , the higher their $\Delta^{33}S$ are relative to S^0 (Fig. 9). In addition, sulfates show a slight $\Delta^{36}S$ depletion relative to S^0 , averaging at $-0.31 \pm 0.26\text{‰}$ (2σ). However, the relative $\Delta^{36}S$ uncertainties are significantly larger than for $\Delta^{33}S$ (table 3), preventing any direct trend with $\delta^{34}S$ values to be observed (Table 3). This is nevertheless the first time that the relationship observed in Fig. 9 is observed in natural samples, and we suggest that it reflects the specific nature of the S^0 oxidation mechanism to sulfate. The mass dependence of an isotope fractionation accompanying a chemical reaction or physical process among more than two stable isotopes is typically given by a power law relationship, e.g., $^{33}\alpha = (^{34}\alpha)^\theta$ where α is the fractionation factor (Craig, 1957; Hulston and Thode, 1965; Matsuhisa et al., 1978; Clayton and Mayeda, 1996; Young et al., 2002). By convention, the reference exponent θ for the relationship between $^{33}\alpha$ and $^{34}\alpha$ is taken to be 0.515, the approximate exponent of mass dependence describing most simple equilibrium isotope exchange reactions (Matsuhisa et al., 1978; Young et al., 2002). Rare exceptions to this rule have been observed, particularly for complex kinetic processes, where exponents of mass dependence differing significantly from the reference exponent of 0.515 were observed and coined “non-canonical” effects (Eiler et al., 2013). For those fractionations, $\Delta^{33}S$ is predicted to depart from a reference across a given process and to be correlated with $\delta^{34}S$ variations. In our case, a mechanism linking S^0 and sulfate would require that the $^{33}S/^{32}S$ fractionation be 0.505 ± 0.005 times that of the $^{34}S/^{32}S$ fractionation.

5.3. Sulfur cosmochemistry

The analyses presented here yield a much larger range of S-MIF in the major S-carrying phases than previously recognized in chondrites. Gao and Thiemens (1993) may have missed identifying the signature because the number of CM chondrites that they studied was small ($n=3$). Repeat analyses of the same meteorites in some cases match well within uncertainty with Gao and Thiemens (1993), but we report a distinctly different bulk S isotope composition for Murchison, suggesting sample heterogeneity. The largest S-MIF signals are found in S^0 , but they are also preserved in sulfide and sulfate – the latter being a water-soluble phase.

Mixing of S from diverse nucleosynthetic origins, such as that associated with ^{32}S -bearing SiC attributed to decay of ^{32}Si produced in supernovae, is not a good mechanism for explaining the observed S isotope anomalies in CMs. SiC grains comprise $30\pm 15\text{ppm}$ of CMs (Davidson et al. 2014), and of these, the grains carrying ^{32}S -excesses ($\Delta^{33}\text{S}$ values down to -500‰) are rare ($\sim 1\text{-}5\%$ - Hoppe et al., 2012; Fujiya et al., 2013; Pignatari et al., 2013). Considering the S abundance of CMs, ^{32}S addition by these grains would only raise the $^{32}\text{S}/^{34}\text{S}$ ratio by $\sim 5\times 10^{-5}\%$, ~ 3 to 5 orders of magnitude too low to account for the $\Delta^{33}\text{S}$ variations in S^0 and sulfide, respectively.

The significant non-mass dependent ($>0.1\text{ ‰}$) ^{33}S variations in phases that condense at different temperatures suggest a photochemical process. During its T-Tauri phase, the young Sun would have emitted significantly greater deep and extreme UV than it does today (Zahnle and Walker, 1982). This UV radiation would have been available for photolysis in the transparent hotter inner parts of the solar nebula (Rai et al. 2005) and along unshaded parts of the surface of the disk, as modeled by Ciesla (2010) and Ciesla and Sandford (2012). Any produced photochemical S-isotopic signature could have been transferred to solids via condensation of S-bearing phases, followed by transportation to the midplane of the disk by vertical mixing (Ciesla, 2010) where it would have been accreted as part of the chondrite matrices.

For the present CM S isotope data, the carrier of the anomaly appears to be related to S^0 or an S^0 -precursor rather than a high temperature sulfide condensate, as was suggested in prior studies (Rai et al., 2005; Rai and Thiemens, 2007; Antonelli et al., 2014), but the production mechanisms of the S^0 or S^0 -precursor remains unclear. The S-MIF signature could reflect direct photochemical production of S^0 , provided that sufficient UV were available in the cooler parts of the disk where S^0 could condense or be captured by grain surfaces.

The observation that $\Delta^{33}\text{S}$ values of S^0 (which is water-insoluble) is correlated with values in water-soluble phases (such as sulfate), in combination with the observation that different pieces of the same meteorite preserve evidence for variable $\Delta^{33}\text{S}$ values (Murchison) implies that the S-MIF signal is variable on a sub-meter scale at least in Murchison. The corollary is that parent body aqueous processing and flow was not sufficient to homogenize the isotopic signals at this scale. This argues against a pervasive fluid flow in the regions where the CM chondrites were formed.

PCA 91084, the only heated CM analyzed here (Alexander et al., 2007, 2013), displays $\delta^{34}\text{S}$ chemistry pattern that differs from the other CMs. We suggest that this may reflect oxidation during heating in the CM parent body (Appendix B). Further study of heated carbonaceous chondrites is needed to validate this hypothesis.

5.4 H₂S Photochemistry as a candidate production mechanism for S-MIF

H₂S photochemistry is considered as a candidate for the S-MIF production because it is thought to be the dominant S-bearing gas phase in the solar nebula (Chakraborty et al., 2013). H₂S absorbs in several regions in the UV, with a broad absorption feature extending from ~317 nm to ~165nm, and a series of banded absorption features that extend from ~165 nm down to ~40 nm with a peak at ~90 nm. This peak includes several bands around Lyman alpha wavelengths at 121.6 nm (i.e., the most intense T-Tauri wavelengths, Zahnle and Walker, 1982, Okabe et al. 1978). The longer wavelength feature appears to be associated with the production of atomic hydrogen and SH, while the shorter wavelength region is associated with the production of atomic H and S (Okabe, 1978).

Farquhar et al. (2000b) report isotopic fractionations associated with photolysis experiments that access the longer wavelength (~317 nm to ~165nm) absorption feature using continuum radiation extending from ~200 nm to the visible. Recently, Chakraborty conducted a series of photolysis experiments of H₂S by UV radiation with wavelengths of 90, 121.6, 139.1, and 157 nm to investigate isotope effects in the shorter wavelength region. These experiments indicate that photolysis at different wavelengths produces S^0 and residual H₂S with different types of isotopic signals, most notably $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios that vary as a function of the wavelength of the incident UV. The experiments undertaken by Farquhar et al. (2000b) yielded positive $\Delta^{33}\text{S}$ values in the produced S^0 , where products and residues lie on

572 a positive $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ array ($\sim +1.7 \pm 1.5$, 2σ , see Farquhar et al., 2000b). On the other hand, the photolysis
573 experiments of Chakraborty et al. (2013) undertaken at discreet wavelengths of 122 nm and 139 nm
574 produced negative $\Delta^{33}\text{S}$ values in S^0 down to $-1.54 \pm 0.02\text{‰}$, and a $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratio of -2.77 ± 0.46 (2σ).
575 Experiments conducted at 90 nm and 157 nm yielded S^0 with positive $\Delta^{33}\text{S}$ values and near-zero $\Delta^{36}\text{S}$
576 values, yielding $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ values of $+1.4 \pm 0.2$ and $+0.1 \pm 0.2$, respectively (Chakraborty et al., 2013). **Note**
577 **that there are no systematic $\delta^{34}\text{S}$ variations between the different mass independent signatures in the**
578 **experiments (Chakraborty et al., 2013). Thus, as opposed to non-canonical mass dependant fractionations**
579 **(section 5.2, Eiler et al. 2013), no systematic $\delta^{34}\text{S}$ variations can be *a priori* expected to correlate with the**
580 **MIF signatures.**

581 In CMs, most S^0 extracts have **homogeneous $\delta^{34}\text{S}$** , negative $\Delta^{33}\text{S}$ values and lie on a $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ slope of -
582 3.1 ± 1.0 (-3.9 ± 2.2 when sulfide and sulfate extracts are taken into account; 2σ ; Fig. 4a and 5). This
583 relationship is similar to that seen in the experimental results in the Lyman alpha region (Chakraborty et
584 al., 2013). Given that this is one of the most intense emission regions in the far ultraviolet of T-tauri stars
585 (Zahnle and Walker, 1982) we suggest a link to the observation of S-MIF in the CM chondrites.

586 The positive $\Delta^{33}\text{S}$ values for S^0 of Murchison and MCY 05230 are associated with near-zero $\Delta^{36}\text{S}$ values,
587 or $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ values of $+0.9 \pm 0.1$ and $+1.3 \pm 0.1$, respectively, suggest a different mechanism. Magnetic isotope
588 effects, producing large $\Delta^{33}\text{S}$ anomalies associated with negligible $\Delta^{36}\text{S}$ variations, could explain these
589 values. It was experimentally shown that S magnetic isotope effects can be produced in highly specific
590 chemical conditions during S reduction processes (Oduro et al. 2011). This process leads to the
591 preferential partitioning of ^{33}S into the products of the reaction (sulfides), leaving behind ^{33}S -depleted
592 sulfates. In the CMs the sulfates, sulfides and S^0 all share positive $\Delta^{33}\text{S}$ anomalies, leaving unexplained what
593 the complement of these isotopic reservoirs would be. It is also unclear why only two of the CMs would
594 have experienced processes allowing the expression of magnetic isotope effect, without affecting any other
595 meteorites. We here argue that the positive $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios can also result from a photodissociation
596 process, since several H_2S photodissociation experiments show positive $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ ratios, including those
597 conducted at both shorter and longer wavelengths than the Lyman alpha wavelengths (Chakraborty et al.,
598 2013). Considering that absorption by gas phase species such as H_2 , CO , CH_4 , N_2 , NH_3 would preferentially

shield shorter wavelengths (Keller-Rudeck et al., 2013), we suggest this change reflects a shift to longer wavelengths after attenuation of Lyman alpha by absorption in the nebula (See Fig. 8). Importantly, variations of $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ from sample to sample (Fig. 5) resulting from the photodissociation processes provide evidence for heterogeneous accretion of S-bearing phases by the parent body of CMs. This rules out parent body processes as the cause for these S isotope variations (through for example the heterogeneous redistribution of some S-MIF-bearing phase *after* accretion).

5.4.1. Model A: sulfides and S^0 are both direct condensates.

One possibility for explaining the S isotope variations in CMs is that when temperatures in the nebula were low enough, any photolytic S^0 carrying S-MIF condensed and the remaining H_2S sulfidized metal to form sulfides following reaction 2 (Zolensky et al., 1995; Lauretta et al., 1996, 1998).

Metal sulfidation experiments show that the reaction 2 leads to the formation of troilite (FeS) at ~ 700 K (Lauretta et al., 1996). At a given H_2S content, the sulfidation rate decreases dramatically with temperature, but this mechanism remains efficient until temperatures are as low as ~ 500 K. Negative $\Delta^{33}\text{S}$ values in S^0 are predicted to be associated with positive $\Delta^{33}\text{S}$ values in H_2S (recorded in sulfides), by mass balance, as observed in H_2S photodissociation experiments (Chakraborty et al., 2013). Negative trends between $\Delta^{33}\text{S}$ values for S^0 and sulfides are hence predicted. However, a clearly positive trend is observed, with a slope of 0.56 ± 0.20 (2σ , Fig. 6b). H_2S photodissociation associated with an open-system Rayleigh distillation process can reconcile the data with the experiments: Any S^0 would carry a negative $\Delta^{33}\text{S}$ value relative to the residual H_2S , **without a significant change in $\delta^{34}\text{S}$** (Chakraborty et al. 2013). In an open-system model, the photolytic S^0 would be distilled out of the system by condensation, continuously or in discrete episodes, and deposited without substantial accumulation in the chondritic matrices. This would enrich both the produced S^0 and the remaining H_2S in ^{33}S . **Assuming a bulk solar composition of $\Delta^{33}\text{S} = 0$, Rayleigh distillation is required to account for the occurrence of both positive and negative $\Delta^{33}\text{S}$ values for S^0 and sulfides** (Fig. 8), as well as the observed positive correlation between sulfide and S^0 (Fig. 6b).

Photolytic processes producing S-MIF under a Rayleigh distillation have been suggested elsewhere, as to occur in the Earth's upper atmosphere for SO₂ photodissociation, explaining the S isotopic composition of sulfate deposits in volcanic ashes from Antarctic ices (Baroni et al., 2007).

Quantitative modelling of S⁰ abundances and isotopic compositions in CMs remains challenging: Experiments for H₂S photodissociation at 121.6 nm and 139.1 nm yielded $\Delta^{33}\text{S}$ fractionations between produced S⁰ and residual H₂S ranging between $-1.54 \pm 0.02\text{‰}$ and $-0.09 \pm 0.02\text{‰}$ without systematic changes in $\delta^{34}\text{S}$ (Chakraborty et al. 2013). A Rayleigh process involving these isotopic fractionations could have produced the fractionations seen in all of the CM chondrites except Murchison and MCY 05230. For the sake of illustration, we model an endmember case with constant $\Delta^{33}\text{S}$ fractionations and negligible $\delta^{34}\text{S}$ fractionations (Fig. 8). The $\Delta^{33}\text{S}$ values for S⁰ in CMs range between -0.107 ± 0.008 and $+0.045 \pm 0.008\text{‰}$, which are consistent with a model where chondrites sampled S⁰ produced by a Rayleigh process with a -0.1‰ $\Delta^{33}\text{S}$ S⁰-H₂S fractionation during H₂S photodissociation. If reaction 2 is ignored, the calculation yields a fraction of remaining H₂S (f) between 0.99 and 0.30 to account for the range of S⁰ isotopic compositions in all the CMs except Murchison and MCY 05230 (Fig. 8). Note that the *ad hoc* -0.1‰ value for the fractionation is consistent with the $\sim 0.1 \pm 0.1\text{‰}$ difference generally observed between S⁰ and sulfide in the CMs (Table 3). A larger magnitude fractionation would reduce the required f range needed to reproduce the data. Using a fractionation of -1.5‰ would require an $f < 0.4$ to satisfy the observations, and all S⁰ produced for $f > 0.4$ would have been lost.

CMs would be required to sample S⁰ that underwent likely $< 10\%$ incremental accumulation after its production, consistent with S⁰ being the smallest S reservoir in the CMs (Table 2). The amounts of S⁰ produced could be calculated after determining f values for each chondrite. For example, GRA 98074 displays a $\Delta^{33}\text{S}$ value of $-0.055 \pm 0.008\text{‰}$ for S⁰, which would correspond to an instantaneous product at a fraction of residual H₂S (f) of 0.65 (Fig. 8). This isotopic value could also be produced by accumulation of all S⁰ for f values ranging between 0.7 and 0.6 (Fig. 8) or between 0.66 and 0.64. The trade-off between these possibilities is dictated by the acceptable amount of S⁰ accreted in this chondrite to match the measured S⁰ content (1000 ± 100 ppm S for GRA 98074, Table 2). For ALH 84029, its S⁰ content is 5500 ± 100 ppm with a $\Delta^{33}\text{S}$ value of $+0.018 \pm 0.008\text{‰}$ (Table 2 and 3). This $\Delta^{33}\text{S}$ value would be reached for $f \approx 0.3$, but the higher

S^0 content would require more S^0 accumulation. However, because the relative rate of photodissociation ($H_2S \rightarrow S^0 + H_2$, Fig. 8) to sulfidation ($H_2S + Fe^0 = FeS + H_2$, reaction 2) is unknown, f values cannot be translated into S^0 concentrations. Nonetheless, this simple model qualitatively accounts for the absence of direct trend between the S^0 isotopic composition and the amount of S^0 observed in a given CM (Table 2 and 3).

The distinct $\Delta^{36}S/\Delta^{33}S$ values for Murchison and MCY 05230, relative to all other CMs, require a change of the photodissociation regime across the S condensation window (section 5.4). This is also consistent with the reversal of the $\Delta^{33}S$ difference between S^0 and sulfide for these two CMs (Table 3, Fig. 8). In this context, the positive $\Delta^{33}S$ values of both S^0 and sulfide in the two meteorites could be explained if these phases were derived from a S reservoir that had already acquired a ^{33}S enrichment. One could speculate that the first photodissociation regime (with $\Delta^{36}S/\Delta^{33}S \sim -3$ and producing increasing $\Delta^{33}S$ values with decreasing f values, Fig. 8) was responsible for the ^{33}S enrichment. In that case, the minimum $\Delta^{33}S$ value of H_2S at the transition between the two regimes would be constrained by the Murchison sulfide value to be at least $+0.156 \pm 0.008\text{‰}$. Figure 8 illustrates the endmember possibility where the first regime ($\Delta^{36}S/\Delta^{33}S \sim -3$) is recorded by most of the CMs, while a second one accounts for Murchison and MCY 05230 only, with a $\Delta^{33}S$ fractionation of $+0.30\text{‰}$. Considering the $\Delta^{33}S$ value of $+0.156 \pm 0.008\text{‰}$ and a $\Delta^{36}S/\Delta^{33}S$ of ~ -3 , the first photodissociation regime would lead the $\Delta^{36}S$ values for Murchison and MCY 05230 to be $-0.45 \pm 0.30\text{‰}$. These two CMs however have near-zero $\Delta^{36}S$ values with only marginal overlap with this prediction (Table 3). While the uncertainties on $\Delta^{36}S$ do not allow us to completely rule out this possibility, below we develop an alternative and preferred model where the isotopic signatures seen in sulfide and S^0 could derive from a common product that contaminated both components. We discuss this interpretation later in this communication.

5.4.2. Other implications and limitations

This model requires both S^0 condensation and FeS formation to occur *coincident with* the photodissociation process. Under canonical nebula conditions, the rate of FeS formation reaction (reaction 2) would have been highest at ~ 700 K (Lauretta et al., 1996, 1998), but non-negligible until temperatures

680 fell below ~ 500 K (Lauretta et al., 1996,1998, Llorca and Casanova 2000). Experimental data suggest a
681 likely sublimation temperature of S^0 allotropes < 370 K, although the only available data were obtained at 1
682 bar and under O_2 -bearing atmospheres (Meyer 1976 and references therein). If relevant to canonical
683 nebular conditions ($P \sim 5 \times 10^{-4}$ bars, with solid grains in suspension), this is below the minimum FeS
684 formation temperature, and would argue against this working hypothesis. Note that we remain cautious
685 about ruling out such a sink for S^0 because it is unclear whether photochemical production of S
686 intermediates that have an affinity for grain surfaces could play a role in sequestering some anomalous S at
687 temperatures above the sublimation temperature of S^0 .

688 In this model, chondrites sample snapshots of the S^0 produced by H_2S photodissociation under a
689 Rayleigh distillation process. While qualitative inferences about the process appear possible, quantitative
690 modelling of S^0 abundances and isotopic compositions in CMs has not been attempted as $\Delta^{33}S$
691 fractionations vary as a function of wavelength without producing systematic $\delta^{34}S$ variations (Chakraborty
692 et al. 2013). We illustrate a simple scenario in Figure 8 using prescribed fractionations, but do not address
693 the issue of incident wavelength or the relationship between isotopic composition and mass balance
694 because the relative rate of photodissociation to sulfidation is unknown. A point in favor of the general
695 Rayleigh model approach is that the range of $\Delta^{33}S$ anomalies, from significantly negative to positive values,
696 is consistent with a Rayleigh distillation mechanism, accompanied by inefficient accretion of S^0 in CM
697 matrices as suggested by S^0 being the smallest S reservoir (Table 2).

698 Model A predicts that the CM with the lowest S^0 $\Delta^{33}S$ value will have a sulfide value that is closest to the
699 bulk composition of the gas (Fig. 8). This is LEW 87022 with a value of $-0.104 \pm 0.012\text{‰}$ for S^0 , and -
700 $0.051 \pm 0.008\text{‰}$ for sulfide (Fig. 7B). The bulk $\Delta^{33}S$ value of the nebula would be between these two values
701 (but probably closer to $-0.051 \pm 0.008\text{‰}$, Fig. 8), i.e., clearly distinct from CDT. This would leave
702 unexplained the observation that only rare differentiated bodies show significantly negative $\Delta^{33}S$ values.
703 While the mantles of the Earth, Mars, and the Moon have near-CDT $\Delta^{33}S$ values, only subgroups of irons
704 display negative $\Delta^{33}S$ values, with an average $\Delta^{33}S$ value of $-0.027 \pm 0.008\text{‰}$ for IIIF (Labidi et al. 2013,
705 Franz et al. 2014, Wing and Farquhar 2015, Antonelli et al. 2014). If the H_2S in the CM formation region had

a CDT-like S isotope composition to begin with, the model fails to explain the isotope composition of LEW 87022.

5.4.3. Model B-1: S-MIFs in chondrites are brought to the CMs by ice accretion

A second working hypothesis posits that at $T > 500$ K, the S^0 vapor produced by photodissociation of H_2S would not condense and be rapidly removed by reaction with H_2 to form H_2S since H_2 is the main gas in the nebula (Lodders, 2003), as follows:

Under this hypothesis, the transfer of S-MIF to sulfide precursors, and ultimately to iron sulfides would be prevented. Some H_2S probably remained in the nebula after troilite formation ($T < 500$ K), accounting for the S content of Jupiter atmosphere (Gautier et al., 2001; Ciesla, 2015). Under this hypothesis, residual H_2S when subjected to UV irradiation at $T < 500$ K would yield S^0 that eventually would be allowed to condense. The variable $\Delta^{33}S$ values in sulfides positively correlated with the S^0 values (Fig. 6b), though, would require some transfer of the MIF carried by S^0 to the sulfides. However, evidence exists only for sulfide oxidation in chondrites, not S^0 reduction (e.g., Gounelle and Zolensky, 2001; Zolensky et al., 1997; Kerridge et al., 1979; Bullock et al., 2005, 2010).

Accretion of ices to the CM matrices could provide a mechanism for transferring S-MIF in both sulfides and S^0 , under this working hypothesis. Late-accretion of nebular S^0 itself by ices is seen as unlikely, as experimental data suggest that it is significantly more refractory than water under any conditions, and hence it is likely to have condensed from the gas phase well before water ice formation (Jimenez-Escobar and Munoz-Caro, 2011). As an alternative, ice accretion could deliver the remaining H_2S (freezing $T < 170$ K, Jimenez-Escobar and Munoz-Caro, 2011) to the CM matrices. In support of this idea, comets have been observed to host a variety of S-bearing molecules, H_2S being the dominant one, representing from 0.2 to 1.5% relative to H_2O (Irvine et al. 2000). This H_2S gas would carry S-MIF after partial photodissociation in the nebula at $T < 500$ K. Its release in the CM parent body during aqueous alteration would have allowed reaction 1 to occur: H_2S would have reacted with Fe^{3+} present in the aqueous fluids that was produced by metal oxidation (Zolensky et al., 1997; Beck et al., 2012; Sutton et al., 2013; Howard et al., 2015). This

reaction, commonly observed in the laboratory (section 5.1.3), would lead to the formation of S^0 with S-MIF.

Observations of the least altered CM meteorite Paris supports the idea that metal would have been available in the first alteration reactions (Hewins et al. 2014). Therefore, the reaction 2 could also occur on the parent body. The competition between the reaction 1 and 2 would have led to the formation of S^0 (reaction 1) as well as a second generation of sulfides (reaction 2), both bearing identical $\Delta^{33}S$ values. It is conceivable that such a process would have resulted in the further sulfidation of troilite, leading to formation of pyrrhotite (Zolensky and Thomas 1995). Regardless, because our extraction process cannot distinguish between the primary sulfides (CDT-like $\Delta^{33}S$ values) and the S-MIF bearing sulfide formed by reaction 2, this scenario would predict bulk sulfides $\Delta^{33}S$ values that are correlated with the values for S^0 , which consistent with our dataset (Fig. 7b).

5.4.4. Model B-2: S-S production resulting from ice irradiation

A variant of this working hypothesis relates to UV irradiation of H_2S -bearing ices. Multiple lines of experimental evidence show that various S^0 species are produced by the irradiation of H_2S ices by UV (or protons) under relevant nebular conditions (Jimenez-Escobar and Munoz Caro, 2011; Jimenez-Escobar et al., 2011; Moore et al., 2007). As H_2S being in a solid (icy) state, it is not known whether its photodissociation would generate a mass-independent anomaly. We note though that the UV irradiation process of the ices in the protoplanetary nebula can be associated with warming of the ices, leading to temperatures allowing H_2S desorption (Ciesla and Sandford, 2012; Jimenez-Escobar et al., 2014). This would allow the photodissociation to have occurred under gas state, leading to production of S-MIF (Chakraborty et al., 2013). If products recondensed on ice, this mechanism could constitute a possible pathway for transferring S-MIFs to the CM parent body.

5.4.5. Multiple implications and limitations of ice-based models

The ices are required to have carried H_2S with heterogeneous S isotopic compositions to account for the varying $\Delta^{36}S/\Delta^{33}S$ values observed from sample to sample (Fig. 5). This hypothesis contrasts with the

suggestion that the ices carried other isotopically extreme but homogeneous components (Alexander et al. 2015). Naively, a correlation between water content and S content (or isotopic composition) might be expected in any ice-based model, but they are not observed (Table 1 and 2). However, some water must have been consumed by metal oxidation (e.g., Wilson et al., 1999; Rosenberg et al., 2001; Alexander et al., 2010, 2012). It is also possible that sulfides and S^0 were less mobile than water (after the ice melted), and/or that H_2S was mostly in the gas phase and moved independently of the water. Thus, the observed lack of a correlation between water and S is not seen as a weakness of this type of model. Model B-1 requires that the H_2S trapped in ices have S isotope compositions consistent with what is observed for S^0 in experiments (i.e., mainly negative $\Delta^{33}S$ values relative to CDT, Chakraborty et al., 2013), and not with the residual H_2S . This might be a weakness of the model, and experimental studies are needed to establish whether H_2S photodissociation can lead to the formation of S^0 with positive $\Delta^{33}S$ values with $\Delta^{36}S/\Delta^{33}S$ values of around -3. Under the model B-2, the ices would end up hosting both H_2S and S^0 with complementary S-MIFs. Both species would be released upon melting of the ice in the asteroid parent body, and H_2S would be left to react with the iron species in the fluids, leading to the further production of S^0 and sulfides (like in model B-1). However, under the current state of knowledge, the proportion of S^0 provided by the ices, relative to the S^0 formed by reaction 1 (whom the ice H_2S is the precursor), is unknown. If the former were dominant, S^0 and sulfides would have uncorrelated $\Delta^{33}S$ values. If the latter were dominant, S^0 and sulfides would have negatively correlated $\Delta^{33}S$ values. In both cases, the positive correlation between the S^0 and H_2S values (Fig. 6b) would be left unaccounted for, constituting a significant weakness of the model. However, we note that B-2 is not mutually exclusive with B-1. A combination of the two models is possible, and would simply produce some of the scatter observed amongst the compositions of the S-bearing components of the various CMs.

Finally, H_2S ice irradiation in the presence of CH_3OH has been shown to lead to the formation of S-bearing organic molecules (Jimenez-Escobar et al., 2014, Mahjoub et al. 2016). This is a critical observation, as if the H_2S photodissociation process occurred during the ice-warming events (associated with H_2S sublimation), it could lead to the production of S-MIF (Chakraborty et al. 2013) and its transfer to organic molecules. This mechanism has been explored for the production of C,N-bearing organics by UV irradiation

of ice at high altitude in the disk, aided by vertical motions in the protoplanetary nebula (Ciesla and Sandford, 2012). Significant S-MIF has been reported for the soluble organic fraction of Murchison (with $\Delta^{33}\text{S}$ values up to $+2.00 \pm 0.05\text{‰}$), but their origin remains unclear (Cooper et al., 1997). The model B-2 presented here, combined with the dynamical considerations of Ciesla and Sandford (2012), possibly accounts for these signatures.

5.5 What are the next steps to test the models?

While both models explored here can explain the general features of S isotopic heterogeneity in the CMs, they also both have significant limitations. To test these models, experimental studies are needed to fully describe the gaseous and aqueous S chemistries. For example, to test model A, experimental studies are needed to constrain the condensation behaviour of S^0 under canonical nebular conditions, with and without UV light. It is also essential to constrain the reaction rate law of reaction 3, to establish whether S^0 in the vapor phase would back react to H_2S . If not, MIF-bearing sulfide could be directly condensed, even in model B-1, without having the formation of late MIF-carrying sulfides as a requirement. Model B-1, in turn, can be tested through studies of the S^0 chemistry in an aqueous environment and in the presence of H_2 . The rates of reactions 1 and 2 under the relevant conditions need to be explored in future studies to test our hypothesis. Finally, to constrain the model B-2, it will be critical to address the possibility that H_2S ice irradiation by UV (or protons), described to produce S^0 and S-bearing organics (Jimenez-Escobar and Munoz Caro 2011, Jimenez-Escobar et al. 2014, Moore et al. 2007, Mahjoub et al. 2016), is associated with S-MIF production.

In general, if the anomalous S isotopic compositions in CMs are linked with the accreted ices, predictions can be made for other types of chondrites: The various chondrites parent bodies did not accrete similar amounts of ice (e.g., Clayton and Mayeda, 1999; Alexander et al., 2012). Consequently, they would in principle have distinct S-MIF signatures. For example, COs are similar to CMs in terms of bulk chemical composition (Wasson, 1988), although they accreted significantly less matrix (Krot et al., 2009 and references therein). The CO parent body, therefore, presumably accreted significantly less ice than the CMs (Clayton and Mayeda, 1999). If the CMs S isotopic signature is linked with ice accretion only, COs would be predicted to host mass dependant S isotopic signatures.

Finally, we also treated all our data as if the CMs are pristine chondrites that were never subjected to impact processes. These chondrites are, however, breccias (Metzler et al., 1992). It is conceivable that S^0 and sulfides would be redistributed during the brecciation process. In that case, the isotopic relationship between S^0 and sulfides may have been obscured. That could explain why Bantén is the only CM studied here that has sulfide with $\Delta^{33}S$ depletion relative to S^0 but lies on a $\Delta^{36}S/\Delta^{33}S$ of around -3. Since varying $\Delta^{36}S/\Delta^{33}S$ between different CMs (Murchison and MCY 05230 versus the other CMs) require some degree of heterogeneous accretion of MIF-bearing sulfides and S^0 , an alternative is that a similar process heterogeneously accreted S-bearing phases to Bantén.

5.6. Implications for sulfur chemistry in the early solar system

A striking feature of the meteoritic sulfur isotope record is the lack of large mass-dependent and mass-independent isotopic signatures, such as those seen for other elements that partitioned into multiple gas phase molecular species. Spectroscopic observations of multiple S-bearing molecules in molecular clouds (e.g., H_2S , OCS , SO_2 , $HSCN$, CH_2S , CH_3S , C_2H_5S , S_3 , C_2S , SO , $HSCS^+$, and SO^+ ; Müller et al., 2005) suggest a rich photochemistry and ion-molecule chemistry for S in the gas phase. As has already been discussed above, photochemical reactions can produce significant S-MIF (up to +1.5‰). The occurrence of significantly smaller S-MIF in chondrites (this study) and achondrites (Farquhar et al., 2000a, Rai et al., 2005; Rai and Thiemens, 2007, Antonelli et al., 2014) suggests that S may have been homogenized to a significant extent in the nebula. The MIF-S signatures in achondrites have been interpreted to reflect such a processing in high-temperature nebular environments, near the Sun (Rai et al., 2005; Rai and Thiemens, 2007; Chakraborty et al., 2013; Antonelli et al., 2014).

The standard model to explain S-MIF in achondrites is based on the observation of a $+0.161 \pm 0.012$ ‰ $\Delta^{33}S$ values in Norton County oldhamites (Rai et al., 2005). The assertion is that sulfide such as CaS could be a refractory carrier of isotope anomalies to asteroids (Rai et al., 2005). If the isotopic composition of oldhamite records photo-processed H_2S (Rai et al., 2005), the production of complementary S^0 carrying negative $\Delta^{33}S$ values was required by this observation. This S^0 must also have escaped condensation consistent with its low condensation temperature, and reaction with H_2 back to H_2S (i.e., reaction 3) as it

843 would otherwise lead to the preservation of a CDT-like $\Delta^{33}\text{S}$ value in the bulk H_2S and in the condensed
844 sulfides. Later on, the CaS grains could have been transported to various nebular regions where they would
845 have been incorporated into meteorite parent bodies, possibly through X-winds (Rai et al., 2005). H_2S
846 photodissociation cannot occur at the nebular midplane as it is where the optical density is the highest
847 (Ciesla, 2010). It would rather occur close to the sun, where optical density allows UV light to interact with
848 gas phases (Rai et al., 2005; Antonelli et al., 2014). Note that in addition, the reduced conditions closer to
849 the sun (produced by H_2O depletion) are required by the occurrence of refractory Ca,Mg-sulfides as
850 canonical C/O nebular conditions would otherwise bind calcium and magnesium to oxygen, not sulfur
851 (Lodders, 2003).

852 Further complications arising with this model are revealed by examination of the oldhamite data from
853 aubrites. Rai et al. (2005) and Defouilloy et al. (2016) report highly variable $\Delta^{33}\text{S}$ values for oldhamite
854 separates coming from the Norton County aubrite. In addition, the incorporation of CaS in the aubrite
855 parent body must have occurred late, likely after the aubrite asteroid differentiation, so that anomalous
856 $\Delta^{33}\text{S}$ values relative to bulk sulfur could be preserved in refractory sulfides (and not mixed during
857 magmatic processes). This has chronological implications on how the disk produces and distributes early-
858 condensed refractory sulfides to asteroids.

859 Refractory sulfides do not contribute to our extracted S (section 3.1). Only the Sutter's Mill CM, that also
860 displays evidence for mixing with enstatite chondrite during brecciation, have been reported to contain
861 oldhamites (Zolensky et al. 2014). CMs only contain Fe-(Ni-)sulfides (and tochilinites), produced by the
862 parent body processing of Fe-sulfides; Fe-sulfides being the principal sulfide phase predicted to form under
863 canonical C/O conditions (Zolensky and Thomas, 1995; Rubin et al., 2007, Lodders, 2003). The direct
864 observation of S^0 carrying most of the $\Delta^{33}\text{S}$ variability, and of sulfide carrying complementary $\Delta^{33}\text{S}$ values,
865 shows that the condensation of refractory CaS is not required to preserve non-CDT $\Delta^{33}\text{S}$ values. In that case,
866 the H_2S photodissociation could occur at the surface of the disk, and provide another way to produce S-MIF.
867 Vertical motion is a natural consequence of realistic disk viscosities (Ciesla, 2010; Ciesla and Sandford,
868 2012). Over timescales of $<10^5$ years, many particles would have experienced significant UV irradiation
869 simply through vertical motions that transported matter from the midplane to high altitudes in the disk

(Ciesla, 2010; Ciesla and Sandford, 2012). We thus suggest the surface of the disk as a viable location for H_2S photodissociation recorded in CMs.

Our observations do not negate the validity of the refractory sulfide model, as these phases are directly observed to carry S-MIF in the aubrite meteoritical record (Rai et al., 2005; DeFouilloy et al., 2016). Rather, our dataset establishes the fact that at least two S-MIF producing process were operating in the solar nebula, one producing the refractory sulfides observed in aubrites, and one producing the variations observed in CMs. The expansion of the refractory sulfide model to iron meteorites (Antonelli et al., 2014) may be valid, but our observation offers an alternative mechanism for S photochemistry that can be achieved under canonical C/O conditions, and possibly at any heliocentric distance provided a mechanism exists for preserving and transferring the S-MIF to planetesimals.

A H_2S photodissociation mechanism, similar to the ones described in our model A does not require the involvement of ice accretion (or any subsequent parent body processes) to transfer S-MIF to asteroids, and could then be extended to meteorite precursors formed in the inner region of the solar system like iron meteorites (Bottke et al., 2006). This scenario would lead to the formation of variable $\Delta^{33}\text{S}$ values for S^0 and FeS . Any deposited S^0 is likely to have experienced reduction to sulfide during differentiation of the parent bodies of meteorites; this is because parent bodies of all known achondrites and iron meteorites have $f\text{O}_2$ only allowing S^{2-} as the stable S-bearing phase (e.g., Metrich et al. 2009). Thus, the heterogeneous distribution of the photodissociation products and residues (like those observed amongst the CMs) could easily lead to the $\sim 0.05\text{‰}$ $\Delta^{33}\text{S}$ variations observed in the achondrites and irons (Farquhar et al., 2000a; Antonelli et al., 2014). This process could also be recorded in the chondrule precursors of ordinary chondrite, accounting for the S-MIF observed in some of these objects (Rai and Thiemens, 2007). In addition to relaxing the requirement of a reduced, hot inner nebula for the production and sequestration of S-MIF in the meteorite record, this model eliminates the need for the redistribution of grains formed near the proto-Sun to the achondrite-forming region. Importantly, this removes any requirement for the X-wind model or other disk winds to explain the occurrence of S-MIF in meteorites that form in distal cooler regions of the nebula.

The ice-based models, in turn, could not be expanded to iron meteorite, as these bodies were likely formed too close to the sun to accrete significant amount of ices (Bottke et al. 2006). However, the potential

of S-MIF production during ice transport (by UV irradiation of the ices: Jimenez-Escobar and Munoz Caro, 2011; Ciesla and Sandford, 2012) could explain the S-MIF observed in the only study of the organic phases of the Murchison meteorite (Cooper et al., 1997). This would relax the hypothesis that interstellar S was involved in meteoritical organic matter (Cooper et al., 1997), and support the idea that UV processing of ices before their accretion to asteroids can be associated with at least a portion of the organic matter present in chondrites (Ciesla and Sandford, 2012).

6. Conclusions

We report the results of measurements of the abundances and the quadruple S isotopic composition of sulfide, sulfate and S^0 in 13 CM carbonaceous chondrites. Our samples include 4 falls and 9 finds, and display an average S content of 2.11 ± 0.39 wt.% S (1σ). The recovered sulfate, S^0 and sulfide contents represent $25 \pm 12\%$, $10 \pm 7\%$ and $65 \pm 15\%$ of the bulk S, respectively (all 1σ).

We report ranges of S-MIFs in carbonaceous chondrites that are larger than previously observed. The largest variations are captured by S^0 , with $\Delta^{33}S$ values ranging between $-0.104 \pm 0.012\text{‰}$ (LEW 87022, 2σ) and $+0.256 \pm 0.018\text{‰}$ (MCY 05230, 2σ). The $\Delta^{36}S/\Delta^{33}S$ values of S^0 are on average -3.1 ± 1.0 (2σ). When sulfides and sulfates are taken into account, the average $\Delta^{36}S/\Delta^{33}S$ value is -3.9 ± 2.2 (2σ). The only exceptions are MCY 05230 and one of two Murchison samples that have $\Delta^{36}S/\Delta^{33}S$ values of $+1.3 \pm 0.1$ and $+0.9 \pm 0.1$, respectively, for their S^0 (note that their sulfides and sulfates display similar positive $\Delta^{36}S/\Delta^{33}S$ values as well).

Non-zero $\Delta^{33}S$ values are also preserved in sulfide and sulfate, and are correlated with S^0 values. The observed trends suggest a genetic relationship between the extracted S-bearing phases. For sulfate, the $\Delta^{33}S$ trend with S^0 values has a slope of 0.86 ± 0.24 (2σ). This slope is consistent with sulfate was produced by S^0 oxidation, not sulfide oxidation, during parent body processing. For sulfide, the slope of the $\Delta^{33}S$ trend with S^0 is 0.56 ± 0.20 (2σ). This suggests that the genetic link between S^0 and sulfide is more complex.

H_2S photodissociation experiments with UV light (wavelength < 150 nm) have previously demonstrated the formation of MIF-bearing S^0 . The sign of our $\Delta^{33}S$ values, and the $\Delta^{36}S/\Delta^{33}S$ values of our S-bearing extracts are consistent with the experimental data. We have explored two types of models, both requiring

H₂S photodissociation, to explain our data. Although imperfect, these models explain the major features of the CM S isotope compositions, and can be tested experimentally in future studies. In model A, sulfides and S⁰ are both condensates produced after incomplete H₂S photodissociation. A distillation process during photodissociation would account for the sign and range of the S-MIF observed in S⁰ and sulfides. This mechanism requires that the product of the photodissociation (S⁰) is removed from the system via condensation immediately after its production. It also requires the troilite formation occurs contemporaneously with S⁰ condensation. The well-documented rate for metal sulfidation would indicate a temperature window for troilite formation between 500 K and 700 K. Although poorly known, the S⁰ condensation temperature inferred from the literature seems too low to allow such process to occur.

In model B-1, H₂S experienced partial photodissociation at T < 500 K. Some of this H₂S would be trapped in ices that were later accreted, along with the condensed S⁰, by the CMs in their matrices. Melting of the ice in the CM parent body would have released this H₂S, enabling it to react with iron in metal and in solution, leading to the formation of a second generation of sulfides, as well as S⁰. These late phases would carry the S-MIF presently observed. This model requires ices to accrete H₂S with heterogeneous S isotopic compositions. A model B-2 includes the possibility of further photo-processing of H₂S in the ices prior to accretion by the CM parent body.

Our observations offer a mechanism for S photochemistry that can be achieved under canonical C/O conditions, allowing revisiting the origin of S-MIF in other meteorites and relaxing the need for invoking the X-wind model. A H₂S photodissociation mechanism, similar to the ones recorded in CMs, would lead to the formation of variable $\Delta^{33}\text{S}$ values in condensed phases, and their heterogeneous distribution could easily lead to the small $\Delta^{33}\text{S}$ variations observed in other meteorite groups, including non-chondrites.

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Table 1

A list of the studied samples, with estimated bulk H contents in water/OH and bulk δD composition, as reported in Alexander et al. (2013). Sample identification is given for falls. BM stands for British Museum, ASU for Arizona State University, and USNM for the Smithsonian institute. All the samples are of CM2 type except PCA 91084, which is a heated CM (Alexander et al., 2007, 2013). Two petrologic classification scales are presented here, after Alexander et al. (2013). On the first scale, the samples are distributed according to their petrologic types using a scale from 2 to 3, based on correlations between bulk H isotopic compositions and the petrologic criteria of Browning et al. (1996) and Rubin et al. (2007). On the other scale, the samples are on a scale of 1 to 3 based on bulk water/OH H contents.

Table 2

The sulfur contents and speciation in the 13 studied CMs, obtained with our wet chemistry technique. Unless stated otherwise, the S contents were obtained by weighing of Ag_2S generated after chemical extraction of the S from the meteorites. The uncertainty in the abundances is ~ 100 ppm (1 σ) and S content estimates for individual meteorites were rounded to the nearest 100. For S^0 , the abundance values obtained via High Performance Liquid Chromatography (HPLC) are also presented. The AVS, step 12 and step 13 pools refer to the fractions of extracted sulfide S using our extraction protocol. The AVS pool (for Acid Volatile Sulfur) is the H_2S generated when the CM powders were processed in hot HCl. Step 12 and 13 reflect the collection of S^0 that had been produced during the AVS step (reaction 1, see section 3.1). These three extracts were pooled by mass balance and considered to represent the bulk sulfide. See sections 3.1, 5.1.3, and Appendix A for details.

Table 3

The sulfur isotopic composition of all S extracts in the 13 studied CMs. We report 2 σ uncertainties of 0.10, 0.012 and 0.25‰ for $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$ values, respectively, for all

measurements with a SF₆ amount > 1 μmol. When SF₆ amount < 1 μmol (n=4), we report 2σ uncertainties of 0.10, 0.018 and 0.35‰ for δ³⁴S, Δ³³S and Δ³⁶S values, respectively.

Table 4

The sulfur isotopic composition of all S extracts in Murchison and Cold Bokkeveld replicates. We report 2σ uncertainties of 0.10, 0.012 and 0.25‰ for δ³⁴S, Δ³³S and Δ³⁶S values, respectively, for all measurements. The δ³⁴S values are given versus V-CDT. The uncertainty in the abundances is ~100 ppm (1σ) and S content estimates for individual meteorites were rounded to the nearest 100.

Table 1

	fall/find	sample ID	petrologic types		H content and isotope composition in bulk sample	
			Based on H content ^a	based on dD ^b	Water/OH H (wt%) ^c	dD (‰) ^d
Banten	fall	USNM 6017	1.7	2.5	0.91	-32.4
Cold Bokkeveld	fall	BM. 1727	1.3	2.2	1.22	-168.3
Murchison	fall	BM.1988,M23	1.6	2.4	0.96	-61.7
Nogoya	fall	ASU #556.2	1.1	2.1	1.31	-181.5
ALH 84029	find	n.a.	1.2	2.1	1.30	-184.1
DOM 08003	find	n.a.	1.1	2.2	1.36	-137.0
DOM 08013	find	n.a.	1.8	2.7	0.85	47.2
GRA 98074	find	n.a.	1.6	2.6	1.00	-14.1
LEW 85312	find	n.a.	1.8	2.9	0.83	126.3
LEW 87022	find	n.a.	1.4	2.3	1.09	-112.9
MCY 05230	find	n.a.	1.8	2.5	0.87	-17.6
<i>PCA 91084</i> ^e	find	n.a.	1.8	2.4	0.85	-74.6
TIL 91722	find	n.a.	1.9	2.7	0.79	53.7

a petrologic type on a scale from 1 to 2, see Alexander et al. (2013); Petrologic type = $3 - H_{\text{water/OH}}/0.7$

b petrologic type on a scale from 2 to 3, see Alexander et al. (2013); Petrologic type = $(dD + 994)/383$

c typical 1 σ uncertainty is < 0.03 wt%

d typical 1 σ uncertainty is < 10 ‰

e heated CM

Table 2

	mass processed (mg)	sulfate	S ⁰	step 13	step 12	AVS	sulfide	sum	S ⁰ HPLC
ALH 84029	206	4,800	5,500	8,500	500	500	9,500	19,800	5,800
Banten	197	6,500	800	11,000	900	700	12,600	19,900	900
Cold Bokkeveld	214-436 ^a	5,300	1,300	12,000	500	200	12,700	19,300	1,100
DOM 08003	194	6,800	2,800	8,600	200	1,000	9,800	19,400	3,700
DOM 08013	192	6,300	3,100	17,600	1,000	2,200	20,800	30,200	3,200
GRA 98074	198	2,400	1,000	13,100	500	100	13,700	17,100	700
LEW 85312	198	6,000	400	12,700	700	1,300	14,700	21,100	500
LEW 87022	206	2,000	1,200	14,100	700	3,100	17,900	21,100	1,200
MCY 05230	202	1,100	1,300	12,300	200	3,100	15,600	18,000	1,300
Murchison	201-202 ^a	5,900	1,600	7,500	600	200	8,300	15,800	12,300
Nogoya	204	3,700	1,400	16,100	800	900	17,800	22,900	1,400
PCA 91084	211	13,000	3,200	10,800	500	100	11,400	27,600	2,100
TIL 91722	208	5,955	1,500	11,000	500	1,900	13,400	20,855	1,300
average		5,400	1,900	11,900	600	1,200	13,700	21,000	2,700
std dev		3,000	1,400	2,900	300	1,100	3,600	4,000	3,200

all abundances are given in ppm S

a: range of values for replicates. See table 4. S abundance estimates are averages of the replicates

Table 3

		ALH 84029	Banten	Cold Bokkeveld	DOM 08003	DOM 08013	GRA 98074	LEW 85312	LEW 87022	MCY 05230	Murchison	Nogoya	PCA 91084	TIL 91722
S ⁰	d ³⁴ S (‰) V-CDT	2.42	4.28	2.88	3.25	3.23	4.06	3.69	5.29	3.17	3.71	3.16	-1.74	3.63
	d ³⁴ S (‰) CDT	2.32	4.18	2.78	3.15	3.13	3.96	3.60	5.19	3.07	3.61	3.06	-1.84	3.53
	D ³³ S (‰)	0.018	-0.001	-0.001	-0.034 (±0.018)	-0.085	-0.055	-0.080 (±0.018)	-0.104	0.256	0.243	-0.002	0.045	0.005
	D ³⁶ S (‰)	0.00	0.04	0.09	0.12 (±0.35)	0.07	0.23 -		0.34	0.32	0.23	0.20	-0.23	0.20
SO ₄	d ³⁴ S (‰) V-CDT	-1.65	-0.66	-0.70	-1.22	-1.68	-0.15	-4.44	0.19	-2.42	-0.64	-1.92	1.75	-0.13
	d ³⁴ S (‰) CDT	-1.75	-0.76	-0.80	-1.31	-1.78	-0.25	-4.54	0.09	-2.52	-0.74	-2.02	1.65	-0.23
	D ³³ S (‰)	0.058	0.040	0.023	0.006	-0.036	-0.019	-0.023	-0.036	0.143 (±0.018)	0.263	0.034	0.016	-0.007
	D ³⁶ S (‰)	-0.28	-0.23	-0.09	-0.21	-0.25	-0.03	-0.30	-0.14	0.26 (±0.35)	-0.11	-0.20	-0.15	-0.33
AVS	d ³⁴ S (‰) V-CDT	0.84	0.73 -		0.55	-0.38 -		0.20	1.15	0.84 -		1.35 -		-0.91
	d ³⁴ S (‰) CDT	0.75	0.63 -		0.45	-0.48 -		0.11	1.05	0.74 -		1.25 -		-1.00
	D ³³ S (‰)	0.027	0.007 -		0.016	0.006 -		0.010	-0.022	0.113 -		0.016 -		0.033
	D ³⁶ S (‰)	0.25	-0.03 -		0.12	-0.26 -		-0.07	0.18	0.28 -		0.25 -		-0.56
step 12	d ³⁴ S (‰) V-CDT	2.18	0.25 -		4.64	-0.03	0.50	1.07	1.15	3.90 -		0.34	0.10	1.53
	d ³⁴ S (‰) CDT	2.08	0.15 -		4.54	-0.13	0.40	0.98	1.05	3.80 -		0.24	0.00	1.43
	D ³³ S (‰)	0.046	-0.050 -		0.000 (±0.018)	-0.027	-0.023	0.015	-0.096	0.118 -		0.033	0.025	0.016
	D ³⁶ S (‰)	0.80	-0.06 -		0.42 (±0.35)	0.02	-0.20	0.20	0.07	1.16 -		0.23	-0.28	0.00
step 13	d ³⁴ S (‰) V-CDT	0.16	-0.06 -		-0.72	-0.50	-0.35	0.20	0.09	0.21 -		0.02	0.20	-0.19
	d ³⁴ S (‰) CDT	0.06	-0.16 -		-0.82	-0.60	-0.44	0.10	-0.01	0.11 -		-0.08	0.10	-0.29
	D ³³ S (‰)	0.047	-0.037 -		0.007	0.013	-0.014	-0.075	-0.049	0.106 -		0.006	0.015	0.009
	D ³⁶ S (‰)	0.12	0.07 -		0.21	-0.10	-0.04	-0.11	-0.11	0.19 -		0.14	-0.03	0.00
bulk sulfideb	d ³⁴ S (‰) V-CDT	0.27	-0.04	-0.53	-0.60	-0.48	-0.31	0.25	0.15	0.28	0.24	0.03	0.19	-0.11
	d ³⁴ S (‰) CDT	0.17	-0.14	-0.63	-0.70	-0.58	-0.41	0.15	0.05	0.18	0.14	-0.07	0.09	-0.21
	D ³³ S (‰)	0.047	-0.038	0.015	0.007	0.011	-0.014	-0.070	-0.051	0.106	0.156	0.007	0.015	0.009
	D ³⁶ S (‰)	0.16	0.06	0.05	0.22	-0.09	-0.04	-0.09	-0.10	0.20	-0.01	0.14	-0.04	0.00
bulk S ^c	d ³⁴ S (‰) V-CDT	0.40	-0.06	-0.32	-0.09	-0.35	-0.04	-1.01	0.43	0.32	0.24	-0.10	0.70	0.15
	d ³⁴ S (‰) CDT	0.30	-0.16	-0.42	-0.19	-0.45	-0.14	-1.11	0.33	0.23	0.14	-0.20	0.60	0.05
	D ³³ S (‰)	0.041	-0.011	0.016	-0.001	-0.009	-0.017	-0.058	-0.053	0.119	0.207	0.011	0.019	0.004
	D ³⁶ S (‰)	0.01	-0.03	0.02	0.06	-0.10	-0.02	-0.27	-0.08	0.22	-0.02	0.09	-0.11	-0.08

typical 2S uncertainties are 0.10‰, 0.012‰, and 0.25‰ for d³⁴S, D³³S and D³⁶S respectively

a for small samples, (< 1mmol SF₆), 2S uncertainties are 0.10‰, 0.018‰, and 0.35‰ for d³⁴S, D³³S and D³⁶S respectively

b estimated by mass balance of AVS, step 12 and 13. 2S uncertainties < 0.10‰, 0.018‰, and 0.42‰ for d³⁴S, D³³S and D³⁶S respectively. Typically 0.10‰, 0.012‰, and 0.25‰

c estimated by mass balance of S⁰, SO₄, AVS, step 12 and 13. 2S uncertainties < 0.35‰, 0.020‰, and 0.50‰ for d³⁴S, D³³S and D³⁶S respectively. Typically 0.30‰, 0.012‰, and 0.25‰

Table 4

		Murchison				Cold Bokkeveld					
		split one	split two	Average of replicates	1s		split one	split two	split three	Average of replicates	1s
powder mass (mg)		201	202				214	436	284		
Sulfur chemistry	sulfate (ppm S)	5600	6200	5900	424		5500	4900	5500	5300	346
	S ⁰ (ppm S)	1100	2100	1600	707		900	1600	1277	1259	350
	step 13 (ppm S)	5400	9700	7550	3041		7800	18400	9900	12033	5613
	step 12 (ppm S)	300	1000 -	-			640	730	100 -	-	
	AVS (ppm S)	pooled with step 12		200 -	-		pooled with step 12		100	300 -	-
	sulfide (ppm S)	5700	10900	8300	3677		8400	19200	10400	12667	5746
	sum (ppm S)	12400	19100	15750	4738		14800	25700	17200	19233	5727
S ⁰	δ ³⁴ S (‰)	4.72	2.69	3.71	1.44		4.31	2.14	2.21	2.88	1.23
	Δ ³³ S (‰)	0.236	0.249	0.243	0.009		-0.007	0.008	-0.003	-0.001	0.008
	Δ ³⁶ S (‰)	0.49	-0.04	0.23	0.38		0.69	0.09 -		0.39	0.42
SO ₄	δ ³⁴ S (‰)	-0.45	-0.82	-0.64	0.26		-0.69	-0.55	-0.87	-0.70	0.16
	Δ ³³ S (‰)	0.261	0.264	0.263	0.002		0.025	0.029	0.014	0.023	0.008
	Δ ³⁶ S (‰)	0.17	-0.39	-0.11	0.40		-0.03	-0.14	-0.09	-0.09	0.06
AVS	δ ³⁴ S (‰)	pooled with step 12		3.39			pooled with step 12		too small	1.00	
	Δ ³³ S (‰)		0.171						0.006		
	Δ ³⁶ S (‰)		-						0.37		
Step 12	δ ³⁴ S (‰)	-3.30	1.78	-0.76	3.59		-1.39	1.14	-2.12	-0.79	1.71
	Δ ³³ S (‰)	0.054	0.186	0.120	0.093		-0.020	0.012	0.027	0.006	0.024
	Δ ³⁶ S (‰)	0.83	0.00	0.42	0.58		0.45	0.13	0.30	0.29	0.16
Step 13	δ ³⁴ S (‰)	0.28	0.25	0.27	0.02		-2.21	0.07	0.48	-0.56	1.45
	Δ ³³ S (‰)	0.141	0.176	0.159	0.025		0.006	0.022	0.020	0.016	0.009
	Δ ³⁶ S (‰)	0.07	-0.14	-0.04	0.15		0.10	0.02	-0.02	0.03	0.06
Bulk sulfide ^a	δ ³⁴ S (‰)	0.08	0.40	0.24	0.22		-2.15	0.11	0.45	-0.53	1.41
	Δ ³³ S (‰)	0.136	0.177	0.157	0.029		0.004	0.022	0.020	0.015	0.010
	Δ ³⁶ S (‰)	0.11	-0.13	-0.01	0.17		0.13	0.02	-0.01	0.05	0.07
Bulk S ^b	δ ³⁴ S (‰)	0.23	0.25	0.24	0.01		-1.21	0.11	0.16	-0.31	0.78
	Δ ³³ S (‰)	0.201	0.213	0.207	0.008		0.011	0.022	0.016	0.016	0.006
	Δ ³⁶ S (‰)	0.17	-0.20	-0.02	0.26		0.11	0.00	-0.04	0.023	0.078

a estimated by mass balance of AVS, step 12 and 13. resulting 2s uncertainties are lower than 0.10‰, 0.018‰, and 0.42‰ for δ³⁴S, Δ³³S and Δ³⁶S respectively. Typically 0.10‰, 0.012‰, and 0.15‰

b estimated by mass balance of S⁰, SO₄, AVS, step 12 and 13. resulting 2s uncertainties are lower than 0.15‰, 0.020‰, and 0.50‰ for δ³⁴S, Δ³³S and Δ³⁶S respectively. Typically 0.10‰, 0.012‰, and 0.15‰

Figure 1

Analytical flow diagram for sulfate, S^0 , and sulfide extraction from CMs. Soluble and insoluble organic compounds were also isolated, but are not studied here. Sulfides compositions are estimated by pooling the AVS, step 12, and step 13 extracts (see sections 3.1, 5.1.3 and appendix A).

Figure 2

Histograms of bulk S, sulfide, sulfate and S^0 contents of the 13 CMs studied here. For all samples except PCA 91084, sulfide is the dominant pool, whereas sulfate and S^0 are minor S-carrying reservoirs.

Figure 3

The quadruple S isotopic compositions of bulk S in the 13 CMs: (a) $\Delta^{33}S$ versus $\delta^{34}S$, and (b) $\Delta^{36}S$ versus $\delta^{34}S$. All the isotope data are given relative to CDT. The shaded areas are representations of CDT values and 2σ uncertainty. Whereas variability in $\delta^{34}S$ $\Delta^{36}S$ remains mostly within the reported uncertainties, resolvable variations are present in $\Delta^{33}S$, with values varying over a $\sim 0.25\text{‰}$ range. Over the 13 CMs, 5 samples have bulk S with non-CDT $\Delta^{33}S$ values.

Figure 4

For the 13 CMs, the quadruple S isotopic compositions of sulfide (yellow triangles), sulfate (red squares) and S^0 (blue circles) in the 13 CMs: (a) $\Delta^{33}S$ versus $\delta^{34}S$, and (b) $\Delta^{36}S$ versus $\delta^{34}S$. All the isotope data are given relative to CDT. Large $\Delta^{33}S$ variations are recorded in the S^0 extracts. The $\Delta^{33}S$ values vary over a $\sim 0.35\text{‰}$ range. This is also observed in the sulfate extracts, but the sulfide extracts mimic the bulk S compositions with moderate $\Delta^{33}S$ variations that range over $\sim 0.2\text{‰}$. In contrast to bulk S, resolvable $\delta^{34}S$ $\Delta^{36}S$ are present in the individual S components. A $\sim 10\text{‰}$ $\delta^{34}S$ range is observed between sulfate and S^0 . The $\Delta^{36}S$ values vary over a $\sim 1\text{‰}$ range.

Figure 5

$\Delta^{33}\text{S}$ versus the $\Delta^{36}\text{S}$ values of individual S-carrying pools in the 13 CMs. All the isotope data are given relative to CDT. The samples show a rough negative trend, with a slope of -3.9 ± 2.2 (2σ). The slope is better defined if only S^0 is considered, with a value of -3.1 ± 1.0 (2σ). Murchison and MCY 05230 are excluded from this main trend, both showing positive $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ values for their sulfide, sulfate and S^0 . The main trend and the deviations from the main trend (for Murchison and MCY 05230) provide information on the type of H_2S photodissociation that occurred in the nebula (see section 5.4).

Figure 6

An evaluation of the genetic links between the S-carrying phases in CMs. The $\Delta^{33}\text{S}$ values of S^0 are plotted against (a) the sulfate, and (b) the sulfide values. The 1:1 slopes are shown in red. The S^0 -sulfate trend is indistinguishable from a 1:1 slope (MCY 05230 is excluded). For all CMs except MCY 05230, this suggests a direct link between sulfate and S^0 (see section 5.2). Sulfide and S^0 may be linked through their condensation sequence or via the delivery of late sulfide to the CMs that partially oxidize to S^0 (see section 5.4)

Figure 7

The $\Delta^{33}\text{S}$ values of S^0 , sulfate and sulfide, in 12 CMs (PCA 91084, the only heated CM, is excluded). The isotope data are given relative to CDT. Chondrites are ranked by order of increasing $\Delta^{33}\text{S}$ values in S^0 . The values for S^0 are compared with (a) sulfate and (b) sulfide.

Figure 8

Schematic representation of the H_2S photodissociation under open-system Rayleigh distillation conditions as described in model A (see section 5.4.1.). The x-axis is the remaining fraction of H_2S in the nebula. The y-axis is $\Delta^{33}\text{S}$, shown for the remaining H_2S and the instantaneous product S^0 . The star symbols are used for illustrating the composition of H_2S . The composition of the initial H_2S reservoir and H_2S likely recorded by Murchison and MCY 05230 sulfide pools are shown. The hexagon symbol is used for

illustrating the composition of produced S^0 for GRA 98074 as an example (section 5.4.1). For the first and second photodissociation regime ($f > 0.2$ and $f < 0.2$, respectively), $\Delta^{33}S$ fractionations are taken at -0.1‰ and $+0.3\text{‰}$, respectively. For most CMs, $\Delta^{33}S$ values of S^0 are lower than for sulfide, as accounted for by the first photodissociation regime. Additionally, it corresponds to $\Delta^{36}S/\Delta^{33}S$ values for CMs at -3.1 ± 1.0 , consistent with H_2S photodissociation occurring at λ between 120 and 139 nm. The one example of GRA 98074 is taken for illustration here. The conclusion does not change if other CMs were taken for illustration (section 5.4.1). For Murchison and MCY 05230, the $\Delta^{33}S$ values of S^0 are higher than for sulfide, and the $\Delta^{36}S/\Delta^{33}S$ values are positive, indicating a change in the main wavelength responsible for the photodissociation (sections 5.4.1. and 5.4.2.). The minimum $\Delta^{33}S$ value of H_2S at the transition between the two regimes requires a low f value (here 0.2) as constrained by the Murchison value of $+0.156 \pm 0.008\text{‰}$. This requires substantial processing of H_2S for its isotopic composition to have evolved significantly from CDT. We suggest here that the photodissociation process recorded by Murchison and MCY 05230 could postdate the recorded in the other chondrites studied here. Note that with a $\Delta^{36}S/\Delta^{33}S$ of ~ -3 , the first photodissociation regime would lead the $\Delta^{36}S$ values for Murchison and MCY 05230 to be $-0.45 \pm 0.30\text{‰}$, which is not seen (these CMs have $\Delta^{36}S$ values closer to zero, Table 3). Although the large uncertainties on $\Delta^{36}S$ values for these two CMs do not allow invalidating the present prediction, a preferred alternative model is developed in section 5.4.3.

Figure 9

The S isotopic relation between sulfate and its potential precursors: S^0 and sulfide. (a) The $\delta^{34}S$ difference between sulfate and S^0 is plotted versus their $\Delta^{33}S$ difference. (b) The difference between sulfate and sulfide. The occurrence of at least three outliers in the trend between sulfate and sulfide argues against a direct genetic link between sulfate and sulfide. There is a direct negative trend between S^0 and sulfate. This suggests a sulfate origin through S^0 oxidation in the CM parent body (see also fig. 6). The ^{34}S depletion in sulfate, relative to S^0 , indicates that the oxidation process is a normal kinetic mechanism. The more sulfates are depleted in ^{34}S relative to S^0 , the higher their $\Delta^{33}S$ are relative to S^0 . We estimate that the $^{33}S/^{32}S$ fractionation is 0.505 ± 0.005 times that of the $^{34}S/^{32}S$ fractionation. As observed for the first time in

82 natural samples, this relationship indicates that the kinetic oxidation process is characterized by a non-
83 canonical mass dependency (see details in section 5.2).

84

85

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

S^0 content (ppm) Ag_2S weighing

$\Delta^{33}\text{S}$ step 2 (‰)