

TRACING THE NEBULAR SNOWLINE WITH SULFUR ISOTOPES IN IRON METEORITES.

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Introduction: The iron meteorite parent bodies formed by the accretion of dust in at least two chemically and isotopically distinct reservoirs [1]. One of the reservoirs is associated with the carbonaceous chondrites (i.e., the CC reservoir), whereas the other reservoir is associated with the non-carbonaceous chondrites (i.e., the NC reservoir) [2]. The CC and NC reservoirs may have been spatially separated by Jupiter by the time at which the iron meteorite parent bodies formed, i.e., < 1 Ma after the formation of CAIs [3]. Given the implications for early solar system evolution models of the possible spatial separation of the NC and CC reservoir by this time, we attempted to better constrain the formation regions of the iron meteorite parent bodies in the protoplanetary disk by determining the S isotope compositions of sulfide inclusions in iron meteorites.

Mas-independently fractionated S (MIF-S) was detected in achondrites and in irons that are associated with the NC reservoir [e.g., 4-6]. MIF-S was also found in sulfonic acids from meteorites that are associated with the CC reservoir [7] and in volatile species that were present in comet 67P/Churyumov-Gerasimenko [8]. The origin of MIF-S in meteoritic materials remains enigmatic, but possibly involves the photolysis of S-bearing gases in the nebula [4-6,9] and chemical reactions in interstellar ices [8]. Both of these explanations imply a possible relation between the presence of MIF-S in meteoritic materials and their heliocentric formation regions. In order to better understand the spatial relation between the NC and CC reservoirs by the time at which the iron meteorite parent bodies formed, and also to better understand the nature of S isotope variations in meteoritic materials in general, we therefore determined the S isotope compositions ($\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$) of sulfide inclusions from iron meteorites that have been ascribed to the CC and NC reservoirs, respectively [e.g., 1,3]. Mass-independent sulfur isotope variations are henceforth expressed with the parameters $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, which are defined here as $\Delta^{33}\text{S} = \delta^{33}\text{S} - 0.515 \times \delta^{34}\text{S}$ and $\Delta^{36}\text{S} = \delta^{36}\text{S} - 1.91 \times \delta^{34}\text{S}$, respectively. The primes indicate that the linearized δ -values were used to calculate the Δ -values [10].

Methods: Sulfide inclusions from six CC irons (i.e., irons from the IIC, IID, IIIF and IVB groups, as well as two ungrouped irons) and from four NC irons

(i.e., irons from the IVA, IIAB, IIIAB, IAB groups) were analyzed, using the analytical setup at the University of California San Diego [11]. In summary, S was extracted from sulfide sample powders as H_2S by reacting the powders with HCl. Sulfur was then precipitated as CdS, which was subsequently reacted to Ag_2S with a solution of 0.1 M AgNO_3 . The sample Ag_2S was then reacted with excess BrF_5 in nickel reaction tubes to SF_6 by heating of the sample for 12 hours at $\sim 580^\circ\text{C}$. The SF_6 gas that was produced by the reaction was cleaned from contaminant gasses by consecutive distillation steps at -119°C using ethanol cold slushes, and was further cleaned with a gas chromatograph. The isotope compositions of the sample SF_6 gas was determined from SF_5^+ fragments using a MAT253 gas source mass spectrometer. The sample gas was measured for at least 6×20 cycles of 8 s integration time. The δ -values of the samples were determined relative to the composition of a reference gas that has been calibrated against the Canyon Diablo Troilite standard (CDT). A sulfide inclusion was extracted from a slab of Canyon Diablo as well and was analyzed relative to the reference gas for comparison. For each sample, at least three replicate extractions were performed.

Results: The $\delta^{34}\text{S}$ values of irons from CC groups in the dataset ($\delta^{34}\text{S} = 0.2\text{-}1.2\text{‰}$) are tentatively higher than $\delta^{34}\text{S}$ values of irons from the NC groups in the dataset ($\delta^{34}\text{S} = 0\text{-}0.4\text{‰}$). Whereas the magmatic irons from the NC groups show uniform and mildly positive $\Delta^{33}\text{S}$ values of $\sim +0.15\text{‰}$, in contrast, irons from the CC groups show variable $\Delta^{33}\text{S}$ values that are in part negative and lower than the NC irons. The lowest $\Delta^{33}\text{S}$ values in CC irons are found in the IIIF group and are $\sim -0.35\text{‰}$. The non-magmatic NC irons in the dataset display a tentatively lower $\Delta^{33}\text{S}$ than the magmatic NC irons by $\sim 0.15\text{‰}$, i.e., in good agreement with previously published data [4]. The $\Delta^{36}\text{S}$ for both CC and NC irons is identical to CDT within the analytical uncertainty (ca. $< 0.15\text{‰}$). Our results for St. Genevieve County, i.e., a IIIF group iron, overlap within uncertainty with previously published data for other irons from this group [4], whereas our measured value for $\Delta^{33}\text{S}$ in Tlacotepec, a IVB group iron, in contrast, is slightly higher by $\sim 0.015\text{‰}$ than a previously published value for $\Delta^{33}\text{S}$ in a IVB iron [4].

Possible origins of MIF-S in CC irons: We propose two possible end member scenarios to explain the variable and in part negative $\Delta^{33}\text{S}$ values in CC irons (Fig. 1). In the first end-member scenario, the CC irons inherited sulfur from nebular gases (e.g., H_2S , CS_2) that had been involved in photochemical reactions [6,7,9]. A reaction that would have been particularly feasible in the early solar system is the photolysis of H_2S at 121.6 nm, i.e., Lyman- α photolysis [e.g., 6,9]. In the inner solar system, elemental S that would have been produced by this reaction would have reacted with H_2 to form H_2S . In the inner solar system, consequently, only minor variations in $\Delta^{33}\text{S}$ (<0.02 ‰) from Lyman- α photolysis of H_2S are expected to have been incorporated in meteoritic materials [6]. To explain the larger $\Delta^{33}\text{S}$ variations that are seen in the CC irons, in contrast, we propose that photolytic S from Lyman- α photolysis of H_2S may have been shielded from reacting with H_2 if H_2S photolysis occurred in ice. We thus propose that the $\Delta^{33}\text{S}$ variations in CC irons formed in parts of the solar system where ice was stable. Upon heating of the ice, e.g., due to parent body accretion processes, the negative $\Delta^{33}\text{S}$ values were then transferred from photolytic S in ice to refractory S species by the reaction of S with dust and organics. Ultimately, S from these refractory species was then incorporated into the cores of the parent bodies of the CC irons.

The variable and negative $\Delta^{33}\text{S}$ values of CC irons are possibly alternatively explained if the parent bodies of CC irons had accreted a component of presolar ice with ^{33}S -depleted sulfur. Such ^{33}S -depleted sulfur that is potentially of presolar origin was detected in volatile S-species (H_2S , OCS , CS_2) from the cometary ice of 67P/Churyumov-Gerasimenko [8]. The interpretation that the parent bodies of CC irons accreted presolar ice is in good agreement with the variable and extreme $\delta^{15}\text{N}$ variations seen in CC irons [12], which may reflect a component of N that was inherited from presolar ice as well. As the volatile S-species from 67P/Churyumov-Gerasimenko carry negative $\Delta^{33}\text{S}$ values by several hundreds of per mill, only a minor contribution of S from presolar ices (i.e., $<1\%$) to the cores of the parent bodies of CC irons would be required to explain the negative $\Delta^{33}\text{S}$ values that are seen in the CC irons.

Implications for solar system evolution models:

Both scenarios that may explain the variable and in part negative $\Delta^{33}\text{S}$ of CC irons require that the parent bodies of CC irons had accreted ice. In contrast, the apparently uniform $\Delta^{33}\text{S}$ values of NC magmatic irons [6, this study] suggest that the parent bodies of NC irons did not accrete significant portions of ice. By implication, the CC and NC reservoirs were therefore

likely separated by the snowline by the times at which the iron meteorite parent bodies formed. This conclusion demonstrates for the first time that the CC and NC reservoirs were spatially separated by the times at which the iron meteorite parent bodies formed (<1 Ma after the formation of CAIs), i.e., in possible agreement with the inferred early formation of Jupiter [3].

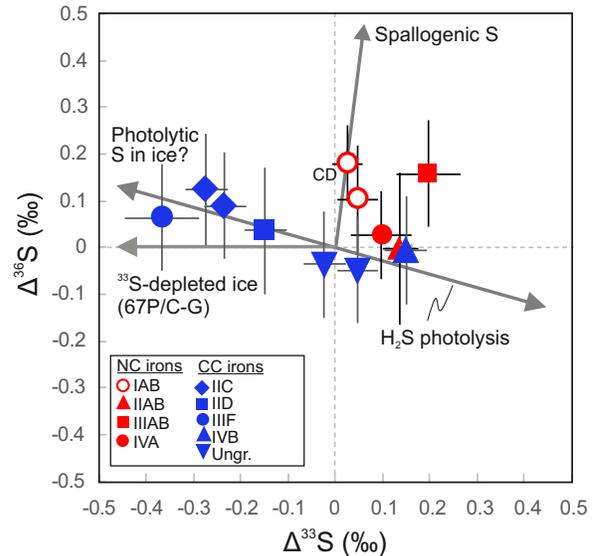


Fig. 1 New sulfur isotope data for sulfide inclusions from carbonaceous (CC) and non-carbonaceous (NC) iron meteorite groups. $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ are reported relative to a reference gas that was calibrated against Canyon Diablo Troilite (CDT; dashed lines); CD = Canyon Diablo. Also shown are the effects of admixing elemental S to CDT that had been produced by Lyman- α photolysis of H_2S in ice [9]; and the effects of admixing presolar ice with a ^{33}S -deficit to CDT, i.e. similar to the ^{33}S -deficits that were observed in 67P/Churyumov-Gerasimenko (67P/C-G)) [8]. Possible effects of the presence of spallogenic S due to meteorite exposure to cosmic rays are also shown [11].

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