

**PHOTOCHEMICAL PROCESSING BY NEARBY STARS RECORDED IN SULFUR ISOTOPES OF COSMIC SYMPLECTITE.** L. G. Vacher<sup>1</sup>, R. C. Ogliore<sup>1</sup>, C. Jones<sup>2</sup>, N. Liu<sup>1</sup> and D. A. Fike<sup>2</sup>. <sup>1</sup>Department of Physics, Washington University in St. Louis, St. Louis, MO 63130, USA. <sup>2</sup>Department of Earth and Planetary Sciences, Washington University in St. Louis, St. Louis, MO 63130, USA. (lvacher@wustl.edu).

**Introduction:** Primitive meteorites display mass-independent (MI) O isotope anomalies that were likely caused by ultraviolet (UV) photochemistry of gas-phase molecules [1]. CO self-shielding is proposed to explain the Solar System's  $\Delta^{17}\text{O}$  variability and may have occurred either (i) in the outer solar nebula by light from the young Sun [1, 2] or (ii) in the parent molecular cloud by light from nearby stars [3, 4]. However, direct constraints on the astrophysical source responsible for photochemical processing are not possible with O isotopes because a range of  $\Delta^{17}\text{O}$  values can be generated by this process [5]. Sulfur isotopes may have also experienced MI isotope fractionation by UV photolysis in the solar nebula or molecular cloud. Photolysis experiments of  $\text{H}_2\text{S}$  at the Lyman- $\alpha$  ( $\text{Ly}\alpha$ ) spectral line (121.6 nm) and larger or smaller wavelengths produce MI anomalies that define distinct  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratios [6]. Young stars have strong emission at  $\text{Ly}\alpha$ , while massive O and B stars dominate the interstellar UV flux [7, 8]. Thus, the photodissociation of  $\text{H}_2\text{S}$  can serve to differentiate between massive stars and young T-Tauri stars as the astronomical source of isotope-selective photodissociation.

Analysis of paired O and S isotope systematics in cosmic symplectite (COS)—a nm-scale intergrowth of  $^{16}\text{O}$ -poor magnetite and pentlandite—in the primitive carbonaceous chondrite Acfer 094 [9, 10] can provide unique insights into photochemical processing of Solar System materials. Acfer 094 shows similarities to cometary material [11] and, therefore, may have formed in the outer Solar System where it could have incorporated  $^{16}\text{O}$ -poor water ice that also contained  $\text{H}_2\text{S}$  ice like that detected in comets [12]. Sulfur in COS may provide insights into the astrophysical environment for the Solar System formation. Here we report the S isotopic composition of COS and determine the likely astrophysical UV source responsible for photochemical processing of Solar System solids.

**Methods:** Oxygen isotopic compositions of COS candidates selected in this study were already described and reported in [12]. On these same COS grains but also four new grains, we analyzed their S isotopic compositions with the Wash U Cameca IMS 7f-GEO using scanning ion imaging. We used a  $\text{Cs}^+$  primary ion beam current of  $\sim 13$  pA and collected  $^{32}\text{S}^-$ ,  $^{33}\text{S}^-$  and  $^{34}\text{S}^-$  on EMs (MRP = 6,000–9,000; raster sizes of  $20 \times 20$  and  $10 \times 10$   $\mu\text{m}$ ). Because of the low primary beam current, the counting statistics of  $^{36}\text{S}^-$  was poor. We, therefore, collected  $^{34}\text{S}^-$  and  $^{36}\text{S}^-$  separately with a  $\text{Cs}^+$  primary ion beams of  $\sim 30$ – $40$  pA to determine the  $^{36}\text{S}/^{34}\text{S}$  isotope

ratio (MRP = 4,000). By multiplying together the mean  $^{34}\text{S}/^{32}\text{S}$  and  $^{36}\text{S}/^{34}\text{S}$  isotope ratios, we determined the mean  $^{36}\text{S}/^{32}\text{S}$  isotope ratio of standards and unknowns. Sulfur isotope ratios of COS were normalized to our in-house pyrrhotite standard ( $\delta^{34}\text{S}_{\text{V-CDT}} = 2.9\text{‰}$ ) and were corrected for dead-time, QSA effect and  $^{32}\text{SH}^-$  hydride contribution ( $<0.6\text{‰}$ ). Data was processed using Matlab code, and regions of interest (ROIs) were defined to include only intrinsic S signals from COS areas.

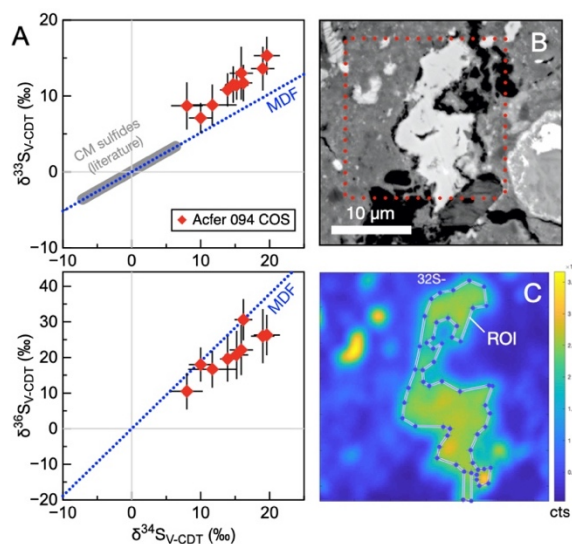


Figure 1: (A)  $\delta^{33}\text{S}$  vs.  $\delta^{34}\text{S}$  and  $\delta^{36}\text{S}$  vs.  $\delta^{34}\text{S}$  plots of COS compared to CM sulfides from [13] ( $2\sigma$  error). (B) BSE image of COS analyzed in this study. (C)  $^{32}\text{S}^-$  ion image for the BSE image (red dotted square) represented in panel B showing the ROI defined in order to extract intrinsic S signals from the COS grain

**Results:** The  $\delta^{33}\text{S}$  and  $\delta^{36}\text{S}$  values of COS grains are  $>10\text{‰}$  larger than those of Fe–Ni sulfides reported in CM chondrites [13] and deviate from the mass-dependent fractionation (MDF) relationship. Our measured  $\Delta^{33}\text{S}$  values vary between  $+1.9$  and  $+6.3\text{‰}$  (weighted mean of  $+3.7 \pm 0.8\text{‰}$ , 2SE) and  $\Delta^{36}\text{S}$  values between  $-0.4$  and  $-11.4\text{‰}$  (weighted mean of  $-5.7 \pm 1.9\text{‰}$ , 2SE) (Figure 1). We calculated the reduced  $\chi^2$  and associated p-value of our data compared to the weighted means for  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$ . The p values of 0.54 for  $\Delta^{33}\text{S}$  and 0.13 for  $\Delta^{36}\text{S}$  imply that our measured COS are consistent with being drawn from a single source reservoir of uniform  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$ .

**Discussion:** Several cosmochemical mechanisms can cause MI sulfur isotope anomalies in meteorites, but only gas-phase photochemistry involving S-bearing gas

(SO<sub>2</sub> and H<sub>2</sub>S) is able to produce S<sup>0</sup> residues associated with positive  $\Delta^{36}\text{S}$  and negative  $\Delta^{36}\text{S}$  values [6]. H<sub>2</sub>S is the major sulfur-bearing species in the solar nebular and molecular clouds [14, 15] and its photochemistry is, therefore, a likely mechanism to produce the S isotopic signature of COS. Since UV photolysis by the protosun or by O and B stars may be able to produce MI sulfur anomalies, we calculated the  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratios generated from these two scenarios to compare with our measurements of  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  in COS (weighted mean =  $-1.4 \pm 0.6$ , 2SE). Then, using (i) the UV spectrum of the TW Hydrae as an analog for the protosun and the interstellar radiation field for the UV radiation from O and B stars [16], (ii) the photodissociation cross sections of H<sub>2</sub>S and (iii) the  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  slopes from H<sub>2</sub>S photolysis experimental data at different wavelengths [6, 17], we calculated the expected  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  values that result from H<sub>2</sub>S photolysis by the young Sun and interstellar UV (Figure 2). We found that photodissociation of H<sub>2</sub>S by the young Sun and interstellar UV generates MI sulfur anomalies that lie on two distinct  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  ratios of  $-2.6 \pm 0.4$  and  $-1.9 \pm 0.3$  (2 $\sigma$ ), respectively. Our measured COS mean value is inconsistent with photochemical processing by the Sun's UV at >95% confidence, but is consistent with irradiation from the interstellar UV spectrum (Figure 2).

A likely interstellar environment to generate MI sulfur anomalies in COS would be photodissociation regions (PDRs) where nearby massive stars irradiate the edges of cold molecular clouds. In PDRs, the gas reaches higher temperature (~100–1,000 K) than the dust (~50–100 K) [19]. UV light from these nearby massive stars will photodissociate gas-phase H<sub>2</sub>S into SH or S<sup>0</sup> and create isotope anomalies in the product S and residual H<sub>2</sub>S. At low temperature, photochemically produced S will adsorb onto molecular cloud dust grains and MI sulfur isotopic anomalies can be preserved in the icy mantles of these grains. CO self-shielding will also take place at the edge of the molecular cloud, producing isotopically heavy H<sub>2</sub>O<sub>(ice)</sub> that also condenses as icy mantles on dust grains [3].

The S and O isotope measurements of COS most likely indicate that the Solar System formed in a large stellar cluster with massive stars (type O and B) in its vicinity. This is a plausible scenario for the Sun's birth environment, since (i) the majority of low-mass sun-like stars form in large clusters relatively close to massive stars [20] and (ii) the presence of short-lived radionuclides in meteorites provides evidence that the Sun formed in a typical massive-star-forming region [21].

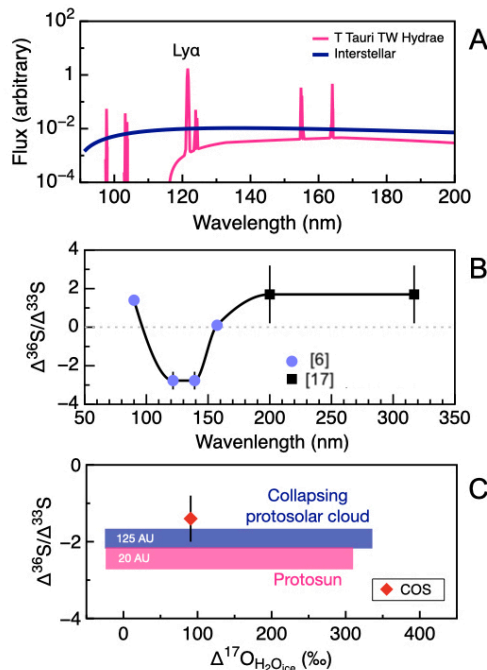


Figure 2: (A) UV spectra of the analog young Sun (TW Hydrae) and the interstellar UV spectrum. (B) Interpolated and measured  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  values produced during H<sub>2</sub>S photodissociation experiments (2 $\sigma$  errors). (C) Measured  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  vs.  $\Delta^{17}\text{O}$  of COS grains (weighted means and 2SE) compared to our calculated photochemical anomalies produced by the protosun and interstellar UV (vertical height is the calculated  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  value  $\pm 2\sigma$  uncertainty). The horizontal range represents the range in  $\Delta^{17}\text{O}$  of water ice produced during CO self-shielding from the protosun in the nebula [18], and that from nearby stars in the collapsing protosolar cloud [3].

**References:** [1] Lyons J. R. and Young E. D. (2005) *Nature*, 435, 317–320. [2] Clayton R. N. (2002) *Nature*, 415, 860–861. [3] Lee J.-E. et al. (2008) *MAPS*, 43, 1351–1362. [4] Yurimoto H. and Kuramoto K. (2004) *Science*, 305, 1763. [5] Huss G. (2012) *M&PSA*, 75, 5294. [6] Chakraborty S. et al. (2012) *PNAS*, 110, 17650–17655. [7] Thalmann C. et al. (2010) *ApJ*, 718, L87–L91. [8] Heays A. N. et al. (2017) *A&A*, 602, A105. [9] Sakamoto N. et al. (2007) *Science*, 317, 231–233. [10] Seto Y. et al. (2008) *GCA*, 72, 2723–2734. [11] Matsumoto M. et al. (2019) *Sci. Adv.*, 5, eaax5078. [12] Vacher L. G. et al. (2020) *LPSC 51st*, abstract #2495. [13] Bullock E. S. et al. (2010) *MAPS*, 45, 885–898. [14] Pasek M. et al. (2005) *Icarus*, 175, 1–14. [15] Rivière-Marichalar P. et al. (2019) *A&A*, 628, A16. [16] Draine B. T. (1978) *Series*, 36, 595–619. [17] Farquhar J. et al. (2000) *Nature*, 404, 50–52. [18] Young E. N. (2007) *EPSL*, 262, 468–483. [19] Esplugues S. et al. (2019) *MNRAS*, 486, 1853–1874. [20] Adam F. C. (2010) *Annu. Rev. Astron. Astrophys.*, 48, 47–85. [21] Young E. D. (2018) *Proc. Int. Astron. Union*, 14, 70–77.