

**OXYGEN ISOTOPIC COMPOSITION OF HIGH-DENSITY PRESOLAR GRAPHITE GRAINS FROM MURCHISON.** Sachiko Amari<sup>1</sup> Noriko T. Kita<sup>2</sup> Frank Gyngard<sup>1</sup> and Maria Lugaro<sup>3</sup>, <sup>1</sup>McDonnell Center for the Space Sciences and Physics Department, Washington University, St. Louis, MO 63130, USA (sa@physics.wustl.edu), <sup>2</sup>WiscSIMS, University of Wisconsin-Madison, Madison, WI, 53706, USA, <sup>3</sup>Konkoly Observatory, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, H-1121 Budapest, Hungary.

**Introduction:** Presolar graphite grains are present only in a few meteorites [1-3]. They show a range of density from 1.6 to 2.2 g/cm<sup>3</sup>. One of the most intriguing characteristics is that isotopic features depend on density. Isotopic analyses of these grains indicate that many low-density graphite grains (1.6 – 2.10 g/cm<sup>3</sup>) originated from core-collapse supernovae (SNe), while high-density graphite grains (2.10 – 2.20 g/cm<sup>3</sup>) originated from low-metallicity asymptotic giant branch (AGB) stars [1, 2].

Four graphite-rich density fractions have been extracted from the Murchison meteorite (CM2): KE3 (1.65 – 1.72 g/cm<sup>3</sup>), KFA1 (2.05 – 2.10 g/cm<sup>3</sup>), KFB1 (2.10 – 2.15 g/cm<sup>3</sup>) and KFC1 (2.15 – 2.20 g/cm<sup>3</sup>). These Murchison graphite grains have been extensively studied using various methods such as noble gas mass spectrometry [4], secondary ion mass spectrometry [1], transmission electron microscopy [5], and Raman spectroscopy [6].

We report C, N, and O isotopic analysis of the grains from KFC1 grains. Many KFC1 grains had already been analyzed for these isotopic ratios. Previous studies focused on analyzing isotopic ratios of as many elements as possible. Consequently analysis of each element was short to preserve grains, sometimes resulting in relatively huge uncertainties in the data.

<sup>18</sup>O/<sup>16</sup>O ratios of many KFC1 grains are normal within errors [1] and it has been attributed to partial equilibrium with normal O either in the meteorite parent body or in the laboratory [1, 7]. In this study, we focused on obtaining high-precision O isotopic ratios to investigate the Galactic chemical evolution and/or mechanisms that might have changed the original O composition of the grains.

**Experimental:** KFC1 grains, deposited onto a gold foil from suspension, were documented for their locations and grain sizes using a scanning electron microscope JEOL JSM-840A at Washington University in St. Louis. Carbon and N isotopic ratios were analyzed using the NanoSIMS 50 at Washington University: <sup>12</sup>C<sup>-</sup>, <sup>13</sup>C<sup>-</sup>, <sup>12</sup>C<sup>14</sup>N<sup>-</sup>, and <sup>12</sup>C<sup>15</sup>N<sup>-</sup> were simultaneously collected. DAG (carbon paint) was used as standard for C isotopes, synthetic Si<sub>3</sub>N<sub>4</sub> for N isotopes.

Oxygen isotopic ratios were analyzed using the CAMECA IMS-1280 (WiscSIMS) at The University

of Wisconsin-Madison. A focused beam of 5pA was used for analysis, and <sup>16</sup>O<sup>-</sup>, <sup>17</sup>O<sup>-</sup> and <sup>18</sup>O<sup>-</sup> were detected with electron multipliers. Terrestrial organic matter containing ~2wt.% of O (WI-STD-64, UWMA1) was used as standard. Since the O isotopic composition of the standard has not been determined yet, we took an average of 23 organic samples ( $\delta^{18}\text{O} = 21.1 \pm 10.8 \%$ ,  $2\sigma$ ) that are similar to the standard and used the average. The errors of the data reported here are  $2\sigma$ .

**Results and Discussion:** Carbon and N isotopic ratios of the grains agree with those of previous studies [1]: many grains have <sup>12</sup>C/<sup>13</sup>C ratios higher than solar and their N isotopic ratios are close to that of air.

Two grains show <sup>18</sup>O excesses. Grain KFC1h-612 has  $\delta^{18}\text{O} = 1480 \pm 26 \%$ , and  $\delta^{17}\text{O} = 35 \pm 10 \%$ . It has a <sup>12</sup>C/<sup>13</sup>C ratio ( $92.7 \pm 3.3$ ) close to solar (89) and a <sup>14</sup>N/<sup>15</sup>N ratio ( $98 \pm 6$ ) significantly lower than that of air (272). The <sup>18</sup>O excess in KFC1h-524 is not so pronounced ( $\delta^{18}\text{O} = 119 \pm 30 \%$ ), with a <sup>12</sup>C/<sup>13</sup>C ratio of  $12.9 \pm 0.4$  and normal N ( $255 \pm 21$ ). These <sup>18</sup>O excesses are indicative of their supernova (SN) origin [1, 2, 8]. The low <sup>14</sup>N/<sup>15</sup>N ratio of KFC1h-612 reinforces its SN origin as many SN graphite grains show <sup>15</sup>N excesses [1, 2].

Except these two grains, the rest of the grains plot around 40 ~ 80 ‰ for  $\delta^{18}\text{O}$  and 10 ~ 60 ‰ for  $\delta^{17}\text{O}$  in a O 3-isotope plot (Fig. 1) regardless of their <sup>12</sup>C/<sup>13</sup>C ratios, which range from 6.7 to 805 (Fig. 2). The average values excluding the two <sup>18</sup>O-rich grains are  $\delta^{18}\text{O} = 55 \pm 12 \%$  and  $\delta^{17}\text{O} = 38 \pm 16 \%$ .

KFC1 grains with <sup>12</sup>C/<sup>13</sup>C ratios higher than 100 are believed to have formed in low-metallicity ( $Z = 3 \times 10^{-3}$  and  $6 \times 10^{-3}$ ,  $Z_{\text{sun}} = 2 \times 10^{-2}$ ) AGB stars [1]. The O isotopic composition of the envelope is altered during the first dredge-up. During the third dredge-up phase, <sup>16</sup>O is produced significantly only in the deeper radiative parts of the He shell. In stars up to  $5M_{\text{sun}}$  stars, AGB nucleosynthesis hardly changes the O isotopic composition of the envelope. It is predicted that  $\delta^{18}\text{O}$  values in the envelope remain negative up to half a solar metallicity, while  $\delta^{17}\text{O}$  values become positive at  $Z = 6 \times 10^{-3}$  ( $3.89 \times 10^{-4}$ ) [1]. Thus, we expect negative  $\delta^{18}\text{O}$  and negative/positive  $\delta^{17}\text{O}$  values in the original O isotopic composition in these grains. The ob-

served O isotopic composition, positive  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values, is not what is expected from AGB stars.

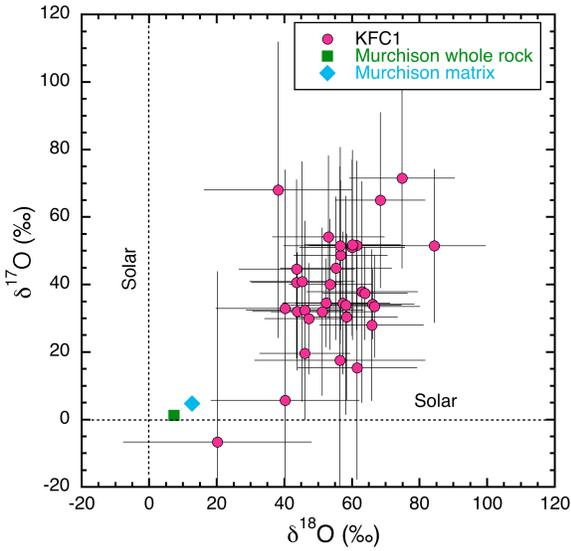


Fig. 1. Oxygen isotopic compositions of KFC1 grains except the two  $^{18}\text{O}$ -rich grains and Murchison [9].

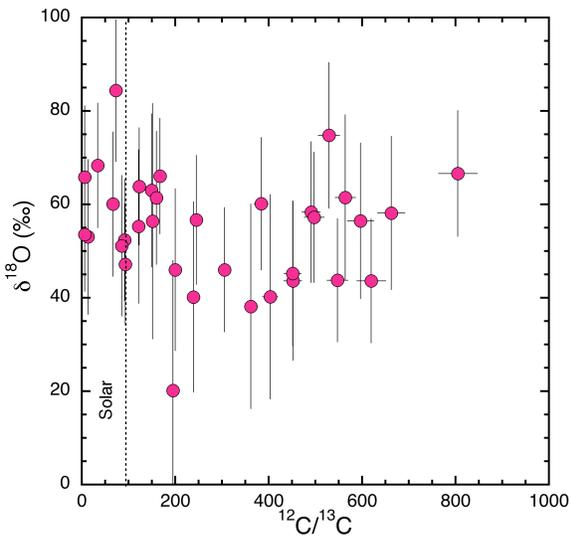


Fig. 2.  $\delta^{18}\text{O}$  and  $^{12}\text{C}/^{13}\text{C}$  ratios of KFC1 grains except the two  $^{18}\text{O}$ -rich grains.

Partial equilibrium of indigenous O and N in graphite grains has been discussed [7]. However, the equilibrium with normal O cannot explain the observed O isotopic composition: if the indigenous O is partially equilibrated with solar O, the  $\delta^{18}\text{O}$  of the grains should still be negative. Partial exchange with the O in Murchison meteorite cannot explain the grains' O isotopic composition, either.  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  of a whole rock and matrix of Murchison are 7.3 ‰ and 1.2 ‰, and 12.7 ‰ and 4.72 ‰, respectively [9].

Sakamoto et al. [10] reported the presence of cosmic symplectite (COS), consisting of magnetite ( $\text{Fe}_3\text{O}_4$ ) and pentlandite ( $\text{Fe}_{5.7}\text{Ni}_{3.3}\text{S}_8$ ) [11], with  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  of  $\sim 180$  ‰. It is interpreted that Fe metal and/or sulfide was oxidized by isotopically heavy water either in the solar nebula or in a meteorite parent body [10]. It remains to be seen whether  $^{17}\text{O}$  and  $^{18}\text{O}$ -rich isotopic composition of the graphite grains is a result of interaction with isotopically heavy water.

**References:** [1] Amari S. et al. (2014) *Geochem. Cosmochim. Acta*, 133, 479-522. [2] Jadhav M. et al. (2013) *Geochem. Cosmochim. Acta*, 113, 193-224. [3] Xu Y. et al. (2016) *Astrophysical J.*, 825:111 (12pp). [4] Amari S. et al. (1995) *Geochim. Cosmochim. Acta*, 59, 1411-1426. [5] Croat T. K. et al. (2003) *Geochim. Cosmochim. Acta*, 67, 4705-4725. [6] Wopenka B. et al. (2013) *Geochem. Cosmochim. Acta*, 106, 463-489. [7] Hoppe P. et al. (1995) *Geochim. Cosmochim. Acta*, 59, 4029-4056. [8] Amari S. et al. (1995) *Astrophys. J.*, 447, L147-L150. [9] Clayton R. N. and Mayeda T. K. (1999) *Geochem. Cosmochim. Acta*, 63, 2089-2104. [10] Sakamoto N. et al. (2007) *Science*, 317, 231-233. [11] Seto Y. et al. (2008) *Geochem. Cosmochim. Acta*, 72, 2723-2734.