

# Carbon isotopic ratios of calcite grains in the LAP 031166 CM chondrite: Implications for possible link between CM and cometary ices.

Wataru Fujiya<sup>1</sup>, Kohei Fukuda<sup>2</sup>, Paula Lindgren<sup>3</sup>, Martin R. Lee<sup>4</sup>, Mizuho Koike<sup>5</sup>, and Yuji Sano<sup>5</sup>

<sup>1</sup>Ibaraki University, 2-1-1 Mito, Bunkyo, Ibaraki 310-8512, JAPAN. (wateru.fujiya.sci@vc.ibaraki.ac.jp),

<sup>2</sup>University of Tokyo, <sup>3</sup>Lund University, <sup>4</sup>University of Glasgow, <sup>5</sup>Atmosphere and Ocean Research Institute, University of Tokyo.

**Introduction:** Carbonate minerals are ubiquitous in CM chondrites, which formed by aqueous alteration in the CM chondrite parent body. Previous studies have shown that C isotopic ratios of CM carbonates are highly variable at whole-rock scales as well as among individual grains in single meteorites [e.g., 1-3]. Despite extensive studies on C isotopic ratios of CM carbonates, the reason for variability in  $\delta^{13}\text{C}$  variation and the origin of the carbonate C remain poorly understood.

Here we report C isotopic ratios of calcite ( $\text{CaCO}_3$ ) in the LAP 031166 CM chondrite (CM 2.1), and discuss the origin of the carbonate C and a possible link between ices in CMs and in comets. The O isotopic ratios of calcite in this meteorite were reported by Lindgren et al. [4].

**Experimental:** Carbon-isotope analysis was performed with the NanoSIMS 50 installed at Atmosphere and Ocean Research Institute, the University of Tokyo, on the calcite grains whose O isotopic ratios were measured previously. Negative secondary ions of  $^{12}\text{C}^-$ ,  $^{13}\text{C}^-$ ,  $^{18}\text{O}^-$ ,  $^{12}\text{C}^{14}\text{N}^-$ , and  $^{28}\text{Si}^-$  produced by rastering a  $\text{Cs}^+$  primary ion beam (20-30 pA,  $\sim 1\ \mu\text{m}$  in diameter) over  $6\ \mu\text{m}^2$  sized areas were detected simultaneously with five electron multipliers.

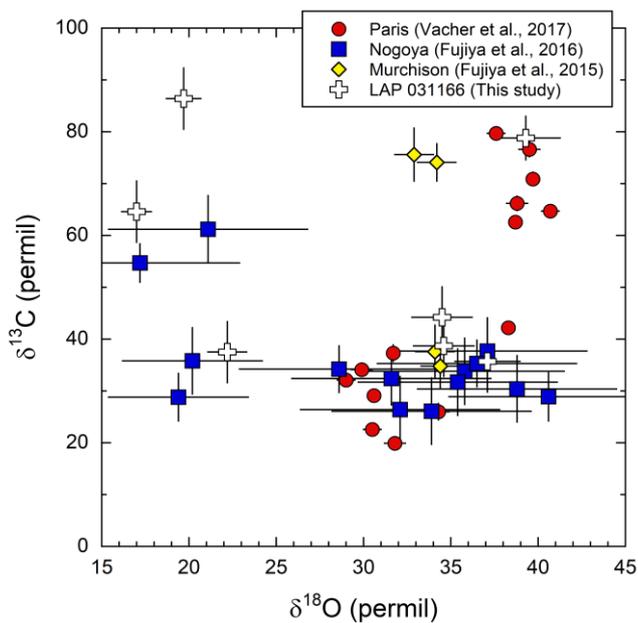
**Results and discussion:** The  $\delta^{13}\text{C}_{\text{PDB}}$  and  $\delta^{18}\text{O}_{\text{SMOW}}$  values of the calcite grains in LAP 031166 are shown in Fig. 1, together with literature data of Ca-carbonate (calcite and aragonite) in the Murchison, Nogoya, and Paris CM chondrites [3,5,6]. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the CM carbonates are highly variable, ranging from  $\sim 20$  to  $80\text{‰}$  and from  $\sim 15$  to  $40\text{‰}$ , respectively, and they do not correlate with each other.

Alexander et al. [1] have suggested that the range in  $\delta^{13}\text{C}$  can be explained by variable formation temperatures (0-130 °C) of CM carbonates which are isotopically equilibrated with gaseous C species dominated by CO (or  $\text{CH}_4$ ). However, this model implies that the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the CM carbonates would correlate, which is clearly not the case as demonstrated by this work (Fig. 1). Instead, the observed  $\delta^{13}\text{C}$  range must be produced under nearly constant temperatures.

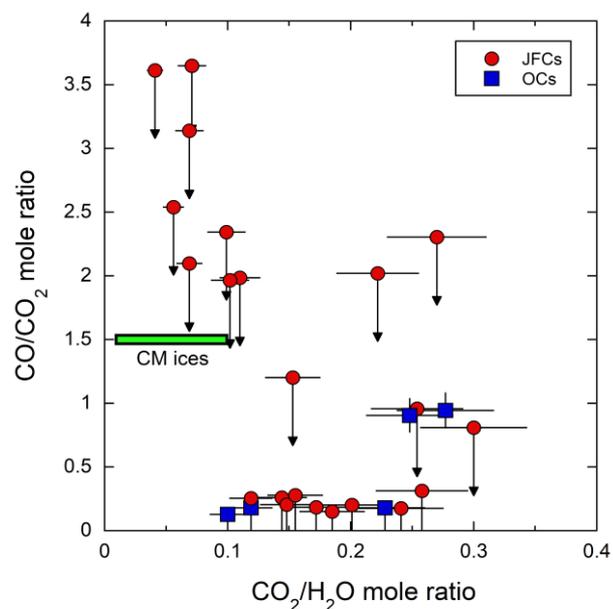
Here we propose a modified version of the model outlined by Alexander et al. [1], where we consider mixing of  $\text{CO}_2$  and CO gases with higher and lower  $\delta^{13}\text{C}$  values, respectively. Because the equilibrium  $\text{CO}/\text{CO}_2$  ratios are  $\ll 1$  for  $f_{\text{O}_2}$  higher than the iron-magnetite buffer, CO should be converted to  $\text{CO}_2$  and the  $\text{CO}/\text{CO}_2$  ratios of gas phases would have decreased with time. As the  $\text{CO}/\text{CO}_2$  ratios decreased,  $\text{CO}_2$  as well as carbonates acquired lower  $\delta^{13}\text{C}$  values. Given  $1000\ln\alpha(\text{calcite}-\text{CO}_2)$  of  $\sim 10$ -14 at 0-30 °C [7], where  $\alpha$  is a C isotopic fractionation factor, the CM carbonates with the highest  $\delta^{13}\text{C}$  values of  $\sim 80\text{‰}$  were equilibrated with  $\text{CO}_2$  with  $\delta^{13}\text{C} \sim 70\text{‰}$ . The  $\delta^{13}\text{C}$  value of the trapped CO in Murchison is  $\sim 30\text{‰}$  [8]. The lowest  $\delta^{13}\text{C}$  values of the CM carbonates are  $\sim 20$ -30‰, which is common for all the CM chondrites analyzed (Fig. 1). Therefore, the gaseous C species which coexisted with the CM carbonates with the lowest  $\delta^{13}\text{C}$  values of  $\sim 20$ -30‰ would have been dominated by  $\text{CO}_2$ , i.e., most of CO was converted to  $\text{CO}_2$ . If correct, the  $\delta^{13}\text{C}$  value of the bulk gaseous C species ( $\text{CO}_2 + \text{CO}$ ) would be  $\sim 10\text{‰}$ . Using the above numbers, mass balance calculation suggests that a  $\text{CO}/\text{CO}_2$  mole ratio of the gaseous C species which coexisted with the CM carbonates with the highest  $\delta^{13}\text{C}$  value of  $\sim 80\text{‰}$  would be  $\sim 1.5$ , which may reflect the  $\text{CO}/\text{CO}_2$  ratio of ice accreted onto the CM parent body. The carbonate  $\text{C}/\text{H}_2\text{O}$  mole ratios of most CMs range from  $\sim 0.01$  to  $0.1$  [1]. These carbonate  $\text{C}/\text{H}_2\text{O}$  ratios may set lower limits on the  $\text{CO}_2/\text{H}_2\text{O}$  ratio of the CM ices because of possible  $\text{CO}_2$  loss. Thus,  $\text{CO}_2$  accounts for at least 1 % of the CM ices.

The inferred  $\text{CO}/\text{CO}_2$  and  $\text{CO}_2/\text{H}_2\text{O}$  mole ratios of the CM ices are shown in Fig. 2, together with those of cometary ices [9]. Unfortunately, only upper limits on the  $\text{CO}/\text{CO}_2$  ratios are obtained for most of the observed comets. Nevertheless, the  $\text{CO}/\text{CO}_2$  ratios of these comets seem lower than unity, and thus, lower than those of the CM ices. Although the possible similarity between ices in CMs and in some comets cannot be ruled out, these observations suggest that ices in the two classes of bodies had a different origin, which is consistent with contrasts in the D/H ratios of water between CMs and comets [10].

**References:** [1] Alexander C. M. O'D. et al. 2015. Meteorit. Planet. Sci. 50:810. [2] Tyra M. A. et al. 2012. Geochim. Cosmochim. Acta 77:383. [3] Fujiya W. et al. 2015. Geochim. Cosmochim. Acta 161:101. [4] Lindgren P. et al. 2017. Geochim. Cosmochim. Acta 204:240. [5] Fujiya W. et al. 2016. Abstract #1712. 47th LPSC. [6] Vacher L. G. et al. 2017. Geochim. Cosmochim. Acta 213:271. [7] Chacko T. et al. 2001. Rev. Mineral. Geochem. 43.1. [8] Yuen G. et al. 1984. Nature 307:252. [9] Ootsubo T. et al. 2012. Astrophys. J. 752:15. [10] Alexander C. M. O'D. et al. 2012. Science 337:721



**Fig. 1.**  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of Ca-carbonates in CM chondrites. Errors are  $2\sigma$ .



**Fig. 2.**  $\text{CO}/\text{CO}_2$  and  $\text{CO}_2/\text{H}_2\text{O}$  mole ratios of the inferred CM ices and comets. Data with arrows represent upper limits. JFCs: Jupiter-family comets, OCs: Oort cloud comets. Only comets which were observed within 2.5 AU from the Sun are shown, where  $\text{H}_2\text{O}$  effectively sublimates from the nucleus of the comet.