

**MN-CR AGE OF DOLOMITE IN THE IVUNA CI CHONDRITE.** W. Fujiya<sup>1</sup>, N. Sugiura<sup>1</sup> and Y. Sano<sup>2</sup>,  
<sup>1</sup>Earth and Planetary Science, The Univ. of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan ([fujiya@eps.s.u-tokyo.ac.jp](mailto:fujiya@eps.s.u-tokyo.ac.jp)), <sup>2</sup>Atmosphere and Ocean Research Institute, The Univ. of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8564, Japan.

**Introduction:** CI chondrites are the most compositionally primitive rocks among the solar system materials [1], although they experienced pervasive aqueous alteration [2]. In order to decipher the geological history, it is important to determine the timescale of the aqueous activity in the CI chondrite parent body.

<sup>53</sup>Mn-<sup>53</sup>Cr systematics (<sup>53</sup>Mn decays to <sup>53</sup>Cr with a half-life of 3.7 Myr) of dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) and breunnerite (Mg(Fe,Mn)(CO<sub>3</sub>)<sub>2</sub>) measured with ion probes have been reported for the Orgueil CI chondrite [3-6]. The initial (<sup>53</sup>Mn/<sup>55</sup>Mn)<sub>0</sub> ratios range from 6.26 to 1.42 x 10<sup>-6</sup> for dolomite and from 3.37 to 0.58 x 10<sup>-6</sup> for breunnerite, which correspond to absolute ages of ~4567-4559 Ma and ~4564-4554 Ma, respectively. The ages seem different not only between dolomite and breunnerite, but also among individual dolomite (and breunnerite) grains. Based on oxygen and carbon isotopic compositions, this is interpreted as a sequential precipitation of carbonates [7]. Then, carbonate precipitation lasted for ~13 Myr at face value. It should be noted that these studies [3-6] used the <sup>55</sup>Mn/<sup>52</sup>Cr relative sensitivity factor (RSF) of silicate standards. Hence the reported (<sup>53</sup>Mn/<sup>55</sup>Mn)<sub>0</sub> ratios likely suffer from systemic errors [8], although the relative age differences may be preserved.

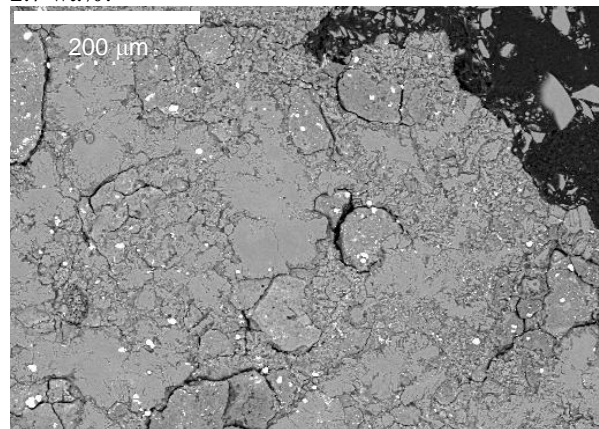
Here we report Mn-Cr systematics of six dolomite grains in the Ivuna CI chondrite. Only one report on Mn-Cr systematics of the Ivuna dolomite has been reported [4]. Hence, further investigations are needed for the accurate Mn-Cr age determination.

**Experimental:** We prepared a polished thin section of Ivuna and determined chemical compositions of dolomite grains with the EDS attached to the SEM.

Mn-Cr isotope measurements were performed with the NanoSIMS installed at Atmosphere and Ocean Research Institute, the Univ. of Tokyo. <sup>43</sup>Ca<sup>+</sup>, <sup>52,53</sup>Cr<sup>+</sup> and <sup>55</sup>Mn<sup>+</sup> were measured in a combined peak-jumping/multi-detection mode with the O<sup>-</sup> primary ion beam (~5 μm beam size, ~1 nA). The magnet was cycled through two field settings 150 times. In the first, <sup>43</sup>Ca<sup>+</sup>, <sup>52</sup>Cr<sup>+</sup> and <sup>55</sup>Mn<sup>+</sup> were simultaneously detected on three EMs (2 seconds), and in the second <sup>53</sup>Cr<sup>+</sup> was measured on the same EM as that for <sup>52</sup>Cr<sup>+</sup> (5 seconds). If possible, multiple measurements were performed for a single dolomite grain depending on its grain size. The <sup>55</sup>Mn/<sup>52</sup>Cr RSF of 0.690 are determined using a synthetic calcite standard doped with Mn and Cr [8]. The standard deviation of the RSF is 7.4% (2σ) for repeat

measurements in this study. Combining the RSF in this study and previous ones ([8] and our unpublished data), a systematic error of 8.1% due to the RSF is applied to the error on the (<sup>53</sup>Mn/<sup>55</sup>Mn)<sub>0</sub>. The standard deviation of <sup>53</sup>Cr/<sup>52</sup>Cr ratios is 4.5‰ (2σ) for the standard, much smaller than the counting errors for the Ivuna dolomite and their <sup>53</sup>Cr excesses. Typical count rates of <sup>52</sup>Cr<sup>+</sup> are 1-20 cps/nA for the Ivuna dolomite depending on Cr concentrations. <sup>52,53</sup>Cr<sup>+</sup> count rates are corrected for dynamic background (~0.03 cps). Errors on <sup>53</sup>Cr/<sup>52</sup>Cr and <sup>55</sup>Mn/<sup>52</sup>Cr ratios are based on the counting errors. <sup>53</sup>Cr excesses of the Ivuna dolomite are represented as permil deviations (δ<sup>53</sup>Cr) from the <sup>53</sup>Cr/<sup>52</sup>Cr ratio of the standard assumed to be 0.1134 [1]. The slope and its error of the isochron are calculated using the York fit program 'Isoplot 3.41' [9].

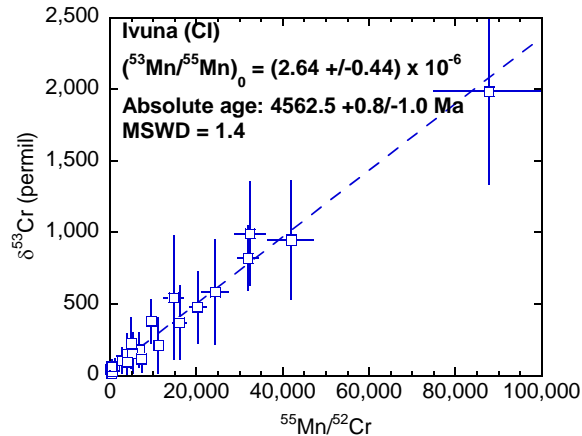
**Results and discussion:** We found many dolomite grains in the polished thin section. Six grains of them were chosen for the Mn-Cr isotope measurements based on their grain sizes and the lack of potential contamination (cracks, oxide and/or sulfide inclusions). Two of six grains are in a clast of ~1 mm<sup>2</sup> in size dominated by dolomite with less abundant phyllosilicate and magnetite (Fig. 1), while the remainders are isolated grains. Their Mn concentrations range from 0.7 to 2.7 wt.%.



**Figure 1:** Back scattered electron image of dolomite in Ivuna. It is in a clast of ~1 mm<sup>2</sup> in size dominated by dolomite with less abundant phyllosilicate and magnetite.

We plot Mn-Cr data for the six dolomite grains in a δ<sup>53</sup>Cr vs. <sup>55</sup>Mn/<sup>52</sup>Cr diagram (Fig. 2). <sup>53</sup>Cr excesses are well correlated with <sup>55</sup>Mn/<sup>52</sup>Cr, which indicates the in-situ decay of <sup>53</sup>Mn. The slope of the best fit line for

whole data corresponds to  $(^{53}\text{Mn}/^{55}\text{Mn})_0$  of  $(2.64 \pm 0.44) \times 10^{-6}$  and all data lie on a single regression line (i.e., no difference among slopes of the six grains is found). If we assume the homogeneous distribution of  $^{53}\text{Mn}$  in the early solar system, we obtain an absolute age of  $4562.5 \pm 0.8/-1.0$  Ma for dolomite in Ivuna using the LEW86010 angrite as a time anchor [10,11].



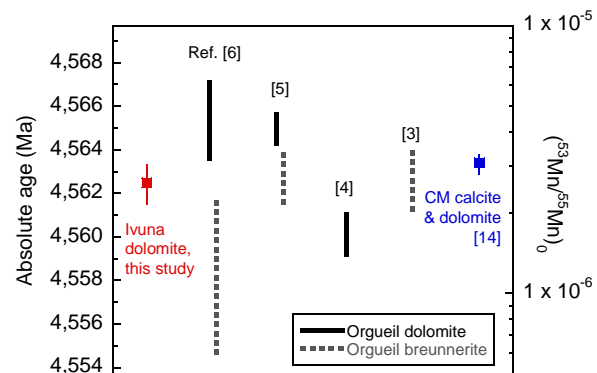
**Figure 2:** Mn-Cr isochron of dolomite in Ivuna. Errors are  $2\sigma$ . The absolute age is  $4562.5 \pm 0.8/-1.0$  Ma.

We show the Mn-Cr age of dolomite in Ivuna, and for comparison, dolomite and breunnerite in Orgueil [3-6] in Fig. 3. Also shown in Fig. 3 is the average Mn-Cr age of calcite and dolomite in four CM chondrites (Murchison CM2.5, Y791198 CM2.4, ALH83100 CM2.1 and Sayama CM2.1; data are from Fujiya et al. [12]). Dolomite in Ivuna is younger than that in Orgueil [5,6]. However, previous studies [5,6] used silicate standards for calibration of  $^{55}\text{Mn}/^{52}\text{Cr}$  ratios of dolomite. If the RSFs are corrected, then the Mn-Cr ages of the Orgueil dolomite [5,6] are consistent with that of the Ivuna dolomite (the bias in ages is  $\sim 1.6$  Myr assuming the RSF of 0.93 for San Carlos olivine [5]). The Ivuna dolomite in this study is older than the Orgueil and Ivuna dolomite in Endress et al. [4], which is unlikely due to the difference in the RSFs. The reason for this discrepancy is unknown at this time.

Our data of Ivuna and CM chondrites indicate that calcite and dolomite in CI and CM chondrites formed around the same time. Because calcite precipitation appears to have preceded dolomite formation, our data imply contemporaneous accretions of the CI and CM chondrite parent bodies and dolomitization occurred soon after calcite precipitation. Based on oxygen isotopic compositions [13], aqueous alteration of CI chondrites likely occurred at higher temperatures than that in CM chondrites and dolomite formed at higher temperatures than calcite. Therefore, similar Mn-Cr ages of carbonates in CI and CM chondrites are consis-

tent with a rapid increase in temperature by decay energy of  $^{26}\text{Al}$  (half-life: 0.73 Myr) [14].

On the other hand, it seems that formation ages of individual breunnerite grains in Orgueil have a range and they are younger than those of dolomite grains [5,6]. The range of ages is preserved even if the different RSFs are used. Therefore, we conclude that the breunnerite formation persisted for at least 7 Myr following dolomite formation at high temperatures. If we assume the Mn-Cr ages in Petit et al. [6] are biased by 1.6 Myr due to the RSFs, breunnerite formation (and therefore, aqueous alteration) in Orgueil lasted until  $\sim 4553$  Myr (at least 10 Myr after dolomite formation in Ivuna). Note that it is possible that the RSFs of dolomite and breunnerite are different from that of calcite. The production of a synthetic dolomite standard doped with Mn and Cr is now in progress in our laboratory and we will check the RSF in the near future.



**Figure 3:** Mn-Cr ages of carbonates in CI and CM chondrites. Black solid and gray dotted lines show ranges of previously reported ages for Orgueil dolomite and breunnerite grains, respectively [3-6].

**References:** [1] Lodders K. et al. (2009) in *Landolt-Börnstein, VI-4B*, 560-598. [2] Brearley A. J. (2006) in *Meteorites and the Early Solar System II*, 587-624. [3] Hutcheon I. D. and Phinney D. L. (1996) *LPS XXVII*, Abstract #1289. [4] Endress M. et al. (1996) *Nature*, 379, 701-703. [5] Hoppe P. et al. (2007) *Meteoritics & Planet. Sci.*, 42, 1309-1320. [6] Petit M. et al. (2009) *LPS XXXX*, Abstract #1657. [7] Zito K. L. et al. (1998) *Meteoritics & Planet. Sci.*, 33, A171. [8] Sugiura N. et al. (2010) *Geochem. J.*, 44, e11-e16. [9] Ludwig K. R. (2003) *Berkeley Geochronology Center Special Publication No. 4*, 1-73. [10] Lugmair G. W. and Shukolyukov A. (1998) *GCA*, 62, 2863-2886. [11] Amelin Y. (2008) *GCA*, 72, 221-232. [12] Fujiya W. et al. (2011) submitted. [13] Clayton R. N. and Mayeda T. K. (1984) *EPSL*, 67, 151-161. [14] Grimm R. E. and McSween, H. Y. Jr (1993) *Science*, 259, 653-655.