

**DURATION AND SEQUENCE OF CARBONATE CRYSTALLIZATION ON THE ORGUEIL PROTOLITH:  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  SYSTEMATICS OF THEIR EVOLUTION IN O AND C ISOTOPIC COMPOSITION.** M. Petitat<sup>1</sup>, K. McKeegan<sup>2</sup>, M. Gounelle<sup>1</sup>, S. Mostefaoui<sup>1</sup>, Y. Marrocchi<sup>1</sup>, A. Meibom<sup>1</sup>, L.A. Leshin<sup>3</sup>. <sup>1</sup>Laboratoire d'Étude de la Matière Extraterrestre, Muséum National d'Histoire Naturelle, 57 rue Cuvier 75005 Paris, France; <sup>2</sup>Department of Earth and Space Sciences, University of California, Los Angeles, CA 90095-1567; <sup>3</sup>Office of the Director, NASA Goddard Space Flight Center, Greenbelt, MD 20771, United States. E-mail: mpetitat@mnhn.fr.

**Introduction:** Aqueous alteration of silicate primary minerals is an important process that occurred in the inner solar system on the parent bodies of meteorites, as evidenced by secondary mineralization such as the formation of carbonates in primitive meteorites (e.g. [1]). Zito et al. [2] measured the oxygen and carbon isotope compositions of individual carbonate grains from the Orgueil meteorite and discovered a clear trend of correlated increasing isotopic values in carbon and oxygen, from breunnerite to dolomite to calcite [2]. The formation of CI carbonates is known to be early from  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  studies [4,5,6] but the duration and sequence of precipitation is not well-constrained by available chronological data.

The goals of the present work are to: (1) refine the timescales of carbonate formation on the Orgueil parent body, and (2) determine if a correlation exists between the measured initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios and O and C isotope compositions measured for the same grain thereby constraining the sequence of carbonate crystallisation during the progressive protolith alteration hypothesized by [2].

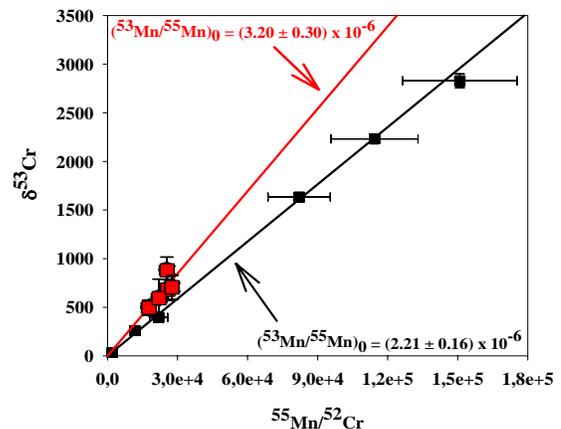
**Experimental methods:** Chemical compositions of Orgueil carbonates were determined at UCLA using conventional SEM and EMPA techniques.  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  data were gathered at MNHN using the NanoSims and at UCLA using the Cameca ims 1270.

**NanoSims:**  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  analyses were made by rastering a 1-3nA  $^{16}\text{O}^-$  primary beam over a  $5 \times 5 \mu\text{m}^2$  area on the polished sample. The secondary ion intensities of  $^{52}\text{Cr}^+$ ,  $^{53}\text{Cr}^+$ , and  $^{55}\text{Mn}^+$  were measured by coupling multi-collection to magnetic peak-switching at high mass resolution sufficient to resolve all molecular ion interferences, including hydrides. The relative sensitivity factor (RSF) for  $^{55}\text{Mn}/^{52}\text{Cr}$  was determined from the mean of analyses of 4 standards: NBS611, San Carlos olivine, T1-G and ATHO-G. Unfortunately, as with previous ion probe investigations, no carbonate standards were available and thus our Mn/Cr ratios may suffer from a systematic error, but they are still comparable to previous results obtained on carbonates.

Mass fractionation was corrected externally, i.e.  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios in the Orgueil carbonates were normalized relative to the average value of the  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios measured for the 4 aforementioned standards and are reported as  $\delta^{53}\text{Cr}$ , expressed as the deviation, in parts per mil, from the reference  $^{53}\text{Cr}/^{52}\text{Cr}$  value of  $0.113457 \pm 0.000001$  [3]. Given the

magnitude of  $\delta^{53}\text{Cr}$  excesses, possible matrix effects on the mass fractionation correction are negligible.

**ims 1270:** Elliptical beam spots of  $\sim 20 \times 30 \mu\text{m}$  were sputtered by a 10 nA  $^{16}\text{O}^-$  beam and  $^{52}\text{Cr}^+$ ,  $^{53}\text{Cr}^+$  and  $^{55}\text{Mn}^+$  were measured in multi-collection mode with  $^{55}\text{Mn}^+$  intensity analyzed by a Faraday cup or electron multiplier depending on the Mn concentration. Although sacrificing spatial resolution compared to the NanoSims, the ims 1270 configuration allowed measurement of high Mn/Cr phases with enough Cr intensity to attain good counting statistics. As previously, measured  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios in the Orgueil carbonates were normalized to those obtained for NBS610 glass and the San Carlos Olivine and the RSF was determined by measuring the same standards (and results agree with those found for the NanoSims). Isotope count rates were corrected for dynamic background and dead time. Uncertainties are expressed in  $2\sigma$ .



**Figure 1.** Mn-Cr isochron diagram for breunnerite 33, Orgueil\_2 (**black squares**) bearing the highest  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio and for dolomite\_5, Orgueil\_1 (**red squares**) grain bearing the lowest initial value from the Orgueil meteorite. Error bars are  $2\sigma$ .

**Results:** Measurements were made for 8 breunnerite grains (100 to 500  $\mu\text{m}$  in diameter) and 3 dolomite grains (80 to 100  $\mu\text{m}$  in diameter) that were previously studied for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  [2] and 8 other breunnerite grains. Elemental and isotopic ratios vary widely within a carbonate grain but are linearly correlated constituting strong evidence for in situ  $^{53}\text{Mn}$  decay (Fig. 1). The slope of this correlation line gives the initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio at the time of carbonate formation. These range from  $(0.58 \pm 0.06) \times 10^{-6}$  to  $(2.21 \pm 0.16) \times 10^{-6}$  for breunnerites and

$(3.20 \pm 0.30) \times 10^{-6}$  to  $(6.26 \pm 0.80) \times 10^{-6}$  for dolomites. The initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios measured for the same carbonate grain using the two different instruments are identical within error.

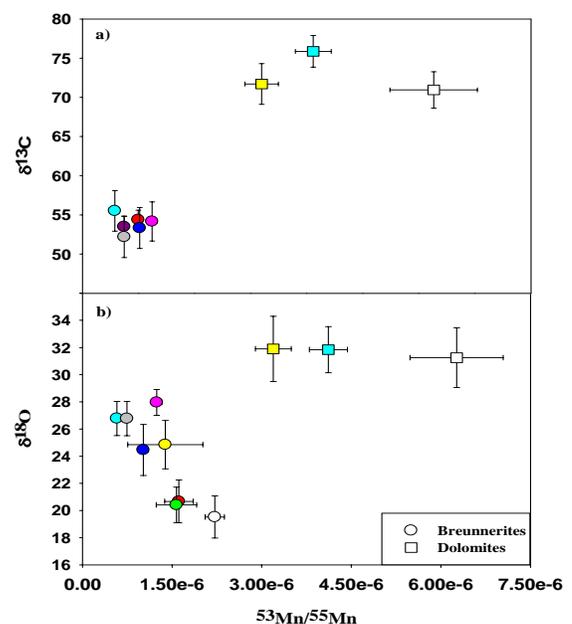
**Discussion:** The initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios inferred for dolomites and breunnerites in this study differ significantly from each other (Fig 2). Our breunnerite average value is similar to the one obtained by [4] and by [5] but is lower than the one from [6]. Our dolomites show similar values within errors with the one calculated by [4] and values for Chainpur [7] and Semarkona [8] chondrules. Because Mn-Cr systematics of CAIs have been disturbed, one needs to rely on other samples to determine *indirectly* the initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio of the solar system [3,9,10]. Here we will adopt the value of  $^{53}\text{Mn}/^{55}\text{Mn} = 8.5 \pm 1.2 \times 10^{-6}$  [9,10] based on bulk rock CCs. It is slightly higher than the initial value proposed by Trinquier *et al.* [11] of  $6.3 \pm 0.7 \times 10^{-6}$ . Assuming an homogeneous distribution of  $^{53}\text{Mn}$  (see [12] for an alternative view) dolomites and breunnerites formed on average  $\sim 3$  Myr and  $\sim 10$  Myr, respectively, after the start of the solar system. Although there is some systematic error in this chronology, due to both uncertainties in the solar system initial value and in the RSF for carbonates, the relative chronology of the carbonates are not affected and we can conclude that on the Orgueil parent body, dolomites formed  $\sim 7$  Myr before the breunnerites. This confirms previous suggestions based on  $^{87}\text{Rb}$ - $^{87}\text{Sr}$  systematics [13] and  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  isotopic systems [i.e. 4,5,6] that dolomite formation predates breunnerite precipitation.

The initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios measured for each carbonate mineralogy is correlated with their respective C and O isotopic compositions (Fig. 2a, 2b) indicating isotopic evolution of the fluids from which the carbonates precipitated [2]. The oxygen isotopic composition of dolomite remains constant ( $\sim 32\text{‰}$ ) over  $\sim 3$  Myr. The O isotopic composition of the first-formed breunnerites had decreased to  $\sim 19\text{‰}$ , reflecting rapid changes in the chemical and isotopic compositions of the fluid. The oxygen isotopic composition of subsequent breunnerite grains then rose gradually to values of up to  $\sim 27\text{‰}$  within a period of  $\sim 7$  Myr.

Aqueous alteration models [e.g., 14,15] assume that older crystals should be isotopically heavier than younger crystals. This is true when comparing the two types of carbonate. However, within the Orgueil breunnerites, a continuous sequence of decreasing  $^{53}\text{Mn}/^{55}\text{Mn}$  with growing  $\delta^{18}\text{O}$  values is observed. It might indicate either multiple carbonate generations or a temperature decrease during the crystallization of these carbonates.

The carbon isotopic composition of dolomites is constant ( $\sim 72\text{‰}$  in average) over a timespan of  $\sim 3$  Myr, while it decreased to  $\sim 53\text{‰}$  when the first breunnerite formed. In comparison to the O isotopic evolution of the fluid, the C isotopic composition remains constant for all the breunnerites analysed.

**Conclusion:** Each of the carbonate type analysed shows a different initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio. The time difference between the formation of dolomite and breunnerite is  $\sim 7$  Myr. Initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios confirm the sequence of precipitation hypothesized by [2] and provide temporal constraints on the evolution of the fluid. Within a time period of at least 10 Myr after the start of the solar system, the fluid evolved, flowing through the CI parent body and eroding primary minerals such as olivine for oxygen and organic matter or pre-solar grains for carbon [16]. As more  $\text{Mg}^{2+}$  was added to the system, dolomite precipitated first, followed by breunnerite, after the  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  ratios of the fluid were sufficiently reduced and the concentration of  $\text{Fe}^{2+}$  (aq),  $\text{Mg}^{2+}$  (aq) and  $\text{Mn}^{2+}$  (aq) were the highest.



**Figure 2.** Correlations for each carbonate grain between the  $^{53}\text{Mn}/^{55}\text{Mn}$  data from this study and the respective average  $\delta^{13}\text{C}$  (a) and  $\delta^{18}\text{O}$  (b) from [2].

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