

**HIGH SPATIAL RESOLUTION ION MICROPROBE MEASUREMENTS REFINE CHRONOLOGY OF ORGUEIL CARBONATE FORMATION.** P. Hoppe<sup>1</sup>, D. Macdougall<sup>2</sup>, and G.W. Lugmair<sup>1,2</sup>. <sup>1</sup>Max-Planck-Institute for Chemistry, Cosmochemistry Department, PO 3060, D-55020 Mainz, Germany (hoppe/lugmair@mpch-mainz.mpg.de); <sup>2</sup>Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA 92093-0220, USA (jdmacdougall@ucsd.edu).

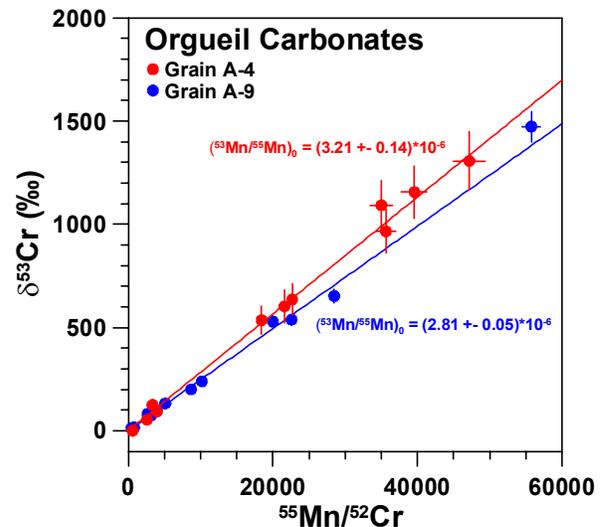
**Introduction:** Carbonates in the CI meteorites occur as discrete crystals and multi-grain fragments and are generally believed to be remnants of hydrothermal vein networks that developed on the parent body and were subsequently disrupted by impacts. Measurements of the Sr isotopic compositions of dolomite and breunnerite from Orgueil first showed that the carbonate-forming episode(s) must have occurred very early in Solar System history [1], and subsequently the detection of <sup>53</sup>Cr from in-situ decay of <sup>53</sup>Mn (half life 3.7 Ma) in some CI carbonates allowed more precise documentation of the timescale of their formation and showed that it must be restricted to the first 15 to 20 Ma of Solar System history [2-4].

In this work we separated carbonate grains from small samples of Orgueil by ultrasonic disaggregation in ethanol followed by hand picking. After initial characterization using the SEM, grains were mounted in epoxy, polished, and Mn and Cr isotopes were measured using the Cameca NanoSIMS 50 at MPI for Chemistry, Mainz.

**Mn-Cr-Isotopic Analyses:** Positive secondary ions of <sup>52</sup>Cr, <sup>53</sup>Cr, <sup>55</sup>Mn, and <sup>56</sup>Fe were measured in a combined multi-detection/peak-jumping mode using a focussed (2-3 μm) O<sup>-</sup> primary ion beam (~1 nA). The analyses were done at a mass resolution m/Δm of ~3500, sufficient to resolve all relevant isobaric interferences. Measured <sup>53</sup>Cr/<sup>52</sup>Cr ratios in the Orgueil carbonates were normalized to those obtained for NIST SRM611 glass, San Carlos Olivine, and Orgueil matrix. Relative Mn/Cr sensitivity factors were determined from measurements on NIST SRM611 glass (<sup>55</sup>Mn/<sup>52</sup>Cr = 1.22) and San Carlos Olivine (<sup>55</sup>Mn/<sup>52</sup>Cr = 10.93). The relative Mn/Cr sensitivity factor was generally close to unity for the different measurement sessions. There is a difference of about 15% between the relative Mn/Cr sensitivity factors obtained for NIST SRM611 glass and San Carlos Olivine and the carbonate Mn/Cr data were normalized using the average relative Mn/Cr sensitivity factor of the two standards. Measurements of the relative Mn/Cr sensitivity factor in synthetic carbonate standards with known Mn and Cr concentrations were unsuccessful because of large spatial heterogeneities in the Mn/Cr ratio.

**Results:** Measurements have been completed for five breunnerites and four dolomites. In each grain, Mn/Cr varies widely, primarily due to variability in Cr

content on a micron to sub-micron scale (the latter can be inferred from smooth variations in Cr intensity as an analysis proceeds at a single spot). Multiple measurements were made for each crystal and in each case <sup>53</sup>Cr is closely correlated with Mn/Cr, constituting strong evidence for in situ <sup>53</sup>Mn decay and age significance for the resulting well-defined isochrons. Figure 1 shows representative data from two of the analyzed grains, a breunnerite and a dolomite.



**Figure 1.** Isochron diagrams for Orgueil breunnerite A-9 and Dolomite A-4. Errors are 1σ.

The data imply <sup>53</sup>Mn/<sup>55</sup>Mn ranging from (1.77±0.15)×10<sup>-6</sup> to (3.88±0.39)×10<sup>-6</sup> at the time of formation of these grains, corresponding to a time span of approximately 4 Ma. In terms of an absolute Solar System timescale [5] this would correspond to the interval between 4564 and 4560 Ma, beginning only some 7 Ma after solar system formation at ~ 4571 Ma. Inferred ages for the measured grains are given in Table 1. The data suggest that dolomite formed first, followed by breunnerite, although within the analytical uncertainty there is some overlap in ages.

**Discussion:** Endress and Bischoff [6] have made the point that carbonates in Orgueil occur both as isolated grains and as fragments, the latter generally occurring between lithic clasts and the former mostly dispersed within the clasts. Because we disaggregated

meteorite samples to obtain carbonates, the petrographic setting of our samples is unknown. However, all appear to be single crystals and probably represent the “isolated grain” variety of carbonate. Their formation must thus pre-date brecciation.

**Table 1.** Orgueil carbonate formation times in millions of years after  $T_0 = 4571$  Ma with  $(^{53}\text{Mn}/^{55}\text{Mn})_{T_0} = 1.4 \times 10^{-5}$  and  $T_{1/2}(^{53}\text{Mn}) = 3.7$  Ma.

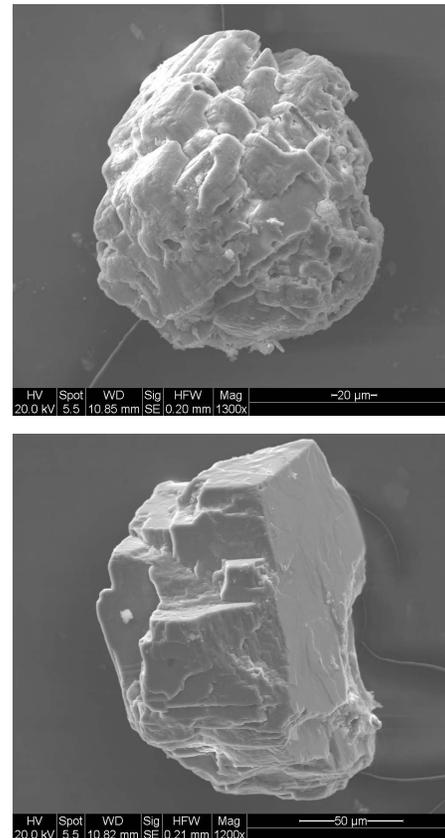
Grain #	Type	Time in Ma
B-10	Dolomite	6.85±0.55
A-3	Dolomite	7.45±0.19
A-4	Dolomite	7.86±0.24
B-8	Dolomite	8.12±0.51
A-9	Breunnerite	8.57±0.10
B-13	Breunnerite	8.63±0.31
OC3-4	Breunnerite	8.81±0.34
OC-1	Breunnerite	10.2±0.38
B-19	Breunnerite	11.0±0.45

The chemical compositions of CI dolomites and breunnerites are consistent with precipitation as an equilibrium two-carbonate assemblage at low temperatures ( $\leq 250^\circ\text{C}$ ) [7]. However, variability, particularly in Mn content of both of these phases, also suggests either temporal or spatial variation in fluid composition, or possibly transport control of Mn precipitation in a static, intergranular fluid [7]. The data presented here favor the former and are consistent with the combined oxygen and carbon isotope data of Zito et al [8]. These show that calcite, dolomite and breunnerite in Orgueil are characterized by distinctly different isotopic compositions, interpreted to be the result of an evolving fluid during alteration. In this scenario, breunnerite would be younger than dolomite, as indicated by our measurements. Furthermore, SEM images of the grains analyzed in our work show dolomites to be rounded and to have an “etched” appearance, while breunnerites have consistently less altered surfaces and frequently show crystal faces (Figure 2), also consistent with breunnerite being a younger phase.

Our data do not distinguish between continuous and episodic hydrothermal activity on the Orgueil parent body, but they do require the occurrence of temperatures well above the freezing point of water over a period of several million years. The most plausible heat source is likely to be impacts, and if so, carbonate formation (and presumably alteration of anhydrous silicates in Orgueil) was most likely episodic. However, latent heat from  $^{26}\text{Al}$  and, particularly,  $^{60}\text{Fe}$  decay may have played a significant role as well. Neverthe-

less, impact mixing must have continued for a significant period after the end of hydrothermal activity in order to produce the small clast size and approximate homogeneity of Orgueil on the scale of a few centimeters.

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**Figure 2:** (a) Dolomite B-10; (b) Breunnerite B-13.

**REFERENCES.** [1] Macdougall J.D., Lugmair G.W., and Kerridge J.F. (1984) *Nature*, 307, 249-252. [2] Endress M., Zinner E., and Bischoff A. (1996) *Nature*, 379, 701-703. [3] Hutcheon I.D. and Phinney D.L. (1996) *LPSC XXVII*, 577. [4] Hutcheon I.D., Phinney D.L., and Hutchison R. (1997) *Meteoritics & Planet. Sci.*, 32, A63-A64. [5] Lugmair G.W. and Shukolyukov A. (2001) *Meteoritics & Planet. Sci.*, 36, 1017-1026. [6] Endress M. and Bischoff A. (1996) *Geochim. Cosmochim. Acta*, 60, 489-507. [7] Johnson C.A. and Prinz M. (1993) *Geochim. Cosmochim. Acta*, 57, 2843-2852 (1993). [8] Zito K.L., McKeegan K.D., Kerridge J.F., Hutcheon I.D., and Leshin L.A. (1998) *Meteoritics & Planet. Sci.*, 33, A171-A172.