

**QUANTIFYING THE INTENSITY OF POST-HYDRATION HEATING OF CM CARBONACEOUS CHONDRITES USING CARBONATES.** M. R. Lee<sup>1</sup>, B. E. Cohen<sup>1</sup> and A. Boyce<sup>2</sup> <sup>1</sup>School of Geographical and Earth Sciences, University of Glasgow, G12 8QQ, U.K. (Martin.Lee@Glasgow.ac.uk). <sup>2</sup>Scottish Universities Environmental Research Centre (SUERC), Rankine Avenue, East Kilbride G75 0QF, U.K.

**Introduction:** Some of the CM carbonaceous chondrites were heated after aqueous alteration [1]. As phyllosilicates are the volumetrically dominant constituent of these meteorites [2], the principal impact of this thermal processing was their dehydroxylation and recrystallization [1,3,4]. Phyllosilicates are typically very finely crystalline and so the effects of heating are normally studied by analysis of bulk samples (e.g., via thermogravimetric analysis and X-ray diffraction), or by characterizing phyllosilicate crystal structures using transmission electron microscope imaging and electron diffraction [e.g., 4].

Carbonates are potentially useful tools for understanding post-hydration heating as they occur in all CMs [5], and their relatively coarse grain size (upto ~100  $\mu\text{m}$ ) makes them amenable to characterisation using a variety of microbeam techniques. Here we have heated samples of the Murray CM carbonaceous chondrite to different temperatures in order to assess how sensitive its calcite grains are to heating, and to document any changes in carbonate microstructure and mineralogy that can be used to quantify heating temperatures. This study has been inspired by recent work on the Sutter's Mill carbonaceous chondrite, which has shown that post-hydration heating of its calcite produced minerals including oldhamite ( $\text{CaS}$ ) and portlandite ( $\text{Ca}(\text{OH})_2$ ) [6].

**Materials and methods:** Five chips of a commercially obtained sample of the Murray meteorite were studied. One was left untreated, whereas the four others were heated to different temperatures (200, 400, 600, 800  $^{\circ}\text{C}$  ( $\pm 5$   $^{\circ}\text{C}$ )). The original masses of the heated chips (in mg) were 24.5, 21.4, 21.1, 20.8 and 34.1, respectively. Each chip was placed in an all-glass vacuum line and heated over the course of ~ 1 hour using a temperature-controlled induction heater to its designated temperature, where it was held for a minimum of one hour. The chips were then left to cool to room temperature over a similar timeframe, then were encased in epoxy resin and one surface was polished without water. After coating with carbon, polished surfaces of the chips were imaged and quantitatively chemically analysed using a Zeiss Sigma SEM. Broad-beam analyses of the matrix avoided coarse mineral grains (e.g., carbonates and sulphides).

**Results:** Heating has caused textural and compositional changes to the meteorite and its calcite grains. The matrix and fine grained rims of the 600  $^{\circ}\text{C}$  and 800

$^{\circ}\text{C}$  chips have abundant fractures and elevated analytical totals (Figs. 1, 2). The only detectable systematic heating-related changes to the chemical composition of the matrix are an increase in Na, and an increase followed by decrease in S (Fig. 2).

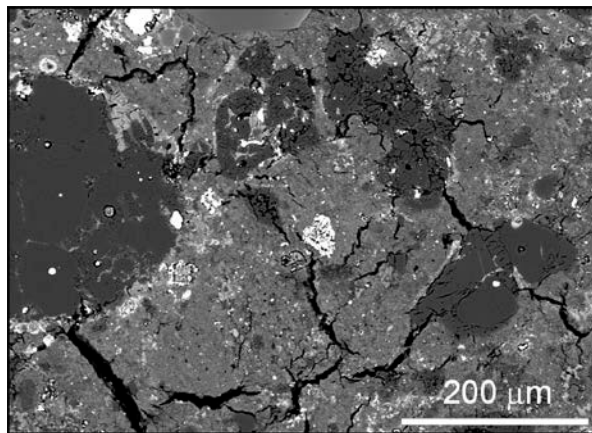


Fig. 1. Backscattered electron SEM image of the 800  $^{\circ}\text{C}$  chip of Murray showing fractures (black) within fine-grained rims and the matrix.

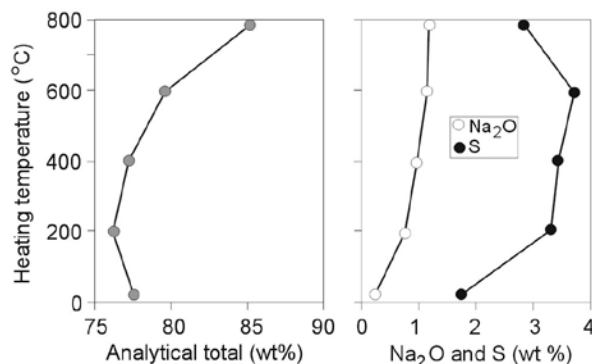


Fig. 2. X-ray microanalyses of the Murray matrix illustrating compositional contrasts between chips heated to different temperatures.

**Calcite mineralogy and texture.** There is no discernable difference in the microstructure or mineralogy of calcite grains between the unheated sample and the chips that were heated to 200 and 400  $^{\circ}\text{C}$  (Fig. 3a). By contrast, calcite grains in the 600  $^{\circ}\text{C}$  chip contain faceted mi-

cropores (Fig. 3b) or have a finely granular microstructure. Calcite is absent from the 800 °C chip. In its place are micropore-rich grains of oldhamite with a patchy rim of troilite (Fig. 3c). The oldhamite crystals are ~500 nm in size.

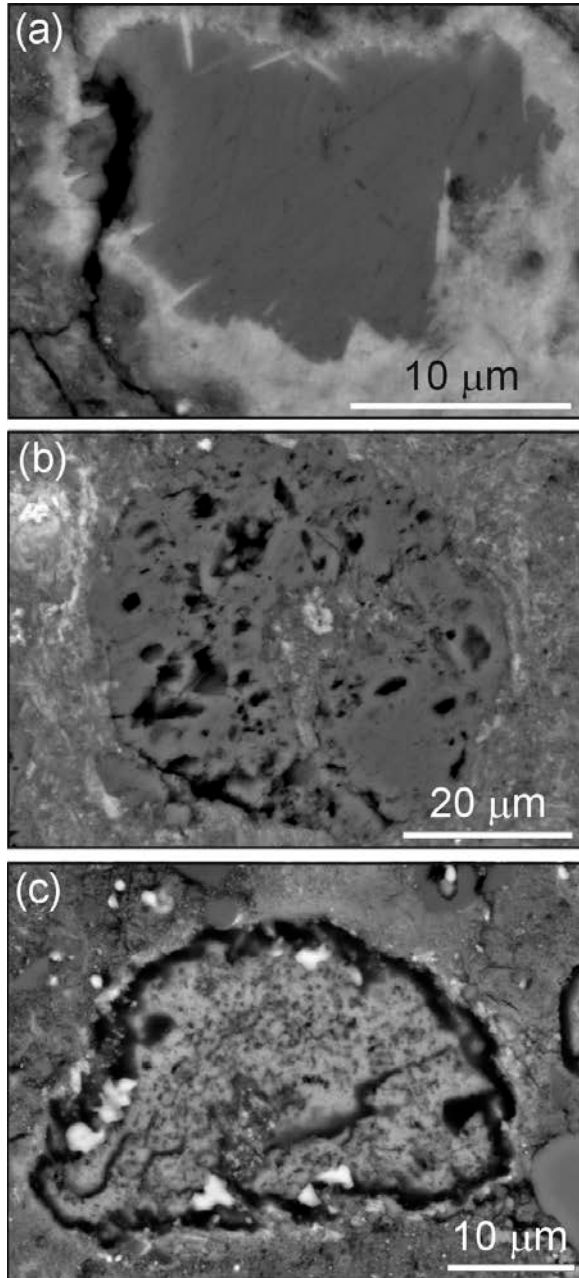


Fig. 3. Backscattered electron SEM images of Murray calcite that has been experimentally heated to different temperatures. (a) A calcite grain in the 400 °C chip with a tochilinite-cronstedtite rim (white). (b) A calcite grain in the 600 °C chip with abundant faceted micropores (black). (c) A grain of oldhamite in the 800 °C chip with troilite crystals (white) at its edge.

**Discussion:** Our experiments have been designed to replicate short-lived heating that would have accompanied an impact into the CM carbonaceous chondrite parent body [7]. Totals from chemical analyses of the matrix increase above 400 °C, reflecting dehydroxylation of phyllosilicates [8], which has also formed the fractures. The increase in matrix Na and S concentrations is interpreted to be due to the breakdown of minerals in chondrules and redistribution of those elements into the matrix. The decrease in matrix S concentrations above 600 °C reflects the formation of new sulphide minerals (e.g., oldhamite and troilite; Fig. 3c).

Calcite grains and their tochilinite-cronstedtite rims change in a systematic matter with progressive heating. The initial breakdown of calcite takes place at between 400 and 600 °C. One consequence of this reaction is the formation of micropores (Fig. 3b) due to the decomposition of calcite ( $\text{CaCO}_3$ ) to lime ( $\text{CaO}$ ) (i.e., calcination) with concomitant loss of  $\text{CO}_2$  (complete loss of  $\text{CO}_2$  from calcite should generate a porosity of 54.2% [9]). This decomposition temperature is lower than for calcite crystals heated in air (whose calcination begins at ~600 °C [10]), probably due to the presence of volatiles that are liberated during heating (e.g.,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$  etc). Addition of S to the grains of lime/calcite at temperatures above 600 °C forms finely polycrystalline oldhamite, and troilite.

**Conclusions:** Our experiments show that the microstructure and mineralogy of calcite is a sensitive indicator of the intensity of heating of carbonaceous chondrites over the higher temperature range. These results also provide new insights into the exchange of elements between various mineral reservoirs accompanying thermal processing. The presence of oldhamite in Sutter's Mill [6] gives confidence that these experiments are a valid analogue for parent body heating, and further work is being undertaken to more precisely constrain the temperature of oldhamite formation.

**References:** [1] Akai J. (1988) *GCA*, 52, 1593–1599. [2] Howard K. T. et al. (2009) *GCA*, 73, 4576–4589. [3] Tonui E. et al. (2014) *GCA*, 126, 284–306. [4] Lee M. R. et al. (2016) *GCA*, 187, 237–259. [5] Lee M. R. et al. (2014) *GCA*, 144, 126–156. [6] Haberle C. W. and Garvie L. (2017) *Am Min*, 102, 2415–2421. [7] Bland P. A. et al. (2014) *Nature Comms.*, 5, 5451. [8] Garenne A. (2014) *GCA*, 137, 93–112. [9] Beruto, D. et al. (2004) *Thermochim. Acta*, 424, 99–109. [10] Rodriguez-Navarro et al. (2009) *Am Min*, 94, 578–593, 2009.

**Acknowledgements:** We thank the U.K. STFC for funding.