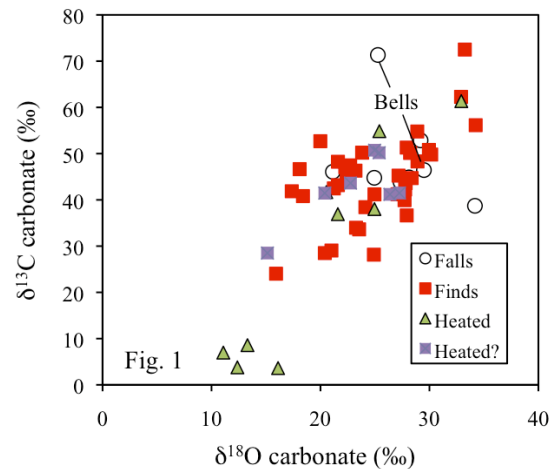**CARBONATE ABUNDANCES AND ISOTOPIC COMPOSITIONS IN CHONDRITES.** C.M.O'D. Alexander[1], R. Bowden[2], M.L. Fogel[2], and K.T. Howard[3]. [1]DTM, Carnegie Institution of Washington, 5241 Broad Branch Road, Washington, DC 20015, USA (alexander@dtm.ciw.edu), [2]GL, Carnegie Institution of Washington, 5251 Broad Branch Road, Washington, DC 20015, USA. [3]Kingsborough Community College of the City University of New York, Brooklyn, NY 11235, USA.
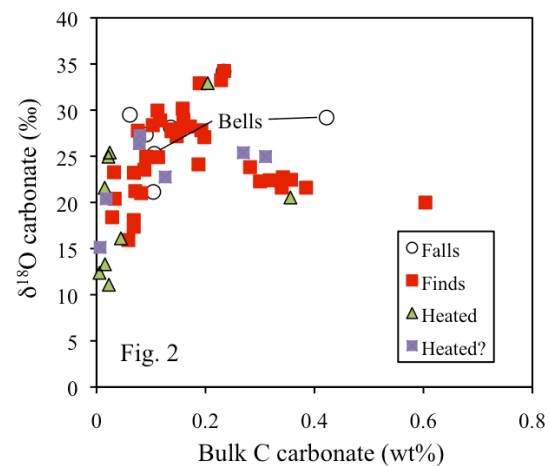
Introduction: Carbonates are secondary minerals that are almost ubiquitous products of the aqueous alteration of chondrites. They cannot have formed from the first fluids as Ca and Mg must first be leached from altering silicates. Nevertheless, carbonates provide important constraints on the temperature, timing and the evolution of fluid compositions during aqueous alteraton [1-4]. The carbonates also constitute the second most abundant C-bearing component in chondrites after the organic matter. The dissolved CO_2 would almost certainly have interacted with the organic matter (e.g., isotopic exchange with carboxyl groups). Gaseous CO_2 may have produced some organic species through FTT-like reactions with H_2 generated during alteration. The source of the CO_2 from which the carbonates formed remains undetermined. Some or all of the CO_2 could have been trapped in accreted ices or, if the ices were heavily irradiated, it could have been produced by oxidation of organics by peroxide.

Past studies of carbonates in chondrites have been limited to a relatively small number of chondrites, and have not been coupled to other studies, e.g., the abundances and isotopic compositions of the water and organics in the same chondrites. We have determined the bulk carbonate $\delta^{13}C$ and $\delta^{18}O$ values, and carbonate C contents for ~80 carbonaceous and ordinary chondrites, although here we focus on the CMs. The measurements were all conducted on relatively large samples with previously determined bulk H, C and N elemental and isotopic abundances [5], and in many cases bulk mineralogies determined by XRD [6].

Samples and techniques: Roughly 100 mg aliquots of bulk meteorite powders were mixed with phosphoric acid in He-flushed containers at 70°C for 24 hrs so that both calcite and dolomite were reacted. The resultant CO_2 was analyzed with a ThermoFinnigan Delta^{Plus} XL via a GasBench II interface with a CombiPAL autosampler. Measured isotopic values were corrected using NBS-18 and NBS-19, and two working standards. The measured $\delta^{18}O$ values must be corrected for an isobaric interference, usually by assuming that the O isotopes lie on the terrestrial mass fractionation line. Chondritic carbonates do not lie on this line [1, 4]. However, the $\Delta^{17}O$ values of chondritic carbonates and other secondary minerals are ≤5 ‰, introducing a $\delta^{18}O$ uncertainty of ≤0.5 ‰.

Fig. 1

Results: Figures 1 and 2 summarizes the results for the CM chondrites, but the results are similar for the the other CCs measured. Our results are broadly consistent with previous studies [1-4]. However, as previously observed, and illustrated here by samples from two Bells stones, carbonate abundances and isotopic compositions can be quite heterogeneous even at the ~1 g scale within a given meteorite.
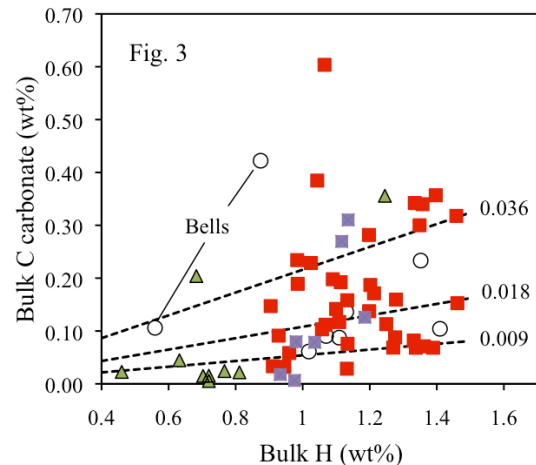

Fig. 2

[5] divided their CMs into unheated falls and Antarctic finds, as well as possibly heated (?) and heated Antarctic finds. Except for the most heated samples, which have lower carbonate contents and lower $\delta^{13}C$ and $\delta^{18}O$ values, most CMs fall on the same trends. Excluding the most heated samples, there is a rough positive correlation between $\delta^{13}C$ and $\delta^{18}O$ values (Fig.

1), although there is a suggestion of two parallel trends. The total range observed for the unheated samples are $\delta^{13}C\approx25\text{-}75$ ‰ and $\delta^{18}O\approx15\text{-}35$ ‰. The $\delta^{13}C$ and $\delta^{18}O$ values exhibit slightly more complex behavior with carbonate content, rising to a maximum at ~0.2 wt% C, and then tailing off slightly (Fig. 2).

Discussion: There is no simple explanation for the correlation between bulk carbonate $\delta^{13}C$ and $\delta^{18}O$ values. The $\delta^{18}O$ values will have been determined by the O isotopic composition of the aqueous fluid and the temperature of precipitation, while the $\delta^{13}C$ will have been determined by exchange with gaseous CO, CO_2, CH_4, etc. and possibly by interaction with organic matter [3]. [3] reported a weak inverse correlation between $\delta^{13}C$ and $\delta^{18}O$ values, the opposite of what we find, but this may simply reflect the smaller number of samples they analyzed (three, with three aliquots of two of them) and the heterogeneity of the meteorites. Our much larger sample size should make our results more robust. [3] suggested that the range of carbonate C isotopic compositions they observed was produced by formation of CH_4 from HCO_3^- and H_2. A process akin to this seems a likely explanation that will be explored further, although not quite as envisaged by [3] since they predicted an inverse correlation. Modification of carbonate inventories during residence in Antarctica [7] may also complicate the interpretation of our results, but we do not observe a systematic difference in either carbonate abundance or isotopic composition between falls and Antarctic finds.

The origin of the CO_2 from which the carbonates formed has received less attention than that of the water present during alteration. If the alteration occurred in a closed system, all the water formed phyllosilicates and all CO_2 ultimately formed carbonate, the bulk H and C contents can be used to estimate the H_2O/CO_2 ratios of the fluid (liquid+gas) system. Fig. 3 plots the bulk H vs. the carbonate C contents for the meteorites analyzed. The bulk H contents are proxies for the extent of alteration, and carbonate abundances do not correlate with them. Also shown are lines for constant CO_2/H_2O molar ratios. Most CMs have ratios of between 0.009 and 0.036. If all the CO_2 were dissolved in the aqueous fluid, these abundances would be equivalent to 0.5-2 M. Such concentrations are probably too high for an aqueous solution, even at low temperatures and after some alteration of has produced a highly alkaline conditions. At least 38-50 % of the original CM water was consumed by oxidizing Fe [8], but this still will not bring CO_2 contents in the aqueous fluids to reasonable levels. If most of the CO_2 were in the gas phase, the observed carbonate abundances would produce pore pressures of up to 4 bars at 25°C and a po-

rosity of 10 %. This is not sufficient to open up fractures that would have allowed the CO_2 to escape. However, the pore pressures due to the H_2 produced by the oxidation of Fe would have been much higher [8], and the escape of the H_2 along fractures would almost certainly have facilitated the loss of some CO_2 as well.

Fig. 3

The water responsible for the alteraton of the chondrites was almost certainly accreted as ice. Cometary ices have $CO_2/H_2O\leq6$, contain comparable amounts of C in CH_4 and CH_3OH, and CO/H_2O of up to 0.15 [9]. This is more than enough C to explain the carbonate contents of chondrites. However, if chondritic ices formed in the warmer inner Solar System [5], the more volatile CO, at least, is unlikely to have condensed and the other volatiles may have only partially condensed.

The carbonate and the organic matter are the two main carbonaceous reservoirs in chondrites. Subtraction of the carbonate contents from the bulk compostions confirms that, contrary to the common assumption, the acid and solvent insoluble organic matter (IOM) only makes up ~50 % of the organic C [5] – this is true across all chondrite groups. The remaining material is too abundant to be accounted for by solvent soluble material. The missing organic C appears to be liberated by acid treatment, either because it is acid-hydrolysable or because it is in very small particles that are lost during IOM isolation (Cody, pers. comm.).

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