

MAJOR AND TRACE ELEMENT DISTRIBUTIONS IN ALH84001 CARBONATE: INDICATION OF A HIGH FORMATION TEMPERATURE. J. D. Gilmour¹, R. A. Wogelius¹, G. W. Grime² and G. Turner¹.

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As part of an ongoing study of the ancient martian meteorite ALH84001 we have performed preliminary proton microprobe (PIXE - Proton Induced X-ray Emission) analyses of a carbonate region and an adjoining maskelynite grain. Major element zoning is similar to that previously reported while some unusual trace element abundances in the carbonate seem most easily explicable if the carbonate formed at high temperature from a carbon dioxide-rich fluid. In this case, the period of elevated temperature during carbonate formation would have reset the Ar-Ar age of the maskelynite, so the two phases would have similar ages. Our preferred age for the carbonate of $3,750 \pm 150$ Ma is based on the Ar released by lasering a sub-microgram carbonate grain [1] and is indistinguishable from the Ar-Ar age of the maskelynite ($3,920 \pm 80$ Ma - weighted mean of stepped heating data [2])

The proton microprobe [3] employs a focussed beam of protons to stimulate X-ray emission in a polished section; analyses are similar to those from an electron probe, except that bremsstrahlung background is greatly reduced allowing a lower detection limit for many elements. The spot size of the proton beam is typically less than $1 \mu\text{m}$, however the beam penetrates $20 \mu\text{m}$ or more below the sample surface so care must be taken to ensure data is not influenced by sub-surface mineral grains. This is achieved with

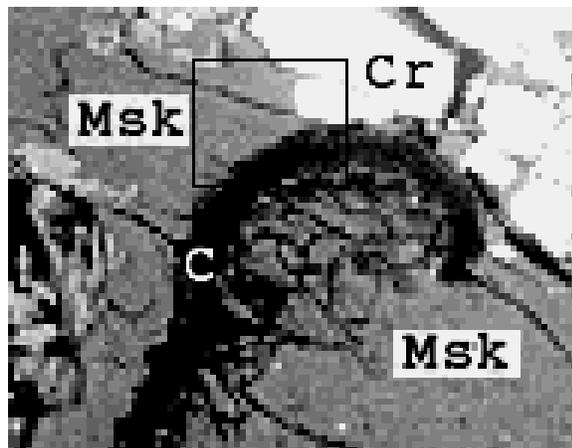


Figure 1. A BSE electron micrograph of a section of sample ALH84001,110. The box highlights the approximate region of figure 2.

Key: Msk=maskelynite, Cr=chromite, C=carbonate.

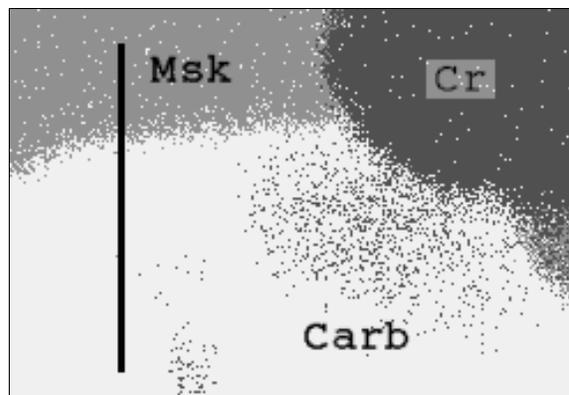


Figure 2: Overlain major element maps (Si = light gray, Cr = black) showing the extent of maskelynite (Msk), chromite (Cr) and carbonate (Carb). The line shows location of the linescan from figure 3. The width of the image is $50 \mu\text{m}$

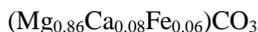
reference to Rutherford back scattering (RBS) spectra acquired simultaneously with point analyses.

Three types of PIXE analyses have been performed: elemental mapping, line scans and point analyses. All data were acquired without an X-ray filter to allow simultaneous analysis of light and heavy elements. A back scattered electron image of the region upon which we have focussed our attention is shown in figure 1. It consists of an area of carbonate that appears to have grown within a crack in a grain of maskelynite. Both carbonate and maskelynite are adjacent to a chromite grain. Major element maps showing the location of the linescan relative to maskelynite and carbonate are shown in figure 2.

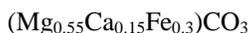
The major element variations along the scan are shown in figure 3. The scan covers the rim of a carbonate region and the interface with maskelynite (the extent of the maskelynite can be seen from the silicon scan). These data do not represent a complete traverse from carbonate core to rim. However, in the region of overlap close to the carbonate rim they are comparable to previously published electron probe data [4], albeit at higher resolution. The magnesite rich region close to the carbonate rim is clearly bounded by zones with higher calcite and siderite components.

Calibration of scans proceeds via Rutherford back-scattering point analyses located along the scan

line. Two analyses of the most magnesium rich region (close to the rim) yield:-



While the iron-rich end of the traverse has composition:-



PIXE point analyses of the carbonate clearly reveal the presence of two unusual trace elements: potassium and chromium (figure 4a - the presence of chromium in these carbonates has been reported previously [7]). Estimated concentrations of both chromium and potassium are 500 ppm. The possibility of contamination by sub-surface maskelynite or chromite grains or both is unlikely given the stoichiometries derived from the RBS spectra (figure 4b) and by the uniform distribution of chromium and potassium counts in the PIXE map of the analysed region of the carbonate. All point analyses show peaks for both of these elements indicating that both potassium and chromium may be widespread in the carbonate. Furthermore, simulations of our RBS spectra incorporating a thin layer of maskelynite (<0.5 μm) are not in good agreement with our data,

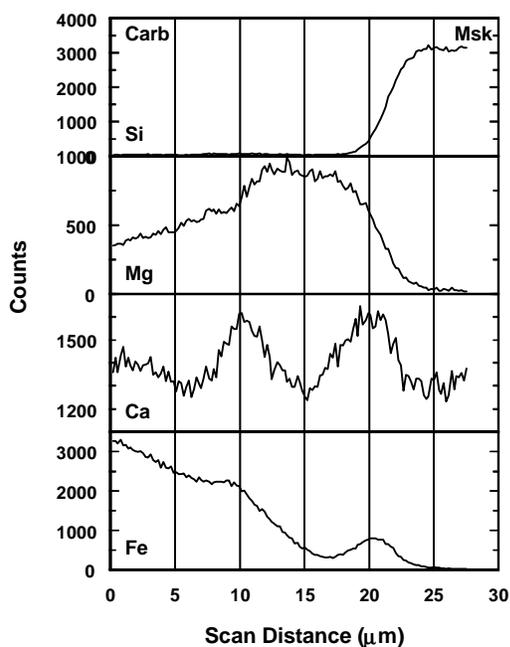


Figure 3. Major element variations along a traverse across a carbonate rim.

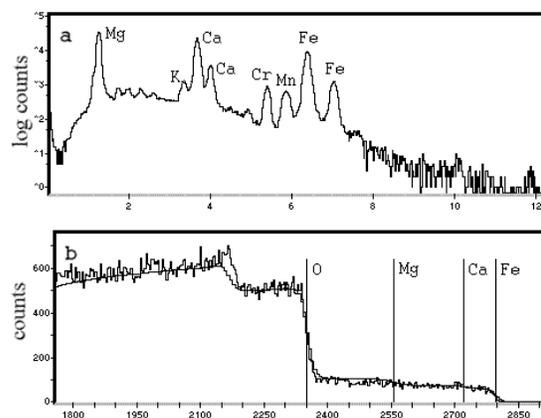


Figure 4. A PIXE spectrum (a) and Rutherford back scattering spectrum (b) for a carbonate analysis.

suggesting that contamination from this source is not the cause. However, further work is underway to verify and further quantify our potassium and trace element abundances. Figure 4a also shows a significant rhodochrosite component in the carbonate.

The presence of potassium and chromium in the carbonate would be hard to account for were the carbonate precipitated from a low temperature aqueous fluid: potassium and chromium concentrations in terrestrial carbonates are usually below the PIXE detection limit (<110 ppm and <40 ppm respectively [5]) and sodium is present at concentrations between 100-200 ppm in marine calcite [6]. In addition, $\text{Cl}/^{36}\text{Ar}$ in ALH84001 is unrealistically low for a martian hydrothermal fluid [1]. However, both the previously reported presence of sodium in the carbonate (0.33 ± 0.07 wt% oxide [7]) and our potassium content are easier to understand if the carbonates were formed rapidly from a (possibly impact-derived) carbon dioxide-rich melt (as suggested in [8] and [9]). In short, our preliminary trace element results are more consistent with the origin of the carbonates being at high temperature than at low temperature.

References [1] Gilmour et al., (1997) *LPSC XXVII*. [2] Turner et al., (1997) *GCA* (in press). [3] Grime et al., (1991) *Nucl. Instrum. And Methods in Physics Res.* **B54** 52-63. [4] McKay and Lofgren (1997) *LPSC XXVII* [5] Wogelius, unpublished data. [6] Veizer, (1983) *Reviews in Mineralogy* (265-300). [7] Mittlefehldt (1994) *Meteoritics* **29** 214-221 [8] Harvey and McSween (1996) *Nature* **382** 49-51. [9] Scott et al., (1997) *LPSC XXVII*.