RARE K-BEARING MICA IN ALH84001: ADDITIONAL CONSTRAINTS ON CARBONATE FORMATION

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Introduction. McKay et al. [1] presented several intriguing observations which suggested that there was evidence of fossil life in martian orthopyroxenite ALH 84001. These exciting and controversial observations have stimulated extensive debate over the origin and history of ALH 84001, but many issues still remain far from being resolved. Among the most important is the question of the temperature at which the carbonates, which host the putative microfossils, formed. Oxygen isotopic data, whilst showing that the carbonates are generally out of isotopic equilibria with the host rock, cannot constrain their temperature of formation [2-4]. Both low and high temperature scenarios are plausible depending on whether carbonate growth occurred in an open or closed system [2-4]. Petrographic arguments have generally been used to support a high temperature origin [5], but these appear to be suspect, because they assume equilibrium between carbonate compositions which are not in contact. Some observations appear to be consistent with shock mobilization and growth from immiscible silicate-carbonate melts at high temperatures [6]. Proponents of a low temperature origin for the carbonates are hampered by the fact that there is currently no evidence of hydrous phases which would be indicative of low temperatures and the presence of a hydrous fluid during the formation of the carbonates. However, the absence of hydrous phases does not rule out carbonate formation at low temperatures because the carbonate forming fluids may have been extremely CO_2-rich, such that hydrous phases would not have been stabilized.

Although phyllosilicates are apparently not present at the scale observable by SEM, they may be present at the submicron scale. However, several detailed TEM studies of ALH 84001 have failed to find evidence of phyllosilicates [1,7]. In this study, I have carried out additional TEM studies of ALH 84001 and have found evidence of very rare phyllosilicates, which appear to be convincingly of preterrestrial origin. At present these observations are limited to one occurrence; further studies are in progress to determine if the phyllosilicates are more widespread.

Results. TEM studies so far have concentrated on fragments of carbonate entrained within feldspathic glass which is widespread throughout ALH 84001. The carbonate fragments have irregular shapes, but examination at high magnification using BSE and TEM imaging show that many grains are faceted and these facets are cleavage surfaces. This observation suggests that these grains are fragments of larger, continuous regions of carbonate which have been fractured, disrupted and entrained within the feldspathic melt during a post-carbonate formation impact and heating event. This is also consistent with the observation that adjacent fragments, separated by regions of glass, have zoning patterns consistent with them originally being part of a single grain. BSE images of the fragments show that they have a range of sizes from ~50 µm down to < 10 µm. TEM observations [8] show that many of these carbonate fragments, despite having relatively Mg-rich compositions contain myriad magnetite particles associated with voids. These magnetite grains have grain sizes and morphologies which are consistent with the magnetites observed by [1] and other workers [6].

A single carbonate fragment within the feldspathic glass contains the phyllosilicates. They occur as highly elongate, parallel to subparallel ribbon-like crystals, typically <10 nm in thickness which extend for several 100s of nanometers through the carbonate grain. The abundance of phyllosilicates within the fragment is difficult to estimate, but is probably of the order of 10 to 20 vol%. It is notable that the phyllosilicate grains are always truncated at the edge of carbonate grains and never extend into the feldspathic glass. It also appears that close to the interface with the glass the phyllosilicates have curved morphologies and some of the smallest grains appear to be amorphous. These observations are consistent with thermal decomposition during the postshock heating which followed fragmentation and entrainment of the carbonate fragments within the feldspathic glass [8,9]. Electron diffraction and high resolution TEM studies of the phyllosilicates show that they have a basal spacing of 1 nm and appear to be well-ordered, with no evidence of stacking disorder or partial interlayers. The composition of the grains has not yet been obtained with any great certainty, because of their very limited thickness and the fact that they are closely intergrown with the carbonate. However, EDS spectra show the presence of Al, Si and K, in addition to Mg, Ca and Fe from the adjacent carbonate. The Al/Si ratio appears to be relatively low. These observations appear to be consistent with this phyllosilicate phase being a K-bearing mica, such as illite.

Implications. A preterrestrial origin for the mica is indicated by several lines of evidence. First, the mica occurs exclusively within the carbonate and does not

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extend into the surrounding feldspathic glass, clearly showing that it predated formation of the glass. If mica had formed after glass formation, it would most likely have formed by replacement of the feldspathic glass, rather than intergrown with carbonate. Second, the mica appears to have been heated and partially decomposed where it is in contact with the glass, again showing that it must have predated glass formation. Third, terrestrial weathering products of meteorites are poorly crystalline clay minerals with an extremely fine-grain size, not well-ordered micas. Fourth, the carbonates appear to be completely entrained within the feldspathic glass and consequently would have been isolated from altering terrestrial fluids. The reasonable conclusion from these observations is that the mica formed prior to ejection of ALH 84001 from Mars.

Although phyllosilicates are not widespread in ALH 84001, the presence of mica clearly indicates that water-bearing fluids were present at some time during the history of ALH 84001. The very close intergrowth of carbonate with the mica suggests that the two phases grew simultaneously or that the mica may have preexisted before carbonate formation. Replacement of preexisting carbonate by long, thin ribbons of phyllosilicates does not seem probable. The very elongate morphology of the mica grains does not seem consistent with unimpeded growth from a solution, but perhaps suggests growth constrained by adjacent growing carbonate grains, i.e. the two phases grew contemporaneously. The presence of illite and its formation from smectite is widely used as geothermometer in terrestrial pelitic rocks which have undergone diagenesis to low-grade metamorphism. However, this approach has been questioned and it may be the case that both illite and smectite are metastable phases with respect to muscovite, but form according to the predictions of Ostwald's step rule [9]. As a consequence, illite can occur under diagenetic conditions and up to temperatures in excess of 250°C. However, at temperatures greater than ~300°C, muscovite would be expected to be the stable K-bearing mica and should form because temperatures are sufficiently high for equilibrium to be attained. This suggests that mica formation in ALH 84001 occurred at temperatures probably <250°C±50°C. At low temperatures, such as occur during diagenesis, clay minerals are extremely fine-grained and are complex submicroscopic intergrowths of different layer lattice minerals such as smectite, illite and chlorite, which are far from thermodynamic equilibrium. The mica grains in ALH 84001 show no evidence of this type of interlayering and hence indicate that they formed at temperatures probably greater than 150°C±50°C. If the mica formed contemporaneously with the carbonate as is indicated by the textural relations, then carbonate formation conditions between 100 and 300°C are indicated. Whilst this is a broad range in temperature, it rules out a high temperature origin for the carbonates that has been proposed by some workers.

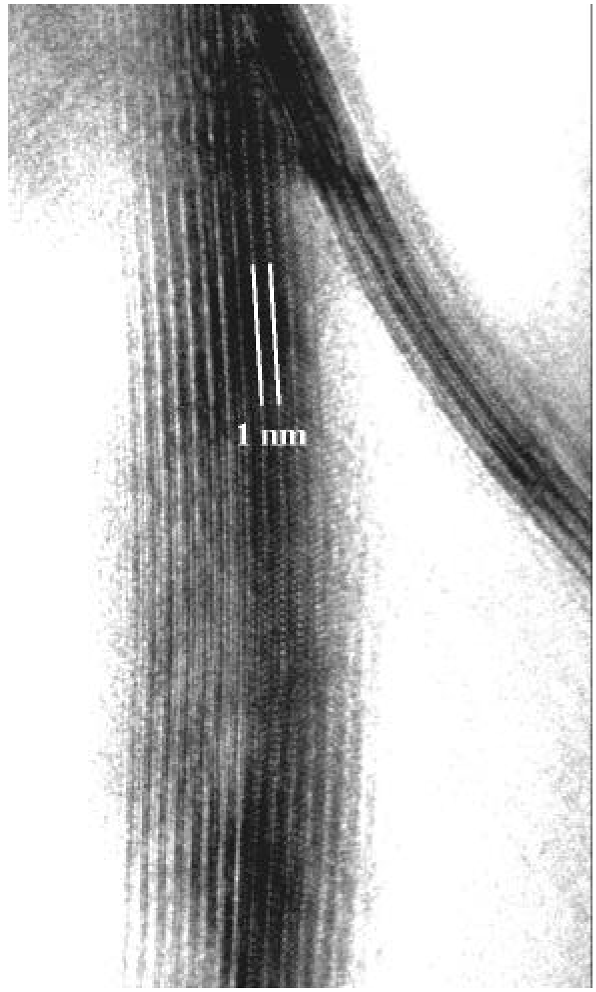

Figure 1. HRTEM image of K-bearing mica from a carbonate fragment in ALH 84001.

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