

CARBONATES IN ALH84001: EVIDENCE FOR KINETICALLY CONTROLLED GROWTH. G. A. McKay¹ and G. E. Lofgren², (NASA Johnson Space Center, SN4, Houston, TX 77058; ¹Gordon.A.McKay@jsc.nasa.gov; ²Gary.E.Lofgren@jsc.nasa.gov).

Introduction. ALH84001, originally classified as a diogenite, was subsequently recognized by [1] as a Martian meteorite. It differs from other Martian meteorites in that it is a coarse-grained orthopyroxene cumulate containing ~1% carbonate [1,2]. It has attained enhanced importance as a result of the recent announcement of possible evidence for relict biogenic activity, especially in the carbonates [3]. The origin of the carbonates is controversial, even to the point of disagreement over the temperature of formation by hundreds of degrees [e.g., 2-5]. Several features of the carbonates suggest kinetic control of growth, which may offer an explanation for why different lines of evidence suggest very different formation conditions. We are undertaking a detailed petrographic and chemical study of the carbonates to assess the role of kinetic control in their formation.

Megascopic observations on chips and microscopic examination of 3 polished thin sections of ALH84001 (,64; ,82; ,88) provide insight into the

modes of carbonate occurrence. Examination of chips reveals the most noticeable occurrence is the orange globules with characteristic white and black rims that were described by [1-4]. These objects vary in shape from highly flattened, pancake-like bodies to thicker elliptical shapes. Granular carbonate is equally common; it is usually orange, similar to the cores of the globules, and is concentrated locally in pockets or veinlets or along fracture surfaces. The grains are nearly equant and subangular to subrounded. Veins of orange carbonate also fill fractures, but are less common. This material is uniform and fine-grained.

Microscopic observations reveal both similarities and differences between types of carbonate occurrences. Fig. 1a is a BSE image of a cluster of globule fragments, and illustrates many typical features. Globules display complex chemical zoning from core to rim (Fig 1a and 1b, discussed below). Although they sometimes occur singly, globules are more often present as clusters or composite globules. Moreover, they are rarely whole, having been brittlely fractured and dispersed. Orthopyroxene, spinel, glass, and Fe sulfide are often found within the globules. Feldspathic glass also crosscuts and surrounds the globules. Orange carbonate is also present as large veins, up to 10 μm thick and extending for 100's of μm , presumably along fractures. (e.g., Fig. 1c, a vein from which the surrounding "country rock" has fractured away on one side). These veins are slightly Fe-enriched at their edges, and are systematically zoned along their lengths (see below). Orange carbonate is also finely dispersed throughout the granulated zones in irregular, angular interstitial patches (Fig 1d). Individual patches such as those indicated by arrows in Fig 1d often show complex zoning similar to that in the globules (Fig. 1e). We observed several large interstitial grains of orange carbonate, one over 175 μm in length. Carbonate is also present within the relatively undisturbed, large orthopyroxene crystals, where it forms pockets and fills micro-fractures. In one case, we could trace these back to a large carbonate vein (Fig. 1f). We found one instance of interstitial carbonate where the zoning was in reverse order from typical globules, having the orange Ca-rich carbonate on the outside and black/white sequence that is typical of globule rims in the center (Fig. 1g).

Chemical zoning is present within all forms of the carbonate. The globules show the most extensive zoning. The top part of Fig. 2 shows zoning profiles along the core-to-rim traverse shown by the arrow in Fig. 1a. This profile is typical of most globules. It has an ankeritic dolomite core that changes rapidly but

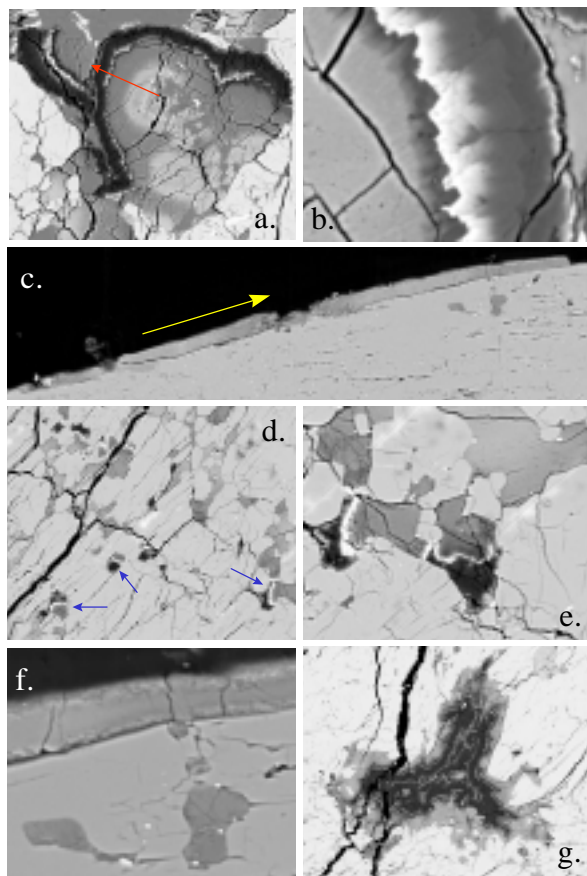


Figure 1. BSE images of carbonates in ALH84001. The width of each image is: a-200 μm ; b-40 μm ; c-450 μm ; d-250 μm ; e-90 μm ; f-60 μm ; g-400 μm .

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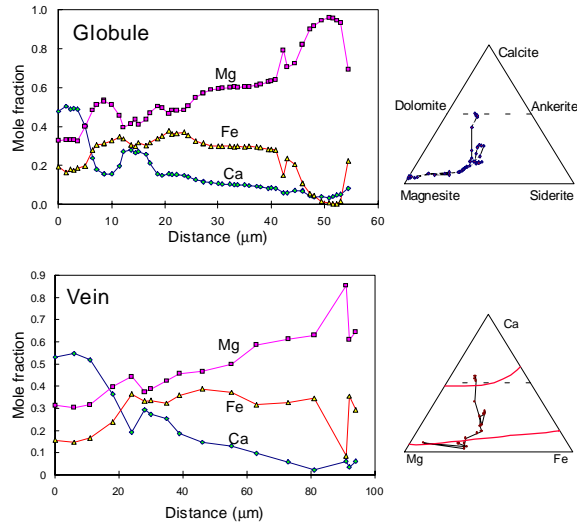


Fig. 2. Zoning profiles in carbonates. 700°C isotherms for dolomite magnesite immiscibility are shown on lower ternary diagram [4].

continuously to ferroan magnesite. (Dolomite is not observed in some globules, presumably because the section missed the center.) We did not observe any of the calcite reported by [4], and conclude it is rare. The core is zoned continuously outwards from the center towards pure magnesite, although there are occasional oscillations back to more calcic compositions. The core is terminated as nearly pure magnesite forms euhedral crystal faces (Fig. 1b). These faces suggest growth slowed enough to form planar interfaces. Renewed growth is markedly Fe-rich in a zone that contains more than one phase, including magnetite, a sulfide phase, and Fe/Mg carbonate [3]. This zone ends abruptly in a transition back to nearly pure magnesite. Another, usually quite thin, Fe-rich zone is the final episode of growth. Only in rare instances is this sequence abridged with the absence of the inner Fe-rich zone. This sequence of Fe-rich and magnesite layers most likely grew quite rapidly. The magnesite appears fibrous.

It is significant that there is continuous zoning of carbonate compositions across the immiscibility gap between dolomite-ankerite and magnesite-siderite (Fig. 2). This must reflect kinetic stabilization of these metastable compositions.

A zoning profile along the portion of the large vein indicated by the arrow in Fig. 1c is shown in the bottom of Fig. 2. This zoning is strikingly similar to the pattern in the globule, suggesting that the vein may be an edge-on section through a pancake-shaped globule, although it is impossible to positively confirm or refute this suggestion.

There are two small pockets of carbonate in the pyroxene underneath the large vein at the right of Fig. 1c that are shown at higher magnification in Fig. 1f. It is clear from this image that the pockets are connected to each other and to the vein via microcracks. The

composition of the carbonate in these pockets is identical, and is the same as the composition of the vein material where the micro-crack intersects it. It is very likely that the vein was the source of the carbonate in the pockets.

Zoning in interstitial patches ranges from simple Fe/Mg variations similar to the cores of the globules to extreme Mg enrichment as magnesite and Fe enrichment as bands that contain high concentrations of sulfur (Fig. 1d and 1e). The Fe-rich zones most likely contain magnetite and Fe/Mg carbonates as in the globules, but contain more Fe sulfide and do not show the same zoning sequence adjacent to this zone, especially the magnesite enrichment with the crystal face development that is typical of globules. The development of the Fe-rich zone is the necessary result of chemical fractionation during growth (i.e., fractional crystallization) and develops as a late-stage phase within any connected interstitial patch. It is difficult to determine how the patches are connected in 3-D. Some interstitial regions appear to have discontinuous concentric stratigraphy just like the globules [2], but others have Fe-rich bands that do not appear related to those in adjacent grains (Fig. 1d, 1e). It is unlikely that zoning develops in exactly the same way in all interstitial patches as it does in the globules, because the zoning patterns differ in detail.

We observed one large interstitial patch that shows the same orange carbonate grading to the black/white rim sequence as in globules, but in the reverse order, from the outside inward (Fig 1g). The outer edge is orange Fe/Mg carbonate and zones inward to nearly pure magnesite with the well developed crystal faces, followed by the Fe-rich and magnesite zones described above. A noticeable difference is the apparently increased amount of magnesite.

Conclusions: The presence of the zoning and the compositions of the carbonate are kinetically stabilized by rapid growth from a melt or fluid. The globules formed where ample space was available and have the most extensive zoning. The large interstitial carbonate shows the effect of more restricted space, but with similar zoning. The smaller interstitial carbonate reflects zoning in closed, fractionating systems. All the carbonate is from a single event and is closely related. The closely associated feldspar-rich glass appears to enclose and is simultaneous with or post-dates the formation of the carbonate

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References: [1] Mittlefehldt (1994) *Meteoritics* 29, 214-221. [2] Treiman (1995) *Meteoritics* 30, 294-302. [3] McKay *et al.* (1996) *Science* 273, 924-930. [4] Harvey and McSween (1996) *Nature* 382, 49-51. [5] Bradley *et al.* (1996) *GCA*, in press.