SHOCK MELTING OF CARBONATE, PLAGIOCLASE, AND SILICA IN THE MARTIAN METEORITE ALH84001.

Edward R.D. Scott, Akira Yamaguchi, and Alexander N. Krot. Hawai'i Institute of Geophysics and Planetology, SOEST, University of Hawai'i at Manoa, Honolulu HI 96822, USA (escott@kahana.pgd.hawaii.edu)

INTRODUCTION. To help understand the origin of carbonates, deformation features in the rock and their relative formation times, we have studied ALH84001,53 using optical and scanning electron microscopy and electron probe analysis. We describe the textures and compositions of plagioclase glass, silica and carbonate grains 2-200 µm in size, focusing on occurrences not previously studied in detail. We infer that carbonate grains presently in ALH84001 did not form by metasomatic replacement of silicates [1-3] or biogenically from low-temperature fluids [4]. Carbonate, plagioclase and silica were probably melted and partly mobilized during a single shock of ~ 50 GPa that also formed the brecciated zones in the rock.

RESULTS. Tiny plagioclase glass grains are widely distributed in the brecciated zones between pyroxene grains and within pyroxene fractures in brecciated and unbrecciated regions. Plagioclase glass forms 2-20 µm rounded blebs and films in healed, irregular fractures in large pyroxenes (Fig. 1a) suggesting that plagioclase melts were injected into pyroxene during shock deformation. The edges of larger glass grains 100-300 µm across, which occur on pyroxene grain boundaries, are ragged indicating that some melt flowed into adjacent fractured pyroxene. Compositions of large glass grains obtained with electron probe beams rastered over >30 μm^2 tend to show poor plagioclase stoichiometry and heterogeneity, as reported by Mittlefehldt [1]. Nearly half our analyses show small deviations from stoichiometry and relatively homogeneous compositions, $An_{32.5\pm2}$, $Or_{3.5\pm0.5}$, but concentrations of up to 1.0 wt.% Cr_2O_3 (due to incipient dissolution of adjacent chromite) and 5.0% K_2O (Or_{30}) were found in regions showing the largest deviations from stoichiometry. Small plagioclase glass blebs analyzed with a focused beam show compositions that are generally comparable to those of large grains. One glass grain show µm-sized vesicles.

Silica occurs as rare blebs on pyroxene fractures (Fig. 1d) and is abundant in a 400 x 600 µm irregularly shaped region composed of a central brecciated zone and the adjacent heavily deformed and fractured edges of three pyroxene crystals. About 100 silica grains 1-10 µm in size are dispersed in pyroxene; other phases are almost absent. Silica grains are compositionally pure and contain only 0.6% FeO. Centrally located grains tend to be subhedral whereas peripheral grains are irregularly shaped.

Numerous 5-200 µm carbonate grains were studied in the brecciated zones and in fractures in large pyroxenes in unbrecciated regions (Fig. 1b). Pyroxene fractures that contain carbonate blebs are not existing fractures but appear to have been resealed at high temperature after the carbonate was introduced. Carbonate grains in pyroxene fractures are rounded and elongated like the plagioclase grains. Some fractures contain both plagioclase glass and carbonate blebs; several mixed carbonate-plagioclase glass grains were also observed (Fig. 1c). All carbonate grains are zoned, typically from nearly pure magnesite, $Mg_{93}Cc_4Sd_3$ to magnesite-siderite-calcite compositions with ~$Mg_{50}Cc_{15}Sd_{35}$. $MnCO_3$ concentrations range from 0-4 mol.% and are positively correlated with Ca. On Mg-Ca-Fe-Mn plots, analyses of poikilitic and fracture carbonates define trends that are indistinguishable. Both types of occurrence lack compositions in the range Sd_{10-20} and contain small regions richer in Ca and Mn.

DISCUSSION. Plagioclase glass in ALH84001 was previously identified as maskelynite [1-4], a glass formed by shock without any change in the shape or composition of the precursor plagioclase grain. Maskelynite like other diaplectic glasses was once believed to have formed by solid-state processes, but melting is now commonly invoked [e.g., 5]. Textural evidence in 84001 for mobilization of plagioclase melts and the poor stoichiometry of many grains suggest that these glasses should not be called maskelynite. Mobilized plagioclase melts have been reported in lunar samples and experimentally shocked rocks [6] but not previously in strongly shocked chondrites and martian meteorites. However in Rose City (H5) we did find melt veins with normative feldspar concentrations of >90%.

Partly because maskelynite was misidentified, Treiman [2] invoked two shocks for 84001 separated by metamorphism. But the presence of micrometer-wide glass films precludes extensive metamorphism. Shocks of >45 GPa are needed to mobilize plagioclase melts in cool non-porous targets [7]. Shock-melted troilite blebs in sealed silicate fractures in shocked L chondrites [e.g., 8] texturally resemble the plagioclase melts in pyroxene fractures in 84001. This suggests that one shock event melted the plagioclase, fractured the pyroxene, injected the melt into fractures and then resealed the fractures. The lack of fractures in glass in the brecciated zones in 84001 indicates that the melt solidified after brecciation. Brecciated zones and melts could easily have formed in one impact as strongly shocked rocks commonly contain sets of shock melt or pseudotachylite veins.

Silica grains in the silica-rich region may have been derived from a grain boundary silica crystal ~30 µm wide that was melted by a shock of >50 GPa [7]. Silica melt was dispersed and injected into neighboring pyroxene crystals when the brecciated zones formed and was subsequently solidified, probably to glass.

Poikilitic carbonates in brecciated zones have essentially the same compositional range as the rounded carbonates on grain boundaries between mm-sized pyroxenes in unbrecciated regions. Treiman [2] concluded that both types of carbonates formed in a single process. Our compositional data for carbonates in fractures and poikilitic carbonates show that fracture carbonates must have formed simultaneously with the other two types.

Existing models for carbonate formation invoke either replacement of olivine, plagioclase or pyroxene by reaction with CO_2-rich fluids [1-3] or formation at low temperatures in pre-existing cracks and pores [4]. Both models fail to satisfy some petrologic constraints. Carbonates that are enclosed by plagioclase glass and pyroxene show the same chemical zoning and are commonly not associated with the silicates that are supposed to have formed or been replaced. In complex intergrowths of carbonate and plagioclase glass, glass tends to sur-

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round carbonate, contrary to theories invoking replacement of glass by carbonate [2]. Nearly all fractures containing carbonates have rounded not angular shapes favoring high temperatures, contrary to [4]. Rounded pores up to 300 μm in size are absent in meteoritic plagioclase glasses, and meteorites shocked to ~50 GPa tend to have low porosities [9].

We conclude that carbonates in fractures and the brecciated zones of 84001 were formed during the impact that melted and mobilized plagioclase. The lack of vugs >1 μm in size in carbonates and the similar sizes and shapes of carbonate and plagioclase in both fractures and brecciated zones favor emplacement of carbonate largely as shock melts. Compositional similarities suggest that all types of carbonate occurrences were shock melted. Sub-micrometer pores in carbonate [4] may result from minor devolatilization. Most shock experiments on carbonates do not report extensive melting, but some do [10]. Small but significant concentrations of SiO_2 in carbonate (0.1 ± 0.1 wt.%) also favor a high temperature origin. The rounded shape of carbonate globules in plagioclase glass in 84001 [2] is consistent with a melt origin as rounded calcites occur in many natural and synthetic igneous silicate-carbonate systems [13].

We cannot explain the inferred crystallization sequence of Ca-Fe-Mg to Mg carbonates but compositions are broadly consistent with formation above 700°C [3]. Crystallization occurred in seconds, possibly while shock pressures decreased. Peridotite xenoliths from Spitzbergen contain analogously zoned carbonate spherules that appear to have formed during quenching in hours [11].

Differences in the inferred crystallinity of carbonate, plagioclase and silica inclusions in fractured and broken pyroxene and minor morphological differences reflect the much lower viscosity of carbonate melts [12]. Shapes of pyroxene-inclusion boundaries reflect the local thermal environment which was controlled by the width, size and local abundance of melt droplets. Slow cooling changed angular boundaries to rounded and subhedral ones. The formation and preservation of nearly monomineralic shock melts of plagioclase, silica and carbonate in 84001 rather than whole-rock or mixed mineral melts may be partly due to quenching of tiny melt volumes (<1%) by large volumes of cooler pyroxene. The post-shock temperature increase of pyroxene for a 50 GPa shock would have been only ~500°C [14]. Reports of possibly discrepant ages for carbonate and plagioclase [15] require further study. Formation by shock melting argues against a biogenic origin [4] for the carbonate crystals presently in ALH84001. Organic compounds may have formed during post shock cooling [16].

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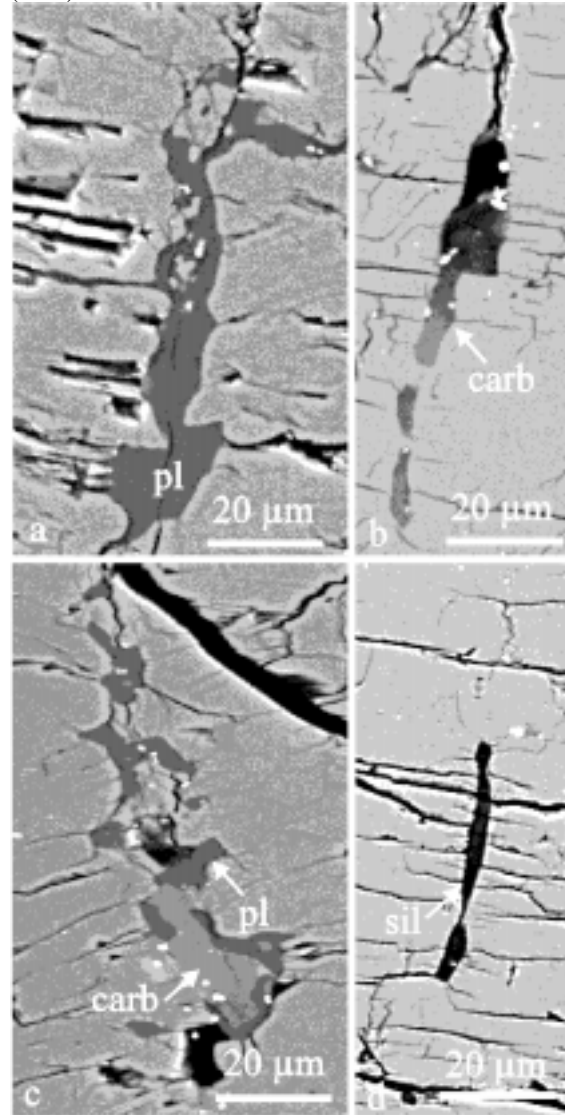

Fig. 1. BSE images of elongated grains of (a) plagioclase glass, (b) carbonate, (c) carbonate and plagioclase glass and (d) silica in fractures in ALH 84001 pyroxene. Carbonate crystal is zoned with Mg-rich portion at top (dark) and Ca-Fe-rich portion at bottom (light).