

ENDOTHERMIC REACTIONS CONSTRAIN DYNAMIC PYROMETAMORPHIC TEMPERATURES IN TWO IRON-RICH INTERPLANETARY DUST PARTICLES.

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The thermal peak and duration of dynamic pyrometamorphism in interplanetary dust particles [IDPs] during deceleration in the Earth's atmosphere depend on atmospheric entry angle and IDP geocentric velocity and mass<sup>1</sup>. Dynamic pyrometamorphism includes loss of volatiles, annealing of solar flare tracks, magnetite decoration of Fe,Mg-silicates and formation of a polycrystalline magnetite rim<sup>2-4</sup>. The density of "aggregated stony" IDPs is 0.2-2.0 g.cm<sup>-3</sup> but "non-aggregated stony" IDPs, such as monosilicate, olivine IDPs<sup>5</sup>, can have  $\rho > \sim 3$  g.cm<sup>-3</sup> (ref.6). The density is determined by IDP morphology (chondritic porous and chondritic smooth IDPs) and composition. In general, the density of Fe,Mg-silicate solid solutions is a function of Fe/Mg ratio with the highest density for the iron endmember. Thus, to a first approximation, iron-rich, "non-aggregated stony" IDPs are likely candidates to investigate metamorphic reactions and temperatures of dynamic pyrometamorphism.

**Experimental.** Serial-ultramicrotome thin sections (~100 nm thick) of particles L2005T12 (ref.4) and L2005U6 were analysed using a JEOL 2000FX analytical electron microscope [AEM] equipped with a TN 5500 EDS for *in situ* microanalysis of elements Z>10 using a 15-20 nm probe. The EDS data have a rel. error of <5%; selected area electron diffraction data have a rel. error of <1.5%. IDP L2005U6 shattered upon sectioning but individual thin sections contain sufficient material to characterise the mineralogy of this particle.

**RESULTS.** Iron-rich chondritic particle L2005T12 (20x18  $\mu$ m in size) is dominated by islands of cronstedtite-rich, serpentine-chlorite mixed layer silicate crystals and their dense, poorly ordered alteration product with high sulfur domains<sup>4</sup>. The particle has a discontinuous rim that consists of (1) a ~140nm wide, polycrystalline, outer zone of maghemite nanocrystals (~10-100 nm in diameter) and (2) a ~150 nm wide zone of chemically-altered IDP with dispersed maghemite nanocrystals (~0.7nm - 2.3 nm, in diameter) abutting on unaltered, high sulfur, domains in the dense alteration material.

Particle L2005U6 has a slightly-elongated form and is 21x19  $\mu$ m, in size. This brittle IDP shattered during thin sectioning. Thus, the exact textural relationship of a ~0.5  $\mu$ m wide, polycrystalline iron-nickel (Ni/Fe (at%) = 0.12 - 0.41) band is not known. This band probably separates the two mineralogically distinct parts of this IDP. The scanning electron microscope image of this particle (JSC Cosmic Dust Catalog 12, 1991) shows two distinct surface textures perpendicular to its long axis: (1) a coarse, scaly texture and (2) a mottled texture of irregular areas that are several hundreds of nanometers in size in a smooth material. The AEM analyses show that the former consists of submicron maghemite plates with rare, Fe,Ni and Fe:Ni:S = 86:4:10 plates close to the Fe,Ni band. The massive part is olivine single-crystals (up to about one micron in size) associated with polycrystalline olivine material with crystallites that are ~0.35 nm, in size. The Mg/(Mg+Fe<sup>2+</sup>), or mg, ratio ranges from 0.53 to 0.76. The mg ratio appears uncorrelated with olivine grain size. Olivine, mg > 0.62, contains < 2 wt% CaO; olivine, mg < 0.62, has ~2 wt% CaO. Rare, Ca-rich olivine crystals, Mg<sub>1.2</sub>Fe<sub>0.67</sub>Ca<sub>0.12</sub>Al<sub>0.1</sub>SiO<sub>4</sub> (6 mole% larnite), are present. Olivine in between large iron-oxide inclusions is transformed into garnet, Mg<sub>0.96</sub>Fe<sub>0.84</sub>Ca<sub>1.24</sub>(<sup>3+</sup>Fe<sub>1.22</sub>Al<sub>0.78</sub>)(Si<sub>2.91</sub>Al<sub>0.09</sub>)O<sub>12</sub>.

Circular, tear-shaped, and rare subhedral, maghemite inclusions (~45 nm in diameter) occur in single-crystal olivine which has a strained lattice at the interface with the inclusions. Circular maghemite grains that are typically <~20 nm in diameter abound in all olivine crystals. Most mg-rich olivines appear to be inclusion-free and have stoichiometric compositions. With decreasing mg-ratio, the sum of cations continuously increases to 3.15 (4O) as a function of increasing Fe<sup>3+</sup>/(Fe<sup>3+</sup>+Fe<sup>2+</sup>) ratio (up to 0.21). This observation is consistent with dispersed nanometer-sized maghemite inclusions but a laihunite component in olivine cannot be excluded. Single-crystal olivine, mg < 0.69, shows a symplectitic texture of olivine and maghemite. In the regular, lamellar, part of this texture in the olivine ac-plane the spacing of maghemite lamellae is 10-15 nm. Maghemite nanocrystals decorate single-crystal olivine grain boundaries.

**DISCUSSION.** The density of both IDPs is inferred from their mineralogy:  $\sim 3.2 \text{ g.cm}^{-3}$  for the iron-rich serpentine-chlorite mixed layer silicate bearing IDP L2005T12<sup>4</sup> and  $\sim 3.6 \text{ g.cm}^{-3}$  for IDP L2005U6. These IDPs belong to the high-density "non-aggregated stony" IDPs<sup>6</sup> that are expected to show intense dynamic pyrometamorphism. The fusion crust on 'traditional' meteorites is ample evidence that melting and evaporation protected the surviving mass against thermal alteration. In the case of the high density, iron-rich IDPs the iron-oxide rims are a new type of atmospheric entry alteration that involves conventional metamorphic reactions. For the unique conditions of dynamic pyrometamorphism, I postulate that these metamorphic reactions are necessarily *endothermic*. In IDPs L2005T12 and L2005U6 the iron-oxide is maghemite rather than magnetite that is reported in other IDPs<sup>3,7</sup>. Nanometer-sized maghemite rather than thermodynamically stable magnetite<sup>8</sup> formed by oxidation of iron below  $\sim 675^\circ\text{C}$  following maximum heating. The medium, maximum atmospheric entry temperature for both particles is  $\sim 1000^\circ\text{C}$  (ref.8).

Olivine in IDP L2005U6 shows two different responses to atmospheric entry heating: (1) **olivine-maghemite symplectite** and (2) **garnet formation**. The symplectite forming reaction that is written as  $1.3\text{Mg}_{1.0}\text{Fe}_{1.0}(\text{}^{3+}\text{Fe}_{0.23}\text{Si}_{0.77})\text{O}_4 = 1.0\text{Mg}_{1.4}\text{Fe}_{0.7}\text{SiO}_4 + 0.9\text{Fe}^0 + 0.6\text{O}_2$  is endothermic at  $1025^\circ\text{C}$  (Note, the reaction is written for Ca-free olivine). Assuming the reaction is diffusion controlled, and using Mg-Fe interdiffusion coefficients in olivine<sup>10</sup> and the spacing of maghemite lamellae, I calculate the symplectite formation time as a function of temperature, viz. 2.2 sec ( $1000^\circ\text{C}$ ) and 0.42 sec ( $1100^\circ\text{C}$ ). Using observed compositions, the garnet forming reaction is written as  $10.3 \text{ Ca-rich olivine (+0.06Si+0.01Al)} + 0.82\text{O}_2 = 7.6 \text{ Ca-free olivine} + 1.0 \text{ garnet} + 0.33\text{Fe}^0$ . At  $925^\circ\text{C}$  this reaction is barely exothermic ( $\sim 4.3\%$  of enthalpy at equilibrium) and although data for garnet at higher temperatures are unavailable the reaction is probably exothermic above  $925^\circ\text{C}$ . Both metamorphic reactions are able to proceed sufficiently rapid with regard to the time interval of maximum entry heating. Both metamorphic reactions in IDP L2005U6 are exothermic at temperatures consistent with predicted peak entry temperatures for this particle (cf. ref.9).

This situation is different in IDP U2005T12 but still consistent with the notion that dynamic pyrometamorphic reactions offer protection to the remainder of the micrometeorite. In this particle, the intimate association of high sulfur domains and the partial maghemite rim suggests iron-sulfide oxidation to form iron-oxide. Of all potential reactions, only the reaction  $2\text{FeS} + 3/2\text{O}_2 = \text{Fe}_2\text{O}_3 + 2\text{S(gas)}$  is endothermic and only below  $\sim 525^\circ\text{C}$ . Phase relations in polycrystalline low sulfur tubes in this particle<sup>4</sup> indicate temperatures of  $\sim 400^\circ\text{C}$  (assuming equilibrium sulfur pressure). I suggest that the thermal regime of dynamic pyrometamorphism was controlled by this endothermic reaction. As a result the effective maximum entry temperature in high density IDP U2005T12 remained well below the calculated temperature based on physical modelling<sup>1,9</sup>. This result could be important to re-assess IDP origin based on physical modelling alone. For example, the mineralogy of probably cometary, carbon-rich chondritic porous IDPs conceivably allows for a greater than calculated atmospheric entry survival rate for these important ultrafine-grained materials.

**Conclusions.** The mineralogy of two high density IDPs constrain the maximum temperature, and duration of the thermal regime, of dynamic pyrometamorphism. The requirement that the metamorphic reactions are endothermic narrowly constrains the types of metamorphic reaction. It also allows detailed analysis of the exact thermal evolution of individual IDPs based on their actual mineralogy. Clearly, the atmospheric entry thermal regime of an individual IDP is not only constrained by its orbital parameters and physical properties but also by its pre-entry mineralogy which might actually be much more restrictive.

**References.** 1. Flynn GJ (1989) Proc. 19th LPSC, 673; 2. Sandford SA & Bradley JP (1989) Icarus 82, 146; 3. Germani MS et al. EPSL 101, 162; 4. Rietmeijer FJM (1992) companion abstract; 5. Rietmeijer FJM & Blanford GE (1988) JGR 93(B10), 11,943; 6. Flynn GJ & Sutton SR (1991) Proc LPSC 21, 541; 7. Fraundorf P (1981) GCA 45, 915; 8. Rietmeijer FJM & Nuth JA (1991) Proc LPSC 21, 591; 9. Fraundorf P (1980) GRL 10, 765; 10. Freer R (1981) Contrib. Mineral. Petrol. 76, 440.

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