

MICROMETEORITE DYNAMIC PYROMETAMORPHISM: NONSTOICHIOMETRIC CLINOENSTATITE (CLEN).

Frans J.M. Rietmeijer, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA.

Polymorphs of enstatite are common phases in many meteorites. They contain clues on their formation and the thermal evolution of their host rock which includes shock metamorphism. Rare, micron-sized, CLEN whiskers and thin platelets in chondritic porous micrometeorites were interpreted as solar nebula condensates that remained unaffected during atmospheric entry flash-heating [1]. This CLEN formed by (1) protoenstatite (PEN) inversion whereby the surface energy of the micron-sized PEN crystals aided the OREN-CLEN transformation or (2) by metastable growth [1]. Ca-poor, Mg,Fe-pyroxene with unequilibrated, intraparticle, Mg/(Mg+Fe) distributions occur in most chondritic micrometeorites [2, for a recent review]. These distributions are a parent body signature that survived dynamic pyrometamorphism [3] because the duration of the thermal spike during atmospheric entry is too short [4] but this conclusion does not consider the ultrafine grain size of micrometeorites. The maximum temperature and duration of the heating event will depend on the kinetic energy and entry angle of the incoming micrometeorite. But lacking detailed petrological data for an individual particle, its thermal profile during atmospheric entry can not be deduced from its mass alone as a function of entry angle [5]. In order to constrain dynamic pyrometamorphism in unmelted micrometeorites I have determined the petrological composition and silicate mineralogy [5] in non-chondritic micrometeorites L2005T13, L2005E40 and L2006A28.

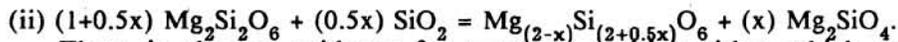
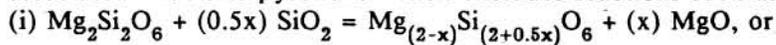
RESULTS. All three particles are coarse-grained with sulfide and silicate grains that are on average between ~0.5 and 1.5 μm , in size. Particle L2005T13 has no distinct iron-oxide rim but Fe-oxide grains that are up to several hundreds of nanometers in size, are scattered along the periphery. Mostly euhedral CLEN single-crystals are elongated along the *a* crystallographic axis. They are up to 1.7 x 0.28 μm , in size with a subequant *bc* cross-section of about 250 x 550 nm. Particles L2005E40 and L2006A28 predominantly consist of Fe,Ni-sulfides. They have a polycrystalline maghemite rim that is distinctly associated with the Fe,Ni-sulfides. This rim is 85-125 nm thick on L2005E40 and much thicker, 220-340 nm, on L2006A28. Both particles have ultrafine-grained (< 100 nm in size), polycrystalline, domains among the coarse sulfide grains. These domains contain rounded and subhedral CLEN, nonstoichiometric Mg-rich olivine and Ca-poor pyroxene, Fe,Ni-sulfides and (probably) iron-oxide nanocrystals in an amorphous matrix. Subhedral CLEN single-crystals in L2005E40 (up to 300 x 220 nm in size) have hollow crystal faces. CLEN in L2006A28 occurs as rounded crystals up to ~75 nm, in size embedded in polycrystalline domains with an almost (CI-) chondritic composition.

CLEN. High-resolution lattice imaging of pyroxene single-crystals in L2005T13 show a disordered phase with CLEN field widths indicating the PEN transformation. The average of 15 single-crystal electron diffraction patterns along different major zone axes yield: *a* (\AA) = 10.9 (\pm 7.5%), *b* (\AA) = 9.9 (\pm 6%), *c* (\AA) = 5.9 (\pm 10%) and β = 111.5° (range 110-113°). These data are consistent with the High-CLEN polymorph. CLEN is chemically pure with a structural formula $\text{Mg}_{(2-x)}\text{Si}_{(2+0.5x)}\text{O}_6$ where *X* = 0.0 - 0.465 (L2005T13) and *X* is up to 1.3 in L2005E40. There appears to be a correlation between CLEN single-crystal size and the value for *X*, whereby *X* increases with decreasing size.

DISCUSSION. The Fe,Ni-sulfide compositions and associate maghemite rims in particles L2005E40 and L2006A28 suggest dynamic pyrometamorphic temperatures up to 1463K [5]. The Fe,Ni-sulfide compositions in L2005T13 suggest temperatures up to ~1173K [cf. 6]. This lower temperature seems consistent with dispersed iron-oxide grains rather than a distinct rim. This temperature in L2005T13 is ~100° below the OREN-PEN transition at 1273K and suggests that PEN did not form during atmospheric entry flash-heating. Citing earlier observations of enstatite in micrometeorites [1], I assume that the PEN-CLEN transformation also predates atmospheric entry heating. This interpretation is consistent with the relic nature the CLEN

grains in L2005E40 and L2006A28. The interrelationships among the enstatite polymorphs as a function of temperature, pressure and shear stress are still open to debate. Unique enstatite polymorph relationships may not exist due to the (probably) small differences in free energy of the polymorphs. It is possible that (sub)micron high-CLEN is a stable polymorph above 1353K in between the PEN and OREN fields, or metastable low-CLEN instead of OREN [7].

The origin of nonstoichiometric CLEN is enigmatic as there is no MgO or forsterite intimately associated with this pyroxene which excludes reactions such as



There is also no evidence for pyroxene melting either which excludes quenching of a fractionated enstatite-SiO₂ melt.

CONCLUSION. Nonstoichiometric enstatite reflects conditions unique to dynamic pyrometamorphism, *viz.* ultrahigh heating and cooling rates. The high rate of atmospheric entry heating may not be conducive to Mg-rich silicate melting in micrometeorites up to ~30 μm in size. I submit that ultrafast diffusion in these (superheated?) silicates determines their behaviour during dynamic pyrometamorphism. The CLEN compositions delineate a reaction: $\text{Mg}_2\text{Si}_2\text{O}_6 + (0.5x) \text{Si} = \text{Mg}_{(2-x)}\text{Si}_{(2+0.5x)}\text{O}_6 + (x) \text{Mg}$. The enthalpy of nonstoichiometric pyroxene in the reaction is probably higher than for CLEN. Diffusion rates in pyroxenes are not well-known but experimental and calculated cation interdiffusion rates in Ca-poor pyroxenes are on the order of $10^{-11} - 10^{-12} \text{ cm}^2 \text{ sec}^{-1}$ at ~1350K [8]. In this case, magnesium diffusion along the c-axis of CLEN in L2005T13 occurs in ~5 sec. This result by no means constrains the dynamic pyrometamorphism event but it indicates that the proposed mechanism is not impossible.

If ultrafast diffusion produced the nonstoichiometric high-CLEN compositions in these particles, it defines a thermal regime that is much higher than that inferred from Fe,Ni-sulfide compositions in L2005T13. It is not inconsistent with the high pyrometamorphic temperatures in L2005E40 and L2006A28 [5]. Local gas phase ratios, silicate-sulfide distributions, mineral reaction rates and the time-temperature profile of atmospheric entry heating will critically determine the ultimate dynamic pyrometamorphic mineralogy. Whilst models of atmospheric entry heating predict temperatures high enough to melt silicate/Fe,Ni-sulfide particles of ~30 μm in size, there is very little evidence for melting in at least four of these particles.

The results suggest that the thermal models might need revision [5]. Or, the four particles on collectors L2005 and L2006 that sampled the stratosphere at the same time are fragments of a micrometeorite that had already slowed down considerably. Hence, the fragments did not reach the high pyrometamorphic temperatures that they would have experienced individually.

REFERENCES. [1] Bradley JP, 1983, *Nature* 301, 473; [2] Rietmeijer FJM, 1992, In *Research Trends in Mineral.* (J Menon, ed), Council Sc. Res. Integration, India, in press; [3] Klöck W *et al.*, 1990, *LPS XXI*, 637; [4] Keller LP *et al.*, 1992, *LPS XXIII*, 675; [5] Rietmeijer FJM, 1993, *LPS XXIV*, companion abstract; [6] Kullerud G *et al.*, 1969, *Econ. Geol. Monograph* 4, 323 (Wilson HDB, ed); [7] Schwab RG & Schwerin M, 1975, *N. Jb. Mineral. Abh.* 124, 223; [8] Rietmeijer FJM, 1983, *Contrib. Mineral. Petrol.* 83, 169.

This work is supported by NASA grant NAG 9-160.