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A TEM study of exsolution in Ca-rich pyroxenes from the Paris meteorite: Determination of type I chondrule cooling rates.

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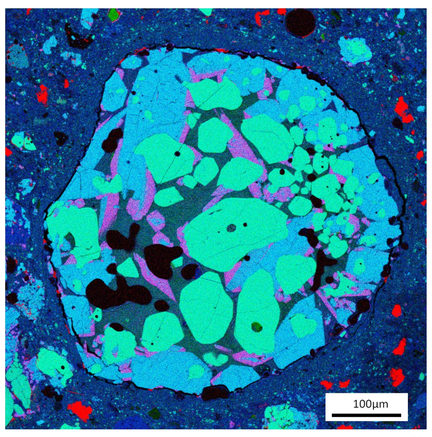
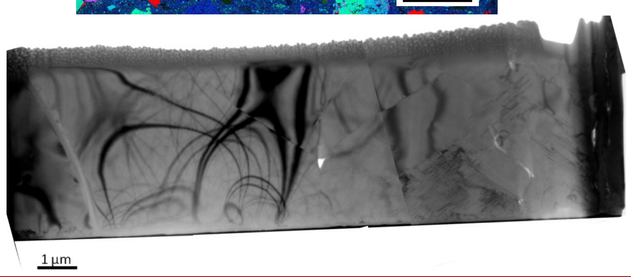
Introduction, Methods, Samples

Cooling rates of meteoritic chondrules are mainly estimated from the study of oxidized chondrules (type II), based on the observation of the texture and Fe-Mg zoning in olivine. Indeed, the study of zonations allows diffusion calculations and/or crystallization modeling, providing access to kinetics of chondrule thermal history [1–4]. However, type II chondrules mainly occur in ordinary chondrites, leaving the thermal history of reduced (type I) chondrules, dominant in carbonaceous chondrites, poorly constrained.

To decipher the thermal history of type I chondrules, other thermal markers need to be established since forsterite is essentially un-zoned. Recently, Cu-Ga diffusion profiles in metal grains were proposed to be useful to determine cooling rates [5, 6]. Another method is based on the observation of the diopside/pigeonite exsolution microstructure in Ca-pyroxenes [7]. Indeed, Ca-bearing pyroxenes' structure and composition depend on thermal history and the study of subsolidus phase transformations may allow the determination of cooling rates within the range of temperature 1200-1400 °C [7–9]. The exsolution process in pyroxene has its origin in the variation with temperature of the miscibility gap between the Ca-rich and Ca-poor pyroxenes.

Here we studied grains of Ca-pyroxene by Transmission Electron Microscopy (TEM) from two chondrules in the Paris meteorite classified as a CM2 chondrite [10]. This meteorite combines both moderately and very little altered zones and is hence less altered than other CM chondrites. Chondrules represent about 45% of the chondrite with mostly type I chondrules.





Type IAB chondrules were selected after a survey of a Paris section by scanning electron microscopy (SEM). SEM-BSE imaging and EDS compositional maps were obtained using a Tescan VEGA II LSU in order to localize Type IAB chondrules containing Ca-rich pyroxene grains.

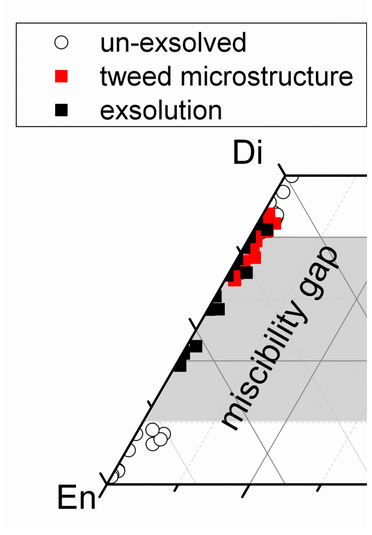
Figure opposite: SEM-EDS map of a type I chondrule. Ca : red, Si : blue, Mg : green. Enstatite grains are in light-blue and Ca-rich pyroxene in pink. (Fe,Ni) metal grains are in black and forsterite in light-green.

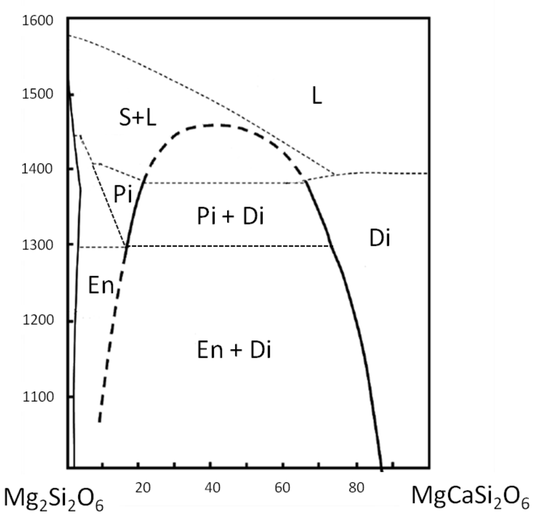
TEM foils (100 nm thick) were extracted from the petrographic section in Ca-rich pyroxenes by the focused ion beam technique using an FEI Strata DB 235 at IEMN (Univ. Lille). Analytical TEM was performed using an FEI Tecnai G2-20 (LaB6 filament) operated at 200 kV and a Philips CM30 operated at 300kV (Univ. Lille1).

Results

Pigeonite $P2_1/c$ exsolved from Augite C2/c host

The studied Ca-rich pyroxene grains have heterogeneous compositions and microstructures. For compositions outside the miscibility gap (Ca/(Ca+Mg) ≥ 0.4 and (Mg/(Ca+Mg) ≥ 0.9), pyroxene is found un-exsolved. Grains with intermediate compositions plot in the two-phase domain and exhibit exsolution lamellae and tweed microstructure.



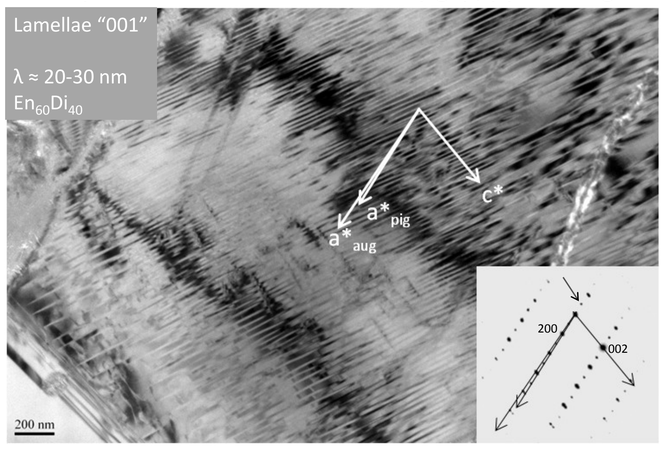


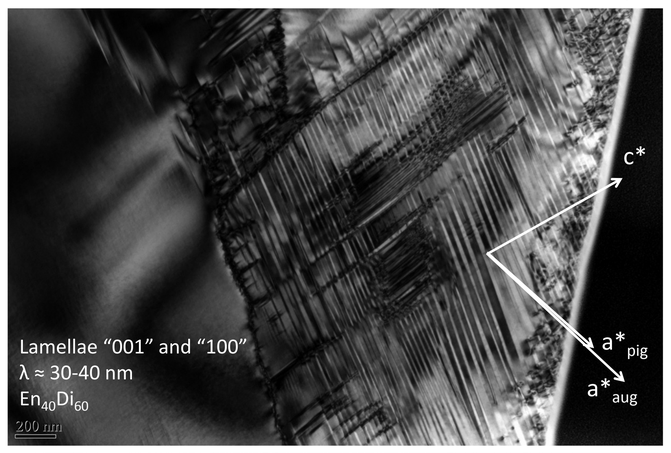
Left: *Pyroxene compositions within the chondrules measured by EDS-TEM and visualized in the Mg-rich portion of the pyroxene quadrilateral. Open circles are for un-exsolved microstructure and solid squares for the two-phase microstructure. Black solid squares are for exsolution microstructure and red square for spinodal decomposition. The two-phase domain is in light grey.*
Right: Simplified enstatite-diopside phase diagram.

The low Ca-pyroxene contains exsolved augite lamellae. They also contain anti-phase boundaries (APB) associated to the transformation C2/c → $P2_1/c$ that occurred at low temperature.

Dark field image showing the APB in pigeonite. The grain also contains augite lamellae along (001) (in dark)

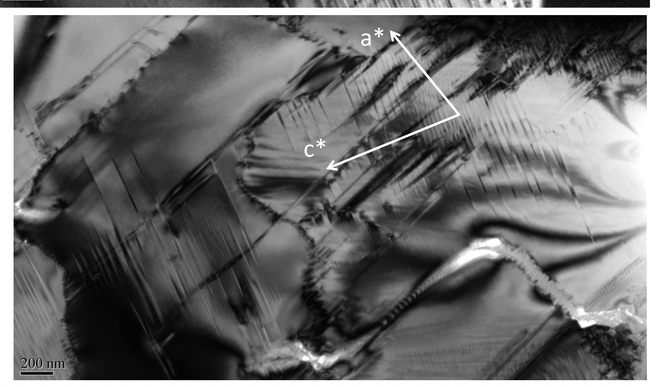
For compositions within the miscibility gap, pyroxene grains exhibit a well developed exsolution microstructure on (001)



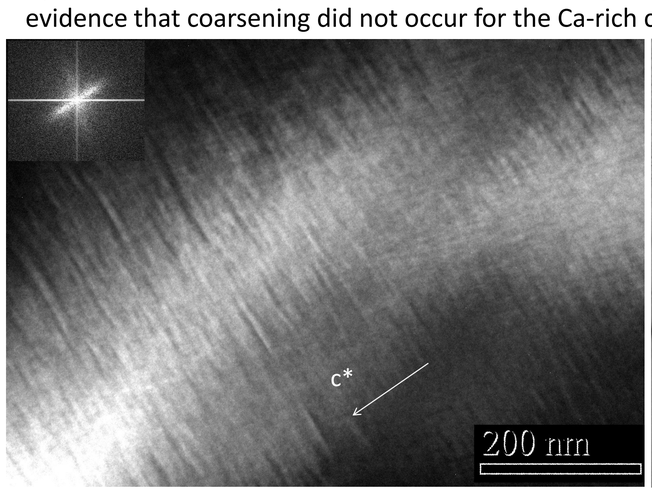


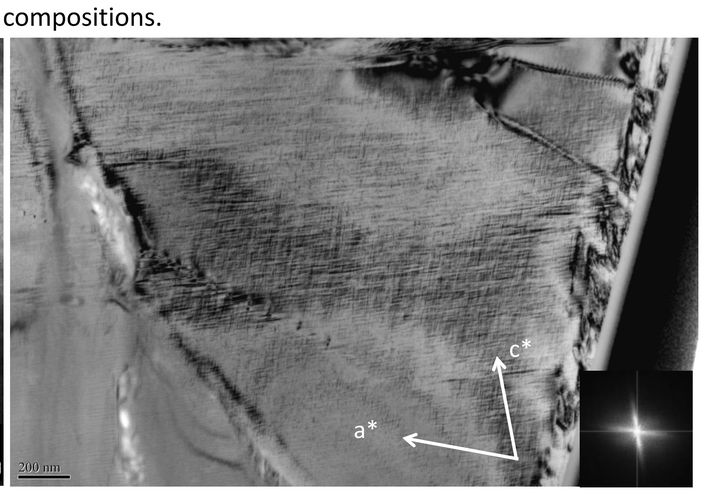
Diffraction patterns reveal that h + k odd reflections are present indicating presence of $P2_1/c$ pigeonite in addition of C2/c augite *(figure up)*. Lamella orientation is predominantly close to the (001) plane and some secondary exolution features are close to the (100) plane *(figures on the left)* .

Δβ between the a* directions of the two phases is about 2°.



Pyroxenes with composition close to Ca/(Ca+Mg) = 0.4 display a tweed microstructure. This microstructure evidence that coarsening did not occur for the Ca-rich compositions.



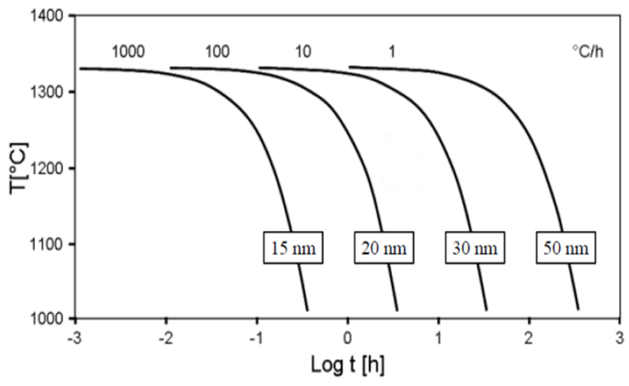


Discussion

Exsolution wavelength is closely related to cooling rates making it a reliable thermal marker. The link between the wavelength, time and temperature has been explored by [7] who proposed a calibration curve to estimate the cooling rate (figure opposite). The cooling rate of the studied chondrules is deduced from the exsolution wavelengths. According to the phase diagram the crystallization temperature is about 1375°C for pyroxene composition between $En_{60}Di_{40}$ and $En_{40}Di_{60}$. Lamellae wavelength (λ) vary within same a chondrule between 20 ≤ λ ≤ 40 nm which correspond to cooling rates within the range 1-100°C/h.

Pyroxene with composition close to Ca/(Ca+Mg) = 0.4 frequently exhibit a tweed microstructure revealing that spinodal decomposition occurred without significant coarsening. Complementary studies are in progress to document the influence of the local composition on the exsolution microstructure.

This study shows that type 1 chondrules have experienced cooling rates comparable to those of type 2 chondrules. Despite the oxygen fugacity environment is clearly different (thus the location formation) for type 1 and 2 chondrules, the comparable cooling rates suggest a common trigger for the formation mechanism.



Time-Temperature-Transformation diagram (TTT) for diopside/pigeonite exsolutions (adapted from [7]) showing cooling rates and the corresponding lamellae wavelength.

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