

**PYROXENE CRYSTAL CHEMISTRY AND THE LATE COOLING HISTORY OF NWA 2737.** B. Reynard<sup>1</sup>, P. Beck<sup>2</sup>, J-A. Barrat<sup>3</sup> and M. Bohn<sup>4</sup>, <sup>1</sup>Laboratoire des Sciences de la Terre, CNRS UMR 5570, Ecole Normale Supérieure de Lyon, 46 allée d'Italie, 69364 Lyon Cedex 7, France. E-mail: breynard@ens-lyon.fr, <sup>2</sup>Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Ranch road NW, DC20015. E-mail:pbeck@gl.ciw.edu. <sup>3</sup>U.B.O.-I.U.E.M., place Nicolas Copernic, F-29280 Plouzané Cedex, France. E-mail: barrat@univ-brest.fr. <sup>4</sup>Ifremer-Centre de Brest, (CNRS-UMR 6538), BP70, 29280 Plouzané Cedex, France. E-mail: Marcel.Bohn@ifremer.fr.

**Introduction:** NWA2737 is the second chassignite ever found after the Chassigny fall in 1815. Its attribution to the Chassigny group is based on petrological similarities, both are dunites with 90% olivine and intercumulus pyroxenes and feldspar, and on a similar geochemical signature [1]. Among these common characteristics, one is a peculiar trend in pyroxene compositions with various Ca/(Ca+Fe+Mg) ratios indicative of chemical zoning during crystallization and Fe/(Fe+Mg) ratios distributed along the equilibrium tie-line [2]. This type of zoning is rare both in terrestrial and extraterrestrial rocks. We propose here a simple petrogenetic model where intercumulus pyroxenes crystallize from a melt whose composition, in particular its Fe/Mg ratio, is controlled by the dominant olivine cumulus crystal through interdiffusion. Kinetic constrains on the Fe/Mg interdiffusion processes are used to discuss the range of cooling rates in the Martian dunites.

**Pyroxene chemistry:** Three pyroxenes are recognized from their chemical analyses and Raman spectra: augite, pigeonite and orthopyroxene [1]. Low-Ca pyroxenes occur as interstitial post-cumulus phases, exhibiting sometimes exsolved augite lamellae (about 1  $\mu\text{m}$  wide). The three types of pyroxenes are not chemically homogeneous. Compositions range from  $\text{En}_{78.5}\text{Wo}_{2.7}\text{Fs}_{18.8}$  to  $\text{En}_{70.5}\text{Wo}_{12.0}\text{Fs}_{17.5}$  for orthopyroxene and pigeonite, which are difficult to separate because of mixed analyses, and from  $\text{En}_{54.6}\text{Wo}_{32.8}\text{Fs}_{12.6}$  to  $\text{En}_{46.7}\text{Wo}_{44.1}\text{Fs}_{9.2}$  for augite. Compositions lying between these two main populations are attributed to mixed analyses at grain boundaries. The quadrilateral composition of pyroxenes shows a broad variation like in Chassigny, along an elongated triangle following tie-lines of Fe-Mg equilibrium among Ca-rich and Ca-poor pyroxenes, which are nearly perpendicular to the two-pyroxene equilibrium isotherms [2].

**Ca thermometry:** A rough estimate of 1100-1200°C is obtained when considering orthopyroxene-pigeonite and lowest Ca augites [2]. Intermediate compositions indicating apparent temperatures of 1300°C are probably due to mixed analyses at grain boundaries between augites and low-Ca pyroxenes. Highest Ca augites indicate apparent temperatures as low as 800-900°C, which is below the eutectic for equilibrium

crystallisation with low-Ca pyroxenes from a mafic melt in the presence of olivine. These high-Ca values are thus explained by a late crystallization out of equilibrium with low-Ca pyroxene, in the Ca-enriched residual melt.

**Fe-Mg augite-olivine thermometry:** We attempted to use the compositions of olivines (considered as constant at  $\text{Fo}_{78.7}$ ) and augites to calculate temperatures from the Fe-Mg exchange [3]. For that purpose, the  $\text{Fe}^{3+}$  content of pyroxene was estimated from stoichiometric and charge balance constrains. Results show a decrease in temperatures from 1120 to 1070°C with increasing Ca content of augite, consistent with a late crystallization of highest Ca augites. The highest temperatures obtained from lowest Ca augites are broadly consistent with those inferred from Ca thermometry in the 1100-1200°C range.

**Discussion:** Similar trends in pyroxene compositions have been reported for terrestrial [4] and lunar rocks [5], and were explained by the metastable growth of crystals under high cooling rates. However, it was alternatively proposed that such "60° trends" result from unresolved analysis of intimately associated augite/pigeonite [6]. The later hypothesis was proposed to explain the chemistry of Chassigny pyroxenes [7]. In the case of NWA 2737, although some of the chemical variability in pyroxene analysis is attributed to mixed analyse at grain boundaries, especially for intermediate Ca contents, a large variability is observed within individual grains from chemical mapping [1], which is attributed to magmatic zoning. Indeed, we can propose that the large range of Ca-content in pyroxenes is due to the immiscibility gap between augite and low-Ca pyroxenes during the cooling and intercumulus crystallization in NWA 2737. If we follow this line of interpretation, pyroxene Ca-contents would record cooling down to about 1100°C on the low-Ca-pyroxene side, and down to 800°C on the augite side. The low temperature obtained from Ca contents of augite probably reflects the fact that these do not grow in equilibrium with low-Ca pyroxene because of the low Ca diffusivity in diopside with respect to Fe-Mg exchange [8], and reflect local variations in melt composition due to crystallization in a closed system. On the other hand, Fe-Mg exchange is very fast with

respect to Ca inter-diffusion in pyroxene (about 3 orders of magnitude, [8] and references therein), and Fe-Mg exchange in olivine is even faster by a few orders of magnitude. The observed decrease of Fe-Mg temperature with increasing Ca in augite is consistent with a progressive crystallization, first along the solvus in equilibrium with low Ca pyroxene, then of augite alone from a Ca-enriched residual melt with Fe-Mg augite-olivine temperatures around 1070°C

In order to quantify these processes, we have used available Fe-Mg interdiffusion data for orthopyroxene and olivine. Complementary constrains are provided by the observations on Ca zoning in pyroxenes and in olivines [9]. From these diffusion laws, we can calculate the closure temperatures  $T_C$  for diffusion [10] as a function of the cooling rate (Figure 1).

During pyroxene crystallization, Fe-Mg exchange with olivine allows equilibration of Fe/Mg ratios in augites, justifying the use of the augite-olivine thermometer [3]. However, the latest crystallized augites (Ca-rich) indicate lower temperatures (down to 1070°C) than the lower-Ca ones (up to 1120°C). This is possible only if Fe-Mg exchange is blocked in augites at the determined temperatures. This is consistent with closure temperature for FeMn-Mg exchange for a minimum characteristic diffusion length of 10  $\mu\text{m}$ , which corresponds to the distance between two EMPA points (Fig. 1).

Subsolidus Ca-Mg diffusion occurs in pyroxenes where exsolution up to a few micron wide are observed, either of pigeonite in augite or of augite in low-Ca pyroxenes. Estimates of closure temperature for Ca-Mg diffusion at the one and ten micron scale are depicted in figure 3. They are consistent with the formation of exsolutions less than a few micron wide at subsolidus temperatures, within the cooling rate range determined from Ca diffusion in olivine (3-30°C/a).

Thus, although error bars on the cooling rates usually amount to about one order of magnitude or more, given the uncertainties on experimentally determined diffusion coefficients, grain size, and other parameters such as temperature and oxygen fugacity, we can build a self-consistent picture of chemical exchange and cooling rates in the NWA 2737 meteorite using various sets of data. In order to constrain the maximum cooling rate, we can use the presence of pyroxene exsolution of a few microns (up to about 5  $\mu\text{m}$ ). and we obtain less than 10°C/a for this diffusion length. Allowing for a one order on magnitude error bar, the maximum cooling rate is 100°C/a. For the minimum cooling rate, we use the interdiffusion of Fe and Mg in augite, which constrain the minimum rate between 0.8 and 3°C/a.

**Conclusion:** This allows to explain the late magmatic evolution of this rock, and especially the intriguing suite of pyroxene compositions, using cooling rates lying in the 0.1-100°C/a range, with a likely value in the 1-10°C/a range. With these values, the late crystallization depth of NWA 2737 is estimated to lie between 50 and 200 meter depth from a simple cooling model of a dyke in cool (0°C) country rocks. This indicates formation in an effusive context such as the base of very thick lava flows or in a subsurface intrusion.

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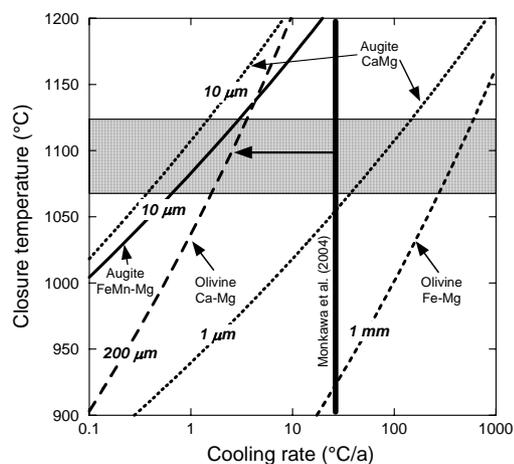


Figure 1: Closure temperatures for Fe-Mg and Ca-Mg exchange in augite and olivine as a function of cooling rate. The shaded area is the temperature range from augite-olivine Fe-Mg exchange thermometry.