OSWALD RIPENING OF CA-RICH PYROXENE. IMPLICATION ON THE VERY LATE COOLING HISTORY OF CHONDRULE MESOSTASIS.

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Introduction: Knowledge of how crystals grow is of fundamental importance for interpreting textures observed in meteorites. However, data on crystal growth of rock-forming silicates for a very small degree of undercooling (< 1°C) are extremely rare. Recently [1], it was demonstrated that these very small degrees of undercooling could be experimentally approached by studying the kinetic of Oswald ripening if this kinetics is not controlled by diffusion. Then, mechanisms and rates of crystal growth of olivine, plagioclase and quartz have been determined [1,2]. The present experimental study was undertaken to investigate growth kinetic of pyroxene at small undercooling. The objective is two fold: (i) determining the diopside growth mechanism, (ii) obtaining quantitative data on the rate of diopside crystal growth.

Experimental techniques: Ostwald ripening experiments are generally conducted with a starting material that is a mixture of crystal powder and glass. In the present study, a particularly of diopside growth is used to develop a non-conventional method to investigate Ostwald ripening. Indeed, it is well known that diopside crystals, but also most of clinopyroxene, grow very quickly with a dendritic habit when a glass is reheated. Experimental protocol used in this study takes advantage of this rapid growth of clinopyroxene during the reheating step. Thermal procedure used in this study is represented figure 1.

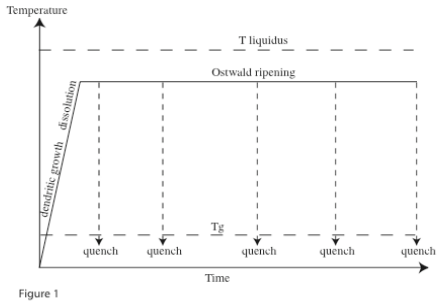

Figure 1

Charges are directly put in the hot spot of the vertical furnace. Geothermometry experiments performed in vertical furnace by Maharaj and Hewins [3] indicate that charges reach 1500°C in 5 s, so faster than indicated by the thermocouple. Dendritic growth of pyroxene occurs during this first step of heating. Figure 2a displays that charge heated only 2 minutes are constituted by dendritic clinopyroxene crystals and liquid (now glass after quenching). Therefore, dendritic clinopyroxene growth is an early phenomenon that produced crystals, which are very far of their equilibrium shape. Dendritic morphology is characterized by a great surface energy. In order to decrease this surface energy with regard to volume energy, dendrites are cut in a multitude of small diopside crystallites. Result of this process after 5 minutes of heating is shown figure 2b where only sparse dendrites survive in the charge. The kinetic of Oswald ripening is studied in these small diopside crystals.

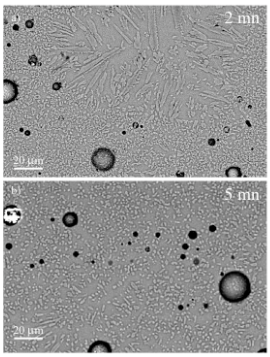

Figure 2

The starting glass material was prepared from a mixture of reagent grade oxides (55.14 wt% SiO_2, 11.61 wt% Al_2O_3, 19.52 wt% CaO, 13.70 wt% MgO), melted in a platinum capsule at 1400°C (about 95°C above the liquidus temperature) for 6 h in air, and quench in water. The glass obtained was then ground in an agate mortar and the resulting powder in a form of a pellet was put onto a platinum wire loop [4] and hung close to the end of a ceramic rod. Then ceramic rod was plunged into the vertical furnace, which was preheated to the run temperature (°C), at the level of the hot spot. At the end of the isothermal experiments (2 mn to 193 h), the charges were quenched by dropping them into water. Then, they were mounted in epoxy and polished. The sections were studied by scanning electron microscope (SEM) and electron microprobe (Cameca SX100) at Université Blaise Pascal (Clermont-Ferrand, France). SEM work was carried out on a JEOL 5910LV equipped with an X-ray analyzer PGT operating in energy dispersive mode (EDS) and with the SPIRIT software that allows to measure directly maximum size of each crystal present in the photo.

Results: Electron microprobe analyses display that after the first step of rapid growth-dissolution, liquid does not evolve with time. Therefore, coarsening of diopside crystals necessary result of Oswald ripening because chemical disequilibrium is nil. The driving

force is the reduction of the surface energy by dissolution of the smaller grains and growth of the larger ones. This result is consistent with the decrease of number of grains with time by more than a factor 30 over 193 h.

Identification of the growth mechanism is possible with a diagram logarithm of 2D mean size versus logarithm of time. A straight line with a positive slope should result. This slope corresponds to 1/n where n is a means to characterize the growth mechanism. Indeed, n equal to 3 when Oswald ripening is controlled by diffusion [5-7] or by the screw dislocation [8-10] and n = 2 if the ripening is controlled by continuous growth-dissolution process. A third type of interface mechanism controlled Oswald ripening must be considered: surface nucleation. In this case, Solomatov and Stevenson [11] have theoretically shown that the mean grain size is proportional to logarithm of time. Therefore, 2D mean grain sizes versus logarithm of time yields a straight line.

Figure 3 displays the two diagrams for diopside experimental data. In a diagram, logarithm of 2D mean size versus logarithm of time, the data yield a straight line with a slope of 0.15 and a correlation coefficient $R^2 = 0.997$ if the 5 minutes experiment is not considered. The value of n obtained is equal to 6.3. The second diagram, 2D mean grain sizes versus logarithm of time, the data yield also a straight line whatever the data considered, with or without 5 minutes experiment: $R^2 = 0.983$ and $R^2 = 0.976$ respectively.

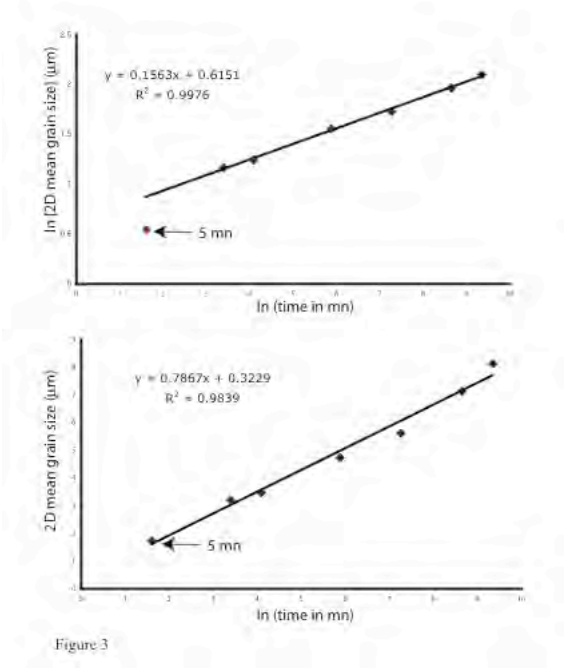

Figure 3

Discussion and conclusion: Ostwald ripening corresponds to dissolution of small grains in order to allow growth of larger ones. This process requires diffusion of the elements between small and large crystal via a liquid phase. Therefore, Ostwald ripening like crystal growth is controlled either by interface mechanisms (continuous growth, spiral growth or surface nucleation) or by diffusion. No sign of concentration gradient had been observed at the interface crystal liquid at the microprobe scale resolution that suggests diffusion is not the limited rate in these Oswald ripening experiments. Moreover, the high value of n (6.3) calculated with the slope obtained in diagram logarithm of 2D mean size versus logarithm of time is not consistent with an Ostwald ripening mechanism controlled by diffusion where n could be equal to 3. This high value of n excludes also a continuous growth and the screw dislocation process. In contrast, the straight line obtained with the 2D mean grain sizes versus logarithm of time suggest that diopside growth mechanism at small degree of undercooling is controlled by surface nucleation.

These experiments may be used to decipher thermal history of several types of igneous extraterrestrial materials. For instance, observation of clinopyroxene dendrites on chondrule mesostasis suggests, on the light of these results, that chondrules didn't experience any high temperature re-heating events.

References: [1] H. Cabane et al. (2005) *Contrib. Mineral. Petrol*. 150, 37. [2] Cabane et al. (2001) *Contrib. Mineral. Petrol*.142, 361. [3] Maharaj and Hewins (1998) *Meteoritics & Planet. Sci.* 34:885. [4] (Donaldson et al. (1975) *Am Mineral* 60: 324. [5] Lifshitz & Slyozov (1961) *J. Phys. Chem. Solids* 19: 35. [6] Wagner (1961) *Z. Elektrochem* 65: 581. [7] Dehoff (1991) *Acta Mettall. Mater.* 39: 2349. [8] Chai (1974) *Carnegie Inst. washington Pub.* 634: 205. [9] Kahlweit (1975) *Adv. Colloid Interface Sci.* 5: 1. [10] Ratke et al. (1995) *Scripta Metall. Mater* 33: 363. [11] Solomatov and Stevenson (1993) *J. Geophys. Res.* 98: 5407.