

SUBSOLIDUS TRANSFORMATION OF AMORPHOUS INTERSTELLAR DUSTS AFTER INJECTION IN A PROTOPLANETARY DISK. M. Roskosz¹, H. Leroux¹, ¹Laboratoire de Structures et Propriétés de l'Etat Solide UMR 8008 CNRS USTL 59655 Villeneuve d'Ascq, mathieu.roskosz@univ-lille1.fr, hugues.leroux@univ-lille1.fr

Introduction: Infrared observations indicate that a dominant fraction of the condensed matter found in the interstellar medium (ISM) is amorphous (silicates, organic matter, ices). On the other hand, similar spectroscopic studies show that silicates are mainly crystalline in protoplanetary disks [1]. Furthermore, cometary material appears also essentially crystalline [2, 3]. Because the ISM dust is the precursor material of protosolar cloud, it appears that structures and compositions of the silicate dust is strongly thermally processed in such environments (e.g. [4]).

Recent dynamical models of accretion disks indicate that turbulent radial mixing probably occurred and that thermally processed silicates from the inner part of the disk were likely transported toward outer regions [5]. With this scheme, reheating and crystallization of amorphous material below solidus temperatures of typical minerals were the first transformations that occurred during the transportation of the interstellar silicate in the protosolar disk.

In this contribution we explore experimentally this subsolidus route of crystallization for amorphous silicates in the CaO-MgO-Al₂O₃-SiO₂ (CMAS) composition system. We found an unexpected diversity of minerals which show that a large redistribution of elements occurs via metastable steps during the crystallization scheme. We finally discuss basic physicochemical mechanisms responsible for the microstructures, compositions and mineralogy of recovered crystallized products.

Experiments: Previous studies showed that silicates in the ISM are amorphous, probably due to irradiation processes [6]. Such amorphous materials cannot be prepared in large amount. Consequently, we used glasses as analogs. Various compositions in the systems CaO-Al₂O₃-SiO₂ (CAS), CaO-MgO-SiO₂ (MAS) and CaO-MgO-Al₂O₃-SiO₂ (CMAS) were studied in order to derive systematic trends for cosmochemically-relevant compositions (pyroxenes, plagioclase, melilite, olivine). Starting materials were either finely crushed in an agate mortar or mm-sized glass chips. These different geometries allowed us to assess the effects of the surface/volume ratio on microstructures and mineralogy of the crystalline phases formed. Samples were heated in a tubular furnace, in air, for 30 min to 15 days at temperatures ranging from 40°C below to 100°C above the glass transition temperature of starting glasses (T_g's). After experimental runs, samples were analyzed by

Scanning Electron Microscopy (SEM), Electron Microprobe (EMP) and Transmission Electron Microscopy (TEM).

Results:

First of all, the microstructure of crystals formed at large degree of supercooling is characterized by a high density of planar defects (Fig.1). Dislocations are observed in diopside but twins are far dominant in other observed minerals. They probably reflect the effect of thermal and mechanical stresses associated with the change of specific volumes and compositions during the formation of crystals from a highly viscous medium. More importantly large samples (mm-sized) exhibit a dendritic to spherulitic growth (Fig.1a). These textures, typical of rapid crystallization upon quench reflect here the difficulty of crystals to grow incongruently from very viscous melts. These textures are however not observed when small grains crystallize. In this latter case, crystals appear relatively euhedral and no preferential orientation is observed (Fig.1b).

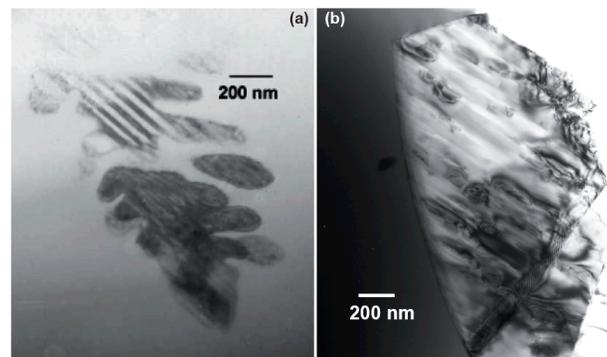


Figure 1: TEM micrograph. a) larnite (Ca₂SiO₄) dendrite crystallized from a glass chip. b) diopside crystallized from a glass powder. Both micrographs also show microstructures with a high density of crystal defects (a. twins and b. dislocations).

A high diversity of crystals formed during the annealing. For instance, starting from a diopside glass (CaMgSi₂O₆), the first phases formed at T_g consist of an assemblage of diopside, akermanite (Ca₂MgSi₂O₇), merwinite (Ca₃MgSi₂O₈) and, even more surprisingly, of Ca-bearing forsterite (Mg₂SiO₄ for the nominal composition). The same trend is observed in the CAS ternary system. For instance, for a glass close to the gehlenite composition (Ca₂Al₂SiO₇) the first phase which crystallizes is

hattrite (Ca_3SiO_5) and not gehlenite as predicted by the phase diagram. The formation of akermanite from a diopside liquid was reported earlier and interpreted as the consequence of the gentle slope of the metastable liquidus curves along the pseudobinary diopside-akermanite join [7]. However, this thermodynamic interpretation cannot be applied to the formation of merwinite and forsterite from a diopside melt and is difficult to apply to the CAS ternary system.

Our annealing experiments at temperature close to T_g show that the crystals that formed have compositions far from nominal stoichiometry of the glass. Aluminous diopside, Ca-rich forsterite, non-stoichiometric melilite, anorthite and wollastonite are frequently observed. More importantly, clear compositional trends are observed for all the starting melts studied (Fig.2). Because these trends also depend on temperature, they allow us to propose a physicochemical mechanism accounting for such subsolidus transformations.

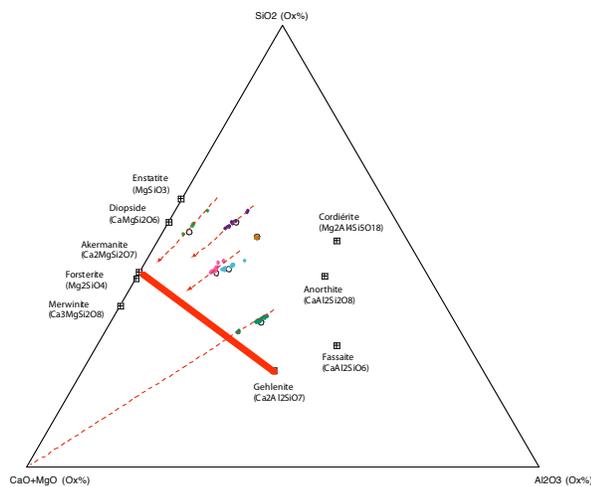


Figure 2: Crystal compositions (determined by STEM) and compositional trends for 6 different starting melts in the CAS system (open circles). Starting compositions were prepared by L. Tissandier, CRPG, France.

Discussion: All our experimental data show that subsolidus crystallization is accompanied by a significant redistribution of cations, especially magnesium and calcium. In the CAS ternary diagram, crystals are essentially enriched in calcium while the Al/Si ratio approach that of the parent liquid. With increasing crystallization temperature (T), the transition to phase composition expected near the solidus takes place via a gradual change of Al/Si, this change being a systematic function of ($T-T_g$) [8]. This feature extends to other systems studied. It may be explained by the decoupling of relative mobility of cations, of which the network modifiers (Ca and Mg)

becomes several orders of magnitude faster than that of the network formers Si and Al around T_g . In addition this crystallization is kinetically favored because the enrichment of the nuclei in low-field strength cations decreases the relative number of strong bonds (i.e. Al-O and Si-O), which need to be reordered to reach a crystalline structure [9].

Our study shows unexpected properties of crystallization behavior of complex amorphous silicate. First of all, dendritic or spherulitic growth only develops for large glass ships (typically mm-sized). Dendritic morphologies are frequently observed in laboratory experiments but only occasionally observed in natural samples. The fact that these textures are not observed in our dust analogs (glass powders) nor in natural samples relevant to this study (cometary grains, IDP's, matrix of chondrites) confirms the relevance of studying low-temperature transformations of amorphous interstellar dust analogs. Second, the mobility decoupling of cations induces a large redistribution of cations, the formation of refractory minerals and non-stoichiometric phases. Unexpectedly, this study shows that subsolidus route to crystallization of amorphous grains produces a relatively large diversity of crystals, a lot of them being typically considered as proxies of direct condensation and/or high-temperature events such as melilite, Ca- and Al-rich phases, Al-diopside and Ca-forsterite.

In this framework, one may hypothesize that relicts of interstellar grains, if present in the fine matrix of chondrites, in cometary materials and IDP's should take the appearance of non-stoichiometric or refractory crystals. As a consequence, they may seem, at first sight, very similar to condensation or high-temperature products whereas their origin differs drastically from CAI's. However, since they did not see very high-temperatures (less than 900°C typically), they may have preserved a discriminating isotopic signature because of limited exchange with their environment. In any case, an extensive work is still required to fully understand the formation conditions of these minerals.

References: [1] Van Boekel et al. (2004) *Nature* 432, 479-482. [2] Crovisier et al. (1997) *Science* 275, 1904-1907. [3] Zolensky et al. (2006) *Science* 314, 1735-1739. [4] Nuth and Johnson 2006, *Icarus*, 180, 243-250. [5] Bockelée-Morvan et al. 2002, *A&A*, 384, 1107-1118. [6] Demyk et al 2001, *A&A*, 368, L38-L41. [7] Kalinina and Filipovich (1995) *Glass. Phys. Chem.* 21, 97-121. [8] Roskosz et al. (2006) *J. Non-cryst Solids*, 352, 180-184. [9] Roskosz et al. (2005) *J. Non-cryst Solids*, 351, 1266-1282.