LABORATORY STUDIES ON SILICATES RELEVANT FOR THE PHYSICS OF TNOS

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Abstract. Silicates are one of the principal components present in Solar System objects. Silicates evolve in space modifying their physical properties according to the astronomical environments they go through. To characterise the nature of TNOs in the framework of the formation and evolution of the Solar System, experiments on structural transitions of silicates have been performed in the laboratory to simulate some of the processing suffered by the dust. The infrared spectral properties of possible silicate candidates thought to be present in TNOs have been studied. The results of thermal annealing of amorphous silicates and amorphisation of crystalline forsterite (pure-Mg olivine) by ion irradiation are presented. The observable properties of TNOs surfaces are inferred.

1. Introduction

It is commonly accepted that small objects in the outer part of the Solar System, comets and Trans Neptunian Objects (TNOs) are a reservoir of partially uncontaminated primordial material from which the Solar System formed about 4.5 billions years ago. Actually, the composition, the physical and structural properties of these objects depend on the formation mechanisms and evolution processes experienced since their accretion. The study of the formation and evolution of TNOs requires knowledge of the dynamical evolution of the proto-solar nebula where they formed. Infrared (IR) signatures observed both by ground observations and by the Infrared Space Observatory (ISO) have successfully been used for the identification of the types of minerals present in Oort cloud comets (Campins and Ryan, 1989; Hanner et al., 1994a, b; Crovisier et al., 1997). These observations have posed clear constraints on the chemical composition of silicates, showing that crystalline olivine and pyroxene are abundant (Wooden et al., 1999; Harker et al., 2002a). The presence of crystalline grains in Oort comet spectra and the absence or un-observability of crystal signatures in the ISO spectra of dense and diffuse interstellar medium (ISM) (Li and Draine, 2001; Demyk et al., 1999) raises the question: does the material present in small objects of the outer Solar System reflect the physical and

Earth, Moon and Planets **92:** 307–313, 2003.

chemical properties of the proto-solar nebula? In fact, many competitive processes experienced by the dust affect the physical and chemical evolution of the grains before and after their coagulation in larger objects. In particular, amorphous and crystalline silicates are separated by an energetic gap which has to be overcome by the atoms to move from one structural configurations to the other. Information on possible transformations suffered by the dust may provide evidence for the possible links between chemical-physical properties of small objects of the Solar System and the interstellar evolution of the dust since the grain's formation around evolved stars.

To understand what the main components of TNOs are, and what processes affected their nature, more detailed observations of these very faint objects and dedicated laboratory experiments have to be performed. Actually, the evolution of silicate structure can be used as a marker of the TNOs history. According to present evolutionary models, silicates coming from the pre-solar cloud and in-falling onto the proto-solar nebula were amorphous. On the other hand, the results obtained from laboratory simulations indicate that amorphous-to-crystalline transformations can occur on time scale shorter than 10^6 years only if annealing temperatures are higher than about 800 K (Brucato et al., 1999). It is, therefore, unlikely that amorphous silicates were converted into crystalline materials in the outer nebula, where comets and TNOs are supposed to have formed and where the temperature is too low (few tens of Kelvin) to favour the amorphous-crystalline transition. Two possible scenarios have been recently proposed that would explain the presence of crystalline grains in comets: turbulent radial mixing in the solar nebula (Bockelee-Morvan et al., 2002) and annealing of dust by nebular shocks (Harker and Desch, 2002b). It has been demonstrated that a flash-heating at temperatures of 1100 K is sufficient to crystallise micrometer sized particles in few minutes, as it has been proposed to happen for pre-chondrules (Rietmeijer et al., 1999). It has also been suggested that the observed amount of crystalline silicates in cometary grains is an indicator of age of cometary formation (Nuth et al., 2000).

Another process which has to be taken into account is that grains suffered, during their life, ion bombardment at various rates sufficient to alter their chemical and structural composition (Strazzulla and Johnson, 1991). This process can affect the nature and the physical properties of the dust and/or of the overall body.

The actual role played by thermal annealing and ion irradiation is studied in laboratory experiments. This information could be the basis to predict the observable properties of TNOs and could be a way to gain more confidence in the modeling of the early Solar System evolution.

2. Thermal Annealing

The experimental procedure used for thermal annealing of silicates is based on two steps. The first is the production of amorphous silicate grains with variable chemical composition by using the laser ablation technique by a powerful Nd-YAG solid state pulsed laser. The second step is annealing the grains for various times at different temperatures, monitoring the crystallisation by IR spectroscopy. The laser targets were terrestrial silicates and oxide mixtures. The composition was that of olivine, with variable contents of Mg and Fe. Terrestrial Mg-rich and Fe-rich olivine, $(Mg, Fe)_2SiO_4$, were used. While terrestrial samples contain inclusions of a few percent of impurities, pure minerals were synthesised in laboratory by using mixtures of oxides (periclase MgO; quartz SiO_2; hematite Fe_2O_3).

Annealing of condensed materials is performed in vacuum (10^{-6} mbar) at temperatures in the range 500–1000 C. The heating rate and the stability in temperature is controlled by an electronic device. The annealing temperatures are reached at a rate of 23 C min^{-1}. For more details see Brucato et al. (1999, 2002).

The transmittance spectral evolution induced by thermal annealing for different time lags and temperatures indicate changes in the structure of the dust. Laboratory experiments on thermal evolution of amorphous silicates were used to derive the activation energy of crystallisation. This parameter describes the crystallisation process, intrinsic to each material, given the temperature and time. Thus, activation energies obtained in the laboratory can be used to model annealing at time scales typical of astrophysical environments. To estimate the activation energy for the samples analysed we used an empirical approach (Brucato et al., 1999; Fabian et al., 2000). The time, t_{hop} that the atoms spend at the temperature, T, to reach long-range order, overcoming the energy barrier for diffusion, can be defined as:

$$t_{\text{hop}} = \nu^{-1} \exp\left(\frac{E_a}{KT}\right),$$

where ν is a characteristic vibrational frequency, and E_a is the activation energy of the amorphous–crystalline transition. The activation energies derived in laboratory are summarised in Table I and compared with those obtained by other authors. These experimental results show that high energy barriers have to be overcame by the atoms of amorphous silicates to reach a more favourable and ordered configuration. The activation energy is, in fact, the parameter that indicates how quick is the crystallisation process once the temperature of the dust is fixed. However, different amorphous configurations, showing the same infrared spectrum, or amorphous structures with metastable energy levels, resulting from very different amorphising effects, could require different activation energies from which, for example, lower crystallisation temperatures could be obtained.

3. Ion Irradiation

Ion irradiation is considered one of the main mechanisms to process material in space (Strazzulla et al., 2000; Baratta et al., 2000; Strazzulla et al., 2002). In this

TABLE I

Activation energy E_a/K (Kelvin)

Compositions	Hallenbeck et al. (1998)	Brucato et al. (1999)	Fabian et al. (2000)	Brucato et al. (2002)
Mg-rich pyroxene	47,500	42,040		
Mg-rich olivine	45,500		39,100	40,400
Fe-rich olivine				26,300
SiO_2			49,000	
$2MgO:SiO_2$				45,800
$1.6MgO:SiO_2:0.5Fe_2O_3$				$\leq$49,700

work, ion irradiation of synthesised thin films of crystalline forsterite was performed by using ions accelerated by a Danphysik (1080–30) ion implanter. Ions are accelerated by 30 kV potential and mean kinetic energies of 30 keV and 60 keV are obtained for single and double ionised ions, respectively. Once extracted, the ions travel through a mass separator where defined m/q are selected by a magnetic field. An electrostatic scanning system is used to deflect the ion trajectories. This irradiates the sample uniformly with a short residence time, avoiding undesirable annealing of the sample. The target assembly is designed for *in situ* spectroscopy. For further details on the experimental apparatus see Strazzulla et al. (2001). Experiments of ion irradiation of thin films of crystalline forsterite samples irradiated with 30 keV H^+, He^+, C^+ and with 60 keV Ar^{++} with ion fluences up to 10^{17} cm^{-2} were performed by Brucato et al. (2004). Light (hydrogen and helium) and heavy (carbon and argon) ions were chosen to study how different classes of ions affect the silicate structure.

The thin films were characterised by Fourier transform infrared spectroscopy (Bruker Equinox 55) in the mid-infrared with resolution of 4 cm^{-1}. Spectra were acquired after laser deposition and thermal annealing and *in situ* during ion irradiation of samples, in order to monitor the chemical and physical evolution of the silicate.

Infrared spectra of forsterite irradiated with 30 keV He^+ at different fluences are shown in Figure 1. With increasing ion fluence, a progressive decrease of the intensities of the crystalline peaks is observed and a large and smooth band around 10 μm, typical of the amorphous silicates, appears in the spectra. The irradiation experiment was extended up to the fluence for which further ion irradiation does not produce any observable variations in the peak intensities. However, residue crystalline peaks are yet observed in the infrared spectrum of the sample irradiated at the highest fluence (Figure 1). This means that the samples, at the end of the process, contain a residual fraction of crystalline forsterite. The possible explanation is that a complete amorphisation did not take place during ion irradiation due

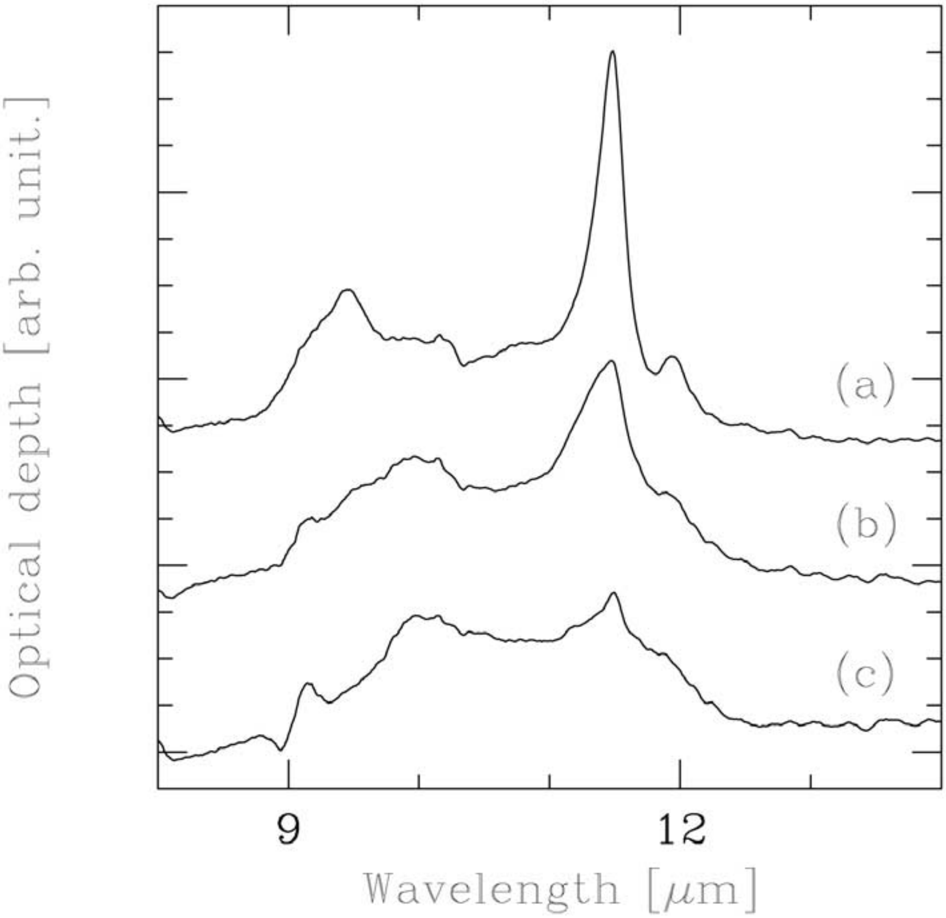

Figure 1. Infrared optical depth spectra of a forsterite thin film before (a) and after irradiation with 4.9×10^{15} (b), and 1.04×10^{17} (c) 30 keV He^+/cm^2.

to a greater thickness of the target with respect to the ions penetration depth. Brucato et al. (2004) demonstrated that the amorphysation process of Mg-pure olivine (forsterite) depends on the energy deposited by the projectile ions through elastic interaction with the target atoms, while any correlation between the amorphysation process and the energy deposited by excitations and ionisations was not observed. However, ion irradiation is an efficient process active in space which is able to explain the presence of amorphous silicates.

4. Conclusions

The results reported in this paper, show that thermal annealing and ion irradiation are two competitive processes able to modify the structure of the silicates giving useful information to predict the nature of TNOs. The values of the activation temperatures, in fact, have a strong impact on the modeling of the possible evolution of materials in the proto-solar system. Taking into account the activation energies measured in laboratory, high temperatures are required to crystallise the amorphous grains present in the molecular cloud where the Solar System formed. This indicates that mixing processes in the pre-solar nebula could be required. Up to now it is not clear to what extent the proto-solar accretion disk suffered mixing between the warmer inner and the cooler outer regions. Then, different regions of the proto-solar nebula could contain different amounts of thermally processed silicates according to the distance from the Sun. This could be used to predict that a considerable fraction of processed material is present in TNOs. However, the ion irradiation process occurs both before the Solar System formation and during the life time of TNOs in the outer regions of the Solar System, possibly increasing the amorphousness of the silicates.

Here particular interest could have the recently discovered Anomalous Cosmic Ray (ACR) components. It is generally accepted that pick-up ions from the solar wind act as a seed population for anomalous cosmic rays originating at the solar wind termination shock. Significant intensities of the anomalous cosmic ray ions are expected throughout the inner Kuiper belt region beyond the termination shock and out to the heliopause (see Cooper, this volume). Cooper et al. (1998) suggested that such a component would significantly affect mantle formation on Kuiper belt objects.

Further theoretical, laboratory and observational works are necessary also to investigate if surface layers of TNO's objects (from which we receive information) being irradiated by cosmic ions contain less crystalline silicates with respect to those observed in cometary comae mostly coming out from internal layers shielded from external radiation. The competing effects of these two processes, crystallisation and amorphisation, on the surface silicate composition of TNOs may be assessable through future IR spectroscopy (e.g., SIRTF) of these faint, distant cold objects.

Acknowledgements

We are grateful to F. Spinella for the technical support given during the ion irradiation experiments, S. Inarta for the collaboration during the SEM analysis and E. Zona for the technical support. This research has been supported by the MIUR and ASI.

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