

**MORPHOLOGICAL AND CHEMICAL SILICATE EVOLUTION UNDER ION IRRADIATION.**

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**Introduction:** Crystalline silicates are present in dust shell around evolved stars and in the protoplanetary discs around young stars [1, 2] whereas the silicate dust is amorphous in the interstellar medium (ISM) [3]. The absence of crystalline silicates in the ISM could be due to the processing in this environment. In supernovae shock waves, atoms or ions of the gas are accelerated with respect to the dust [4]. The result of this acceleration is an irradiation of the dust which results in an efficient sputtering [5, 6] and amorphization of the dust components as demonstrated by experimental studies [7, 8, 9]. These irradiations can also induce changes in the composition of the silicate dust, but their extents have not yet been evaluated. The morphological changes of the silicate surface under ion irradiation are still unknown. Recent experiments have shown the formation of gas bubbles in irradiated samples which suggest that the surface morphology can be significantly modified by ion irradiation [8]. This topic is important since the chemical reaction of gas species in the ISM occurs on grain surfaces.

The aim of this study was to investigate the chemical and morphological modifications of silicates under low energy ion irradiation. Silicate samples were irradiated and analyzed "in-situ" in an X-ray photoelectron spectroscope (XPS) in order to determine the effect on the chemical composition and bonding configuration of the upper and sub-surface region. The morphological changes were studied using an atomic force microscope (AFM) at the nm-scale.

**Experimental:** The samples used for this study are natural olivine single crystals and thin amorphous films synthesized by electron beam evaporation of olivine and deposition onto an aluminium substrate [9]. All samples have the following composition:  $Mg_{1.8}Fe_{0.2}SiO_4$ . The samples were bombarded by  $He^+$  (1keV, 4keV),  $H^+$  (1keV) and  $Ar^+$  (1keV) ions with fluence rates of  $3.3 \cdot 10^{12}$  to  $12 \cdot 10^{14}$  ions  $cm^{-2} s^{-1}$ . Ion irradiation experiments were performed under vacuum, at room temperature, in-situ in XPS. The chemical surface modifications induced by irradiation were recorded by taking XPS measurements at regular time interval. After the irradiation experiments, the morphological changes of the surface were investigated by AFM.

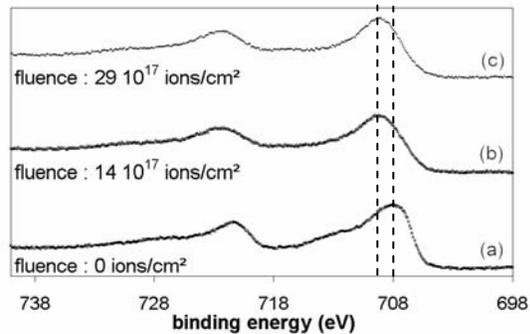
**Results and discussion:** The first effect measured

by XPS after irradiation is a shift of all the peak positions towards lower binding energies. This shift is due to a charging effect, as previously reported [10]. It concerns all elements with the same amplitude, showing that the electron binding energies are not significantly modified by irradiation except for iron (see next paragraph). The peak shape of the magnesium, silicon and oxygen are unchanged confirming that their chemical bonds are not strongly modified and suggesting that the local environment of these elements is not fundamentally disrupted. In order to minimize this charging effect, in some experiments we used a low energy electron gun in order to compensate the charge deposited on the surface by the incident ions but the results are the same. For the thin amorphous films deposited onto aluminium substrates, this charging effect is reduced since the charges can be dissipated via electron transfer into the underlying Al substrate. The charging effect is found to decrease with decreasing film thickness due to ion sputtering.

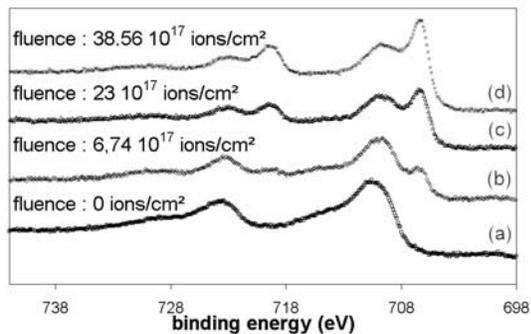
The chemical state of iron is strongly modified by ion irradiation. During  $H^+$  and  $He^+$  irradiations with low fluxes, Fe oxidation has been observed (figure 1). In contrast, iron displays a reduction trend during  $Ar^+$  and  $He^+$  irradiations with high fluxes (figure 2). A comparable Fe reduction phenomenon under irradiation has already been reported by Dukes et al [10]. The reduction is probably due to the breaking of oxygen bonds because of the high energy deposition rate onto the sample at high fluxes. A charge transfer occurs between the free oxygen and iron species, according to the reaction:  $Fe^{2+} + O^{2-} \rightarrow Fe^0 + 1/2O_2$ . At low flux, the charge transfer might occur directly with the incident ions since the chemical bond is not significantly destroyed, according to the reaction:  $Fe^{2+} + He^+ \rightarrow Fe^{3+} + He^0$ . This effect does not appear to be fluence dependent.

Despite changes in chemical bonding have not been evidenced (except Fe), modification of the surface composition has been observed. The surface composition has been calculated by normalization of the elemental peak areas with the Si 2p peak. We observed a progressive increase of magnesium, oxygen and iron as a function of the irradiation fluence. Particularly, the study of the Mg 1s and Mg 2p peaks deserves interest because of the large difference in their kinetic energies which give information about the Mg depth

distribution. The evolution of these two peaks suggests a segregation of Mg in the upper-surface region. This result could be explained by the formation of a positive charge inside the sample due to ion implantation. The corresponding charged layer would repel the positive species toward the surface. Since Mg is probably the most mobile cation in the sample, the polarization leads to its segregation on the surface. This explication makes sense because of the charge effect underlined by the shift of the peak position of the different elements.



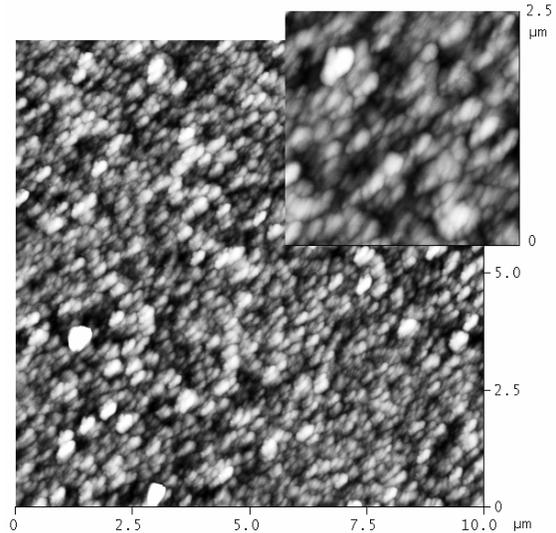
**Figure 1:** XPS spectra of Fe2p region showing an oxidation during a  $\text{He}^+$  (4keV) irradiation with a flux of  $4 \cdot 10^{14} \text{ ions.cm}^{-2}.\text{s}^{-1}$  on olivine. The position and the shape are characteristic of a  $\text{Fe}^{2+}$  state (a), and progressively move to a  $\text{Fe}^{3+}$  signature (b, c) with lower flux irradiation.



**Figure 2:** XPS spectra of Fe2p region showing a reduction during a  $\text{He}^+$  (1keV) irradiation with a flux of  $6 \cdot 10^{14} \text{ ions.cm}^{-2}.\text{s}^{-1}$  on a thin amorphous film. The position and the shape are characteristic of a  $\text{Fe}^{2+}$  state (a). The appearance and the development of a peak in the low binding energy are due to the progressive change to  $\text{Fe}^0$  (b, c, d).

After irradiation and XPS characterization, the samples were studied by AFM, the observations showed different morphological modifications. First the pre-existing defects (such as polishing features) are found to be smoothed. Secondly, a specific morphology develops in flat areas with the formation of hill-

ock-like structures or anisotropic oriented structures (Figure 3). These evolutions are a function of the sample, the nature and the energy of the incident ions.



**Figure 3:** AFM image of the olivine surface after  $\text{He}^+$  (4keV) irradiation.

**Conclusion:** These results confirm that low energy ion irradiation can induce chemical and morphological modification to dust during processing in the ISM. Charge implantation in the sample during irradiation has been demonstrated to induce a charge-driven diffusion process leading to a segregation of cation species onto the surface. The importance of grain surface chemistry and fine scale morphology has already been pointed out since the formation of molecular species occurs on grain surface in the ISM. Irradiation-induced surface modification could influence the nature and kinetics of the catalytic processes. Further experiments are in progress to estimate the surface reactivity of the surface when exposed to a reactive gas.

**Reference:** [1] Waters L. B. et al. (1996) *A&A*, 315, L361-L364. [2] Waelkens C. (1998) *ASS*, 255, 25-33. [3] Kemper F. et al (2004) *ApJ*, 609, 826. [4] Ellison D. C. et al (1997) *ApJ*, 487, 197. [5] Tielens A. G. G. M. et al (1994) *ApJ* 431, 321. [6] Jones A. P. et al (1996) *ApJ*, 469, 740. [7] Demyk K. et al (2001) *A&A*, 368, L38-L41. [8] Carrez P. et al (2002) *M&PS*, 37, 1599. [9] Djouadi Z. et al (2005) *A&A*, 440, L179-L184. [10] Dukes C. A. et al (1999) *JGR*, 104, 1865-1872.