

Proton-Stimulated Redistribution of Fe Atoms in Quartz: Experimental Modeling of the Space Radiation Effect

S. N. Shilobreeva^a, L. L. Kashkarov^a, M. Yu. Barabanenkov^b,
A. N. Pustovit^b, V. I. Zinenko^b, and Yu. A. Agafonov^b

Presented by Academician E.M. Galimov, February 21, 2006

Received February 21, 2006

DOI: 10.1134/S1028334X06090297

Space objects (interstellar and interplanetary dust; surfaces of asteroids, meteorites, and the Moon; and others) are affected by various kinds of radiation, e.g., flows of accelerated protons, ions of helium and heavier elements, and others. The radiation impact may induce structural and chemical modifications of the surface of objects (“space weathering”), in particular, the alteration of their optic reflectance. Modification of olivine, enstatite, and diopside crystals under radiation effects that simulate certain types of space radiation was studied, for example, in [1–3].

As is known, both amorphous and crystalline silicates are important constituents of many space objects. The simplest silicate phase, such as quartz and/or more complex SiO₂-bearing phases, is rather abundant. For example, SiO₂-bearing chondrules are identified in ordinary chondrites. These phases contain up to 1 wt % Fe [4]. Quartz was detected in enstatite [5] and iron meteorites [6]. Furthermore, modeling of the mineral composition of interstellar dust has shown that quartz can occur therein along with olivine, native iron, and periclase [7]. Silica polymorphs (cristobalite, tridymite, and quartz) are known on the Moon [7].

In this communication, we report the results of the first study of radiation-stimulated redistribution of implanted Fe atoms in quartz, which was subsequently irradiated by accelerated protons at temperatures simulating outer space conditions.

The experiment was performed on samples of amorphous quartz glass with microcrystalline silica inclusions detected by IR spectroscopy. ⁵⁴Fe⁺ ions were

implanted into all these samples at room temperature (23°C) on an Extron/Varian ion accelerator (dose $5.2 \cdot 10^{13}$ Fe⁺/cm², energy 85 keV, and current density ~ 0.5 μA/cm²). The samples were divided into pairs. Each pair (except one control pair) was subjected to proton irradiation (10^{16} or 10^{17} H⁺/cm², energy 40 keV, and current density ~ 10 μA/cm²) at different temperatures: 100 K, room temperature ($T_i = 23^\circ\text{C}$), and elevated temperature ($T_i = 300^\circ\text{C}$). One sample of each pair was annealed at 900°C for 72 h in air atmosphere.

Distribution of Fe atoms with depth in quartz samples was established with secondary ion mass spectroscopy (SIMS). The results are shown in Figs. 1–4.

DISCUSSION

Following [9], the intensity of the SIMS signal, which corresponds to Fe⁺ ions, was normalized to the intensity of the signal of Si ions, whose concentration in quartz is known. The area beneath the normalized Fe spectra (0.5 ± 0.1 nm⁻²) is consistent with an implantation dose of 0.52 Fe⁺/nm². The consistence of the implantation dose and the area beneath SIMS spectra allows us to conclude that Fe atoms were not lost due to desorption from the sample surface. Fe atoms either diffuse within the quartz body or interact at the sample surface to make up a compositionally modified surface layer. Fe atoms lose their mobility in the course of chemical interaction. The thickness of such a modified layer is shown in the figures by vertical arrows. While considering the redistribution of Fe atoms (Figs. 1–4), it is necessary to keep in mind the occurrence of randomly arranged microcrystalline inclusions within quartz samples. These inclusions can serve as centers of Fe atom entrapment, i.e., spatially distributed drainage. The drained Fe atoms are excluded from the diffusion process. It is evident that if the spatially distributed drainage is sufficiently thick, the concentration profiles of Fe atoms will markedly differ from diffusion profiles

^a Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, ul. Kosygina 19, Moscow, 119991 Russia

^b Institute of Microelectronic Technology and Ultrahigh-Purity Materials, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia

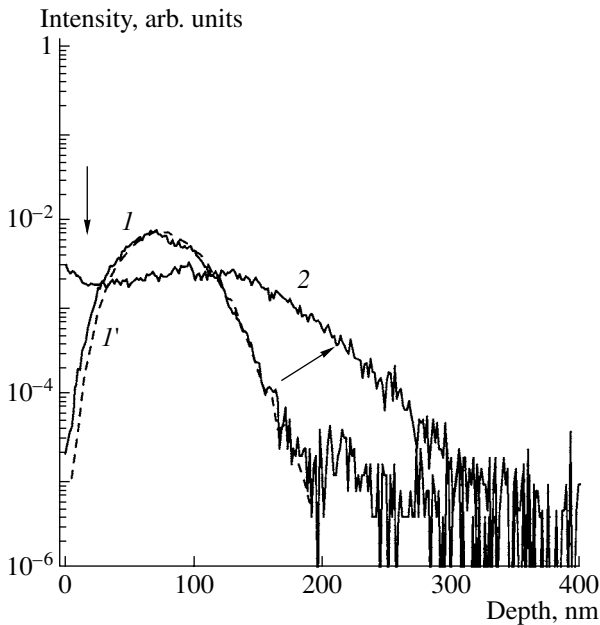


Fig. 1. SIMS concentration profiles of Fe atoms before (curve 1) and after (curve 2) annealing of quartz samples irradiated by Fe⁺ ions (dose $5.2 \cdot 10^{13}$ Fe⁺/cm², energy 85 keV, $T_i = 23^\circ\text{C}$). Curve I' is the range of Fe⁺ ion path calculated with the SRIM software. The vertical arrow shows a surface layer ~15 nm thick.

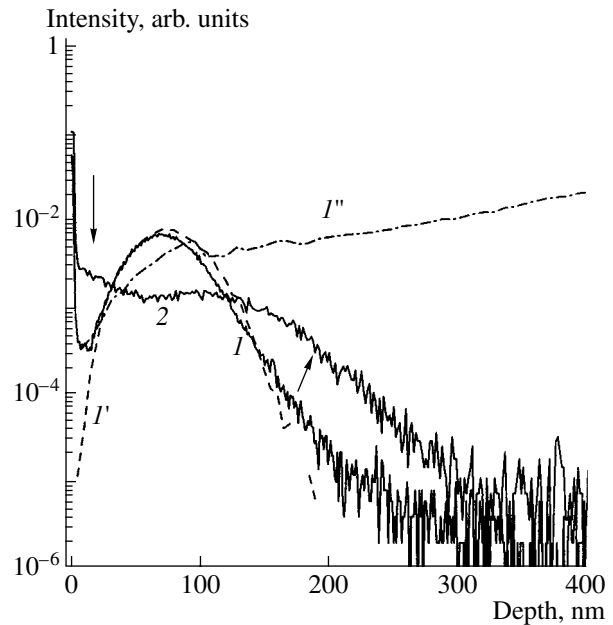


Fig. 2. SIMS concentration profiles of Fe atoms in quartz samples consecutively irradiated by Fe⁺ ions ($5.2 \cdot 10^{13}$ Fe⁺/cm², 85 keV, $T_i = 23^\circ\text{C}$) and protons (10^{16} H⁺/cm², 40 keV, $T_i = 100$ K). Curve 1 corresponds to the sample heated to room temperature after proton irradiation. Curve 2 was recorded after annealing. Curve I'' is the SRIM software-based distribution of oxygen vacancies (in quartz) generated during the braking of protons. The vertical arrow shows the surface layer ~15 nm thick. The inclined arrow indicates the change in the concentration profile of Fe atoms during annealing.

in a homogeneous medium. The physical concept and mathematical description of the “diffusion–drainage processes” are given, for example, in [10].

Figure 1 illustrates the distribution of the range of accelerated Fe⁺ ions (curve 1) and redistribution of the concentration of Fe atoms after the annealing of the control quartz samples. As can be seen, the range distribution may be adequately calculated with SRIM software [11]. In the course of annealing, the atoms partially drain to the sample surface and partially diffuse into the sample. It is noteworthy that curve 2 (Fig. 1) extends above curve 1 into a zone deeper than 150 nm. Such redistribution is typical of the diffusion–drainage process, when atoms of the diffusant are captured by drainage channels, dispersed on their surface, and excluded from the diffusion process.

Chemosorption of iron with formation of a modified phase occurs at the surface of the control sample (Fig. 1, curve 2). Before annealing, the concentration of Fe atoms in the modified surface layer is virtually independent of temperature during proton irradiation (Figs. 1–4) and amounts to ~20% of the implanted dose of Fe ions. After annealing, the concentration changes drastically depending on temperature during proton irradiation. In other words, the proton irradiation creates a cryptic state of the quartz atomic system that is developed during subsequent annealing as a transformation of the concentration profile of Fe atoms. For example, approximately one-half (54%) of previously implanted Fe is concentrated in the surface layer owing to anneal-

ing of the samples after proton irradiation at 100 K (Fig. 2, curves 1 and 2). It should be noted that the radiation-stimulated diffusion due to proton irradiation provides the segregation of only 20% Fe atoms at the surface (Fig. 2, spectrum 1). The shape of curve 2 (Fig. 2) at a depth of >150 nm may be treated as the segregation of Fe atoms on some centers, which can be represented by either quartz-hosted oxygen vacancies [11] generated by accelerated protons (Fig. 2, curve I'') or the aforementioned crystalline inclusions. Furthermore, intensification of proton irradiation of “frozen” samples leads to the complete inhibition of drainage of Fe atoms at the sample surface and intensification of radiation-stimulated migration of atoms inside the sample (this effect is not shown in the figures).

Figure 3 demonstrates redistribution of Fe atoms in quartz subjected to proton irradiation at room temperature. As a result of radiation-stimulated diffusion, the surface layer (shown by a vertical arrow) contains 20% of the implanted Fe atoms (Fig. 3, curve 1). This fraction increases to 48% after annealing. Note that even a greater amount (52%) of Fe atoms accumulates in the surface zone if the dose of protons is increased by an order of magnitude, but the sample is not annealed.

One more substantial observation should be noted. The mode of spectrum 1 transformation into spectrum 2 (Fig. 3) due to annealing principally differs from other

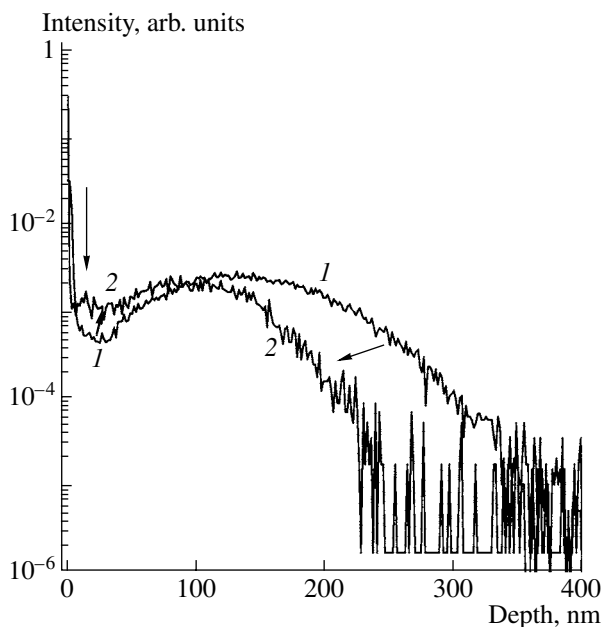


Fig. 3. SIMS concentration profiles of Fe atoms in quartz samples consecutively irradiated by Fe^+ ions ($5.2 \cdot 10^{13} \text{ Fe}^+/\text{cm}^2$, 85 keV, $T_i = 23^\circ\text{C}$) and protons ($10^{16} \text{ H}^+/\text{cm}^2$, 40 keV, $T_i = 23^\circ\text{C}$). Curves 1 and 2 were recorded before and after annealing, respectively. The vertical arrow shows the surface layer ~ 15 nm thick. The inclined arrow indicates the change in the concentration profile of Fe atoms during annealing.

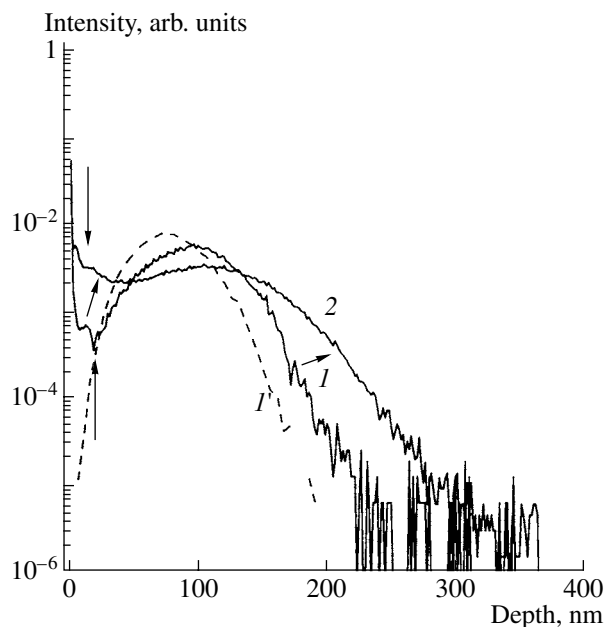


Fig. 4. SIMS concentration profiles of Fe atoms in quartz samples consecutively irradiated by Fe^+ ions ($5.2 \cdot 10^{13} \text{ Fe}^+/\text{cm}^2$, 85 keV, $T_i = 23^\circ\text{C}$) and protons ($10^{16} \text{ H}^+/\text{cm}^2$, 40 keV, $T_i = 300^\circ\text{C}$). Curve 1 corresponds to the sample cooled to room temperature after proton irradiation; curve 2 was recorded after annealing. Vertical arrows mark the surface layer ~ 15 nm thick (before annealing) and ~ 25 nm thick (after annealing). The inclined arrow indicates the change in the concentration profile of Fe atoms during annealing.

changes of the spectrum considered above. Fe atoms migrate toward the surface over the entire irradiated region of the sample as shown by two inclined arrows in Fig. 3. Thereby, in a depth interval from 15 (vertical arrow in Fig. 3) to 40 nm, the concentration of Fe atoms remains approximately constant (curve 2) and is greater than the concentration before annealing (curve 1 is located higher than curve 2 in Fig. 3). The presence of a saturation zone near the abrupt surficial concentration of Fe atoms may be interpreted in the following way. Fe atoms readily drain to the surface during annealing. However, the chemical composition of the surface layer is modified in a kinetic regime; i.e., the rate of the process is constrained by the duration of a certain solid-phase chemical reaction rather than the diffusion supply of the reagent.

Despite the apparent similarity, the transformation mode of concentration spectra of Fe atoms during the annealing of quartz samples subjected to proton irradiation at 300°C (Fig. 4) markedly differs from the scenario of quartz irradiation at room temperature (Fig. 3). Three differences may be pointed out. First, at a depth of >150 nm, Fe atoms migrate during annealing in opposite directions (inclined arrows in Figs. 3, 4). Second, the modified surface layer thickens from 15 to 25 nm (two opposite vertical arrows in Fig. 4). However, despite almost twofold thickening of the modified layer, the concentration of Fe atoms increases insignif-

icantly (from 12% before annealing to 13% after annealing). Hence, the surface layer loosens. Third, the surface zone of the sample subjected to a higher dose of proton irradiation ($10^{17} \text{ H}^+/\text{cm}^2$) is similar in thickness to such a zone in the sample subjected to a dose of irradiation an order of magnitude less and subsequent annealing.

Finally, comparison of concentration profiles of Fe atoms in the samples affected by the same dose of irradiation at different temperatures (Figs. 2, 4, curves 2 for $T_i = 100 \text{ K}$ and 300°C , respectively) shows that the low temperature characteristic of space conditions provides more efficient migration of Fe atoms to the quartz surface.

CONCLUSIONS

This communication presents the first experimental data on the induced migration of Fe atoms in quartz with random inhomogeneities initiated by irradiation-thermal impact. The nonmonotonic distribution of Fe concentrations was created by implantation of Fe ions into quartz. The migration-stimulating radiation impact was provided by irradiation with accelerated protons at a temperature range of 100 K to 300°C . The thermal diffusion in quartz occurred during annealing at 900°C in air. The efficiency of redistribution of Fe atoms between surface and volumetric (microcrystalline

inclusions) drains depends on the temperature of quartz and the intensity of radiation impact. The radiation-stimulated migration of Fe atoms is more efficient at a lower (100 K) temperature. The observed redistribution of Fe atoms in quartz is interpreted in terms of the diffusion–drainage solution of the problem. The data obtained may serve as a basis for development of a kinetic model of physicochemical processes in surface zones of some space objects.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 04-05-64930.

REFERENCES

1. P. Carrez, K. Demyk, P. Cordier, et al., *Meteorit. Planet. Sci.* **37**, 1599 (2002).
2. F. Guyot, H. Leroux, P. Carrez, et al., *Geochim. Cosmochim. Acta* **66** (15a), A300 (2002).
3. S. N. Shilobreeva and L. B. Kuz'min, *Astronom. Vestn.* **38** (1), 1 (2004).
4. A. J. Bradley and R. H. Jones, in *Planetary Materials* (Washington, 1998), pp. 3–37.
5. B. M. Kupletskii, *Meteoritika*, No. 1, 55 (1941).
6. V. D. Kolomenskii, *Mineralogy of Meteorites* (Ural. Nauchn. Tsentr Ross. Akad. Nauk, Sverdlovsk, 1987) [in Russian].
7. H.-P. Gail and E. Sedlmayr, *Astron. Astrophys.* **347**, 594 (1999).
8. J. W. Frondel, *Lunar Mineralogy* (Wiley, New York, 1975; Mir, Moscow, 1978).
9. K.-M. Wang, B.-R. Shi, H.-Y. Guo, et al., *J. Appl. Phys.* **68**, 3191 (1990).
10. B. Ya. Lyubov, *Diffusion in Heterogeneous Solids* (Nauka, Moscow, 1981) [in Russian].
11. J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Range of Ions in Solids* (Pergamon Press, New York, 1985).
12. H. Hosono, *J. Non-Cryst. Solids* **187**, 457 (1995).