Alteration of glasses: Isotope tracing using ^{29}Si and ^{18}O

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The Commissariat à l'Energie Atomique (CEA) has developed a vitrification process in order to store radioactive wastes the result of which is a borosilicate glass; the french R7T7 nuclear waste glass. Storage of this glass in a geological respository requires an understanding of corrosion mechanisms in an aqueous medium.

In contact with water, the surface of R7T7 nuclear waste glass develops a leached layer, which preferentially traps network forming cations and some radionucleides. Understanding the alteration process requires a study of how the leached layer forms. In order to model the mechanisms (hydrolysis, precipitation, condensation,..) responsable for the formation of the leached layer (Vernaz and Dussossoy, 1992), we performed leaching experiments using a solution highly enriched in ^{29}Si and ^{18}O. Such isotopic tracing was aimed at: i) understand reactions involving silicon-oxygen bonds in the leached layer; ii) following the real exchange

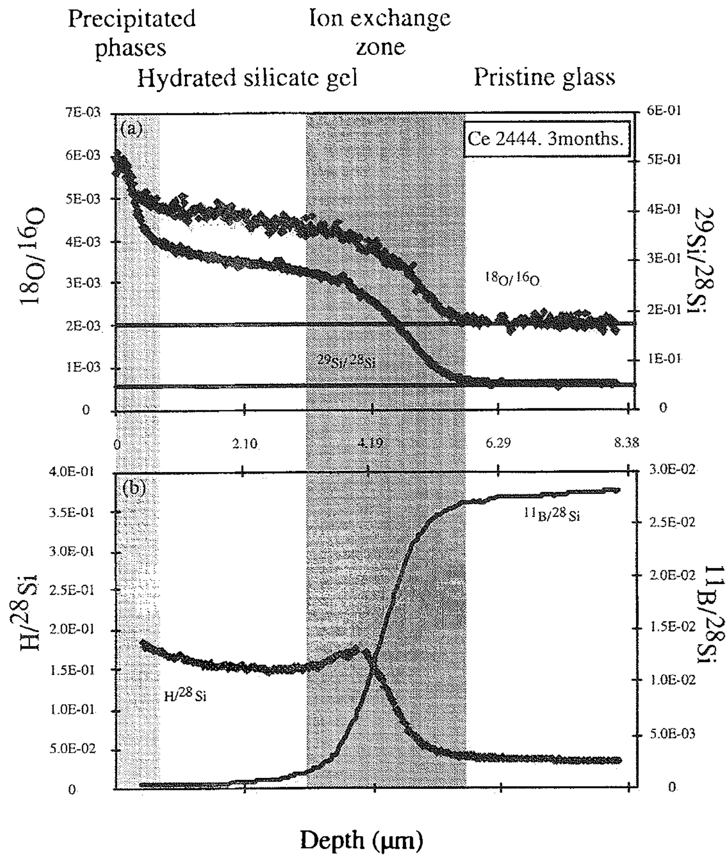

FIG. 1. SIMS depth profiles showing for a glass altered over 3 months: (a) the $^{29}Si/^{28}Si$ and $^{18}O/^{16}O$ isotopic ratios, for which the horizontal line on the diagram represents the value of $^{29}Si/^{28}Si$ and $^{18}O/^{16}O$ in the pristine glass (respectively 5.10^{-2} and 2.10^{-3}): (b) the $H/^{28}Si$ and $^{11}B/^{28}Si$ ratios.

between solution and glass during alteration processes.

Experimental

Glass samples were altered with water enriched in ^{29}Si and ^{18}O under dynamic conditions. The isotopes of silicon and oxygen were chosen because they are the main constituants of unaltered glass and the leached layer. The $^{29}Si/^{28}Si$ and the $^{18}O/^{16}O$ ratios of the solution were respectively 1.13 and 1.10^{-2}. These values are higher than those of pristine glass which has a natural ratio of $^{29}Si/^{28}Si = 5.10^{-2}$ and $^{18}O/^{16}O = 2.10^{-3}$. The solution flow rate used was 12 ml/day and the experiments were conducted at 90°C and a pH of 8. Although this experiment is scheduled to last 2 years, we present here the results concerning the first 6 months of study. Aliquots of leachates were sampled every 2 weeks, and were analysed by ICP-MS and ICP-AES. Glass samples were removed from the solution after 1 week, 2 weeks, 1, 3 and 6 months. Element and isotope variations in the altered glass layer were measured by ion-probe using a depth profiling technique.

Results

Analysis of leachates: Analyses of silicon isotopic ratios were performed on leachate precipitates using the Cameca IMS 3f ion microprobe. The results show a decrease of $^{29}Si/^{28}Si$ in the first 20 days to around 0.47 then, a steady-state is reached. Such a decrease is proportional to the square root of the time. Using both element and isotopic analyses of leachates, the real exchange between the solution and the glass as alteration proceeds can be evaluated. While element analysis diplays a loss of Si from the glass to the solution, isotopic measurements reveal, in contrast, a gain of ^{29}Si in the glass.

Analysis of altered glasses: Depth profiling techniques using secondary ion mass spectometry (Schweda *et al.*, 1997) has been used to measure the $^{29}Si/^{28}Si$ and $^{18}O/^{16}O$ atomic concentration ratios in the altered glasses. SIMS profiles, obtained for R7T7 glass altered for 3 months, are shown in fig.1.a where both silicon and oxygen isotopic ratios are plotted against depth. It should be noted that all glass studied present similar alteration profiles. For both isotopic systems, the highest values of the ratio are observed at the surface of the leached glass. From rim to core of the glass, each profile shows a decrease in $^{29}Si/^{28}Si$ and $^{18}O/^{16}O$ ratios, with a sigmoïdal shape, which approach values representative of the pristine glass. These results suggest a transport of ^{29}Si and ^{18}O from the solution into the altered glass and similar behaviour for the two isotopes.

For the same glass, hydrogen and boron exhibit a contrasting behaviour clearly defining an ion exchange zone (Fig. 1b). Na and Li profiles are not presented here, but are similar to boron profiles. Therefore, three main zones can be observed in these altered glasses: an ion exchange zone in contact with the pristine glass; a hydrous silicate gel; a precipitated phase at the surface (smectite like precipitates).

Profiles, recorded at different time of alteration show an increase of the depth of the altered layer as time increases; a thickness of 6 μm was measured after 3 months of alteration.

Conclusion

This preliminary study shows that SIMS has been successfully applied for the determination of the isotopic ratios in leachates and the characterization of altered glasses. We will show that these results provide important insights into glass alteration mechanisms and exchange rates between solution and glass.

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References

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