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5. A 25-year-old study clearly shows that the metamictization of zircon is due to α recoils and not to α particles [P. Pellas, *Bull. Soc. Fr. Mineral. Cristallogr.* **77**, 447 (1954)]. In addition, the direct visualization of etched α-recoil tracks in mica [W. H. Huang and P. M. Walker, *Science* **155**, 1103 (1967)], which is known to be similar to glass with respect to the registration of tracks due to energetic ions, strongly suggests that α-recoil tracks could be formed in glass.
6. E. Dartyge, J. P. Duraud, Y. Langevin, M. Maurette, *Geochim. Cosmochim. Acta* **9** (Suppl.), 2375 (1978).
7. Our work suggests further clues about these complex processes. In particular, if α-recoil "tracks" are indeed registered in glass, the thermal annealing of such tracks could trigger the formation of tiny crystallites, which would grow upon heating in accelerating glass devitrification. The formation of such track crystallites in dielectric minerals has been discussed elsewhere [J. C. Dran, J. P. Duraud, M. Maurette, L. Durrieu, C. Jouvet, C. Legressus, *Geochim. Cosmochim. Acta* **3** (Suppl.), 2883 (1972)].
8. An extensive fracturing of the storage glass probably results from the cold-water showering of their host metallic containers, which is intended for decontamination purposes. We have evaluated an upper limit for the contribution of this effect by dropping into cold water a hot (500°C) chunk of glass loaded with a 0.5 percent (by weight) uranium. The use of a scanning electron microscope to both measure the size distribution of the residual fragments and evaluate their degree of residual fracturating yields the value of 0.20 m^2 g^{-1}.

9. We thank Dr. R. Klapisch, G. Goutière, and J. Chaumont for their active interest. Supported by the Commissariat à l'Energie Atomique.

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A New Irradiation Effect and Its Implications for the Disposal of High-Level Radioactive Waste

Abstract. *Materials containing alkali metals or alkaline earths are sensitized by bombardment with either ions, electrons, or photons to chemical attack by atmospheric moisture. The implications of this effect on the proposed immobilization and long-term storage of high-level nuclear waste in glass or similar materials is discussed.*

Recent observations in this laboratory have led to the recognition of a new mechanism, through which a large range of materials containing alkali metals or alkaline earths can be rendered susceptible to chemical attack and breakdown by atmospheric moisture. As reported in (*1*, *2*), this degradation process can be induced by particle bombardment or by irradiation with energetic photons, and the effect has been shown to occur both in ionic crystals and in glasses. Although the breakdown mechanism was discovered in the course of experiments quite unrelated to the problem of nuclear waste disposal, the fact that it is effective in vitreous as well as in crystalline materials has obvious implications for the current proposal to incorporate high-level radioactive waste in massive glass blocks for permanent storage. It is the purpose of this report to draw attention to these implications and to point out the need for further investigation before this disposal technique is adopted.

The various chemical reactions in the breakdown process will occur only if they are promoted at catalytically active centers on the surface of the material. These centers are activated by the irradiation at sites of suitable structural irregularity, such as may occasionally be produced by incidental mechanical surface damage. In crystalline materials the sites are primarily associated with crystallographic ledges (*1*), whereas in vitreous substances they are usually found at the boundary between separated phase particles and the main matrix of the glass (*2*). To achieve activation, the sites must receive a minimum irradiation dose *D*, enabling them to act as locations for electron transfer, so that a cation M^+, which diffuses from its normal position in the solid to an active center, can there be neutralized to an atom M.

I shall illustrate the degradation mechanism by discussing the breakdown of a simple sodium silicate glass. As a first step, let us consider Na^+ associated with a nonbridging terminal structure of the well-known type $[\text{-Si-O-Si-O}^-Na^+]$ within the silica network. Even at room temperature Na^+ is fairly readily detached by the application of heat, although detachment can also be effected by irradiation, which may thus act in a second role, additional to its function in the activation of catalytic centers.

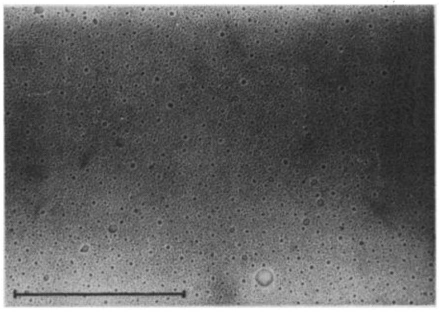

Fig. 1. Corrosion sites on crown glass (Schott type B 270). The photograph was taken 24 hours after exposure to laboratory air, following bombardment by 1.6-keV Ar ions. The bombardment intensity was 2.5 × 10^{14} ions per square centimeter per second; the total ion dose was 1.5 × 10^{17} ions per square centimeter. Scale bar, 100 μm.

After electron transfer at an active site, to which the ion has diffused, the now neutral Na atom will react with atmospheric moisture according to the reaction

$$\mathrm{Na} + \mathrm{H_2O} \rightarrow \mathrm{NaOH} + \mathrm{H}\uparrow \qquad (1)$$

yielding H_2 as a gaseous reaction product. The terminal structure, now truncated by removal of the Na^+, acts effectively as a cation that dissociates another H_2O molecule in the reaction

$$[\text{-Si-O-Si-O}^-] + \mathrm{H_2O} \rightarrow [\text{-Si-O-Si-OH}] + \mathrm{OH}^- \qquad (2)$$

At a suitable surface site the OH^- radical formed in this way is able to break a siloxane bond in the continuous network of the glass, a reaction represented by

$$[\text{-Si-O-Si-}] + \mathrm{OH}^- \rightarrow [\text{-Si-OH}] + [\text{-Si-O}^-] \qquad (3)$$

The $[\text{-Si-O}^-]$ thus produced now reacts with another H_2O molecule in the manner of Eq. 2, so that a cyclically repeated corrosion reaction is set into motion.

A similar process takes place with alkali metals other than Na and, with a slight modification, also with the alkaline earths. Apart from the evolution of H_2, the overall result is the formation of products that are not only water soluble but also readily detachable from the bulk of the glass. This is clearly undesirable; particularly since, when we are dealing with a waste storage glass, among the major constituents of these soluble degradation products will be substances such as ^{137}Cs and ^{90}Sr, whose immobilization the glass is intended to ensure and which contribute a large portion of the total radioactivity within the waste during the first 100 years or so of its storage (*3*).

To illustrate the degradation effect, Fig. 1 shows the accumulation of corrosion sites on the surface of a crown glass (Schott type B 270). As discussed in (*2*), the decomposition occurs preferentially at the location of minority phase particles, and since in the multiconstituent glasses now under investigation for waste storage, phase separation is very pronounced (*4*-*9*), the irradiated glass surface is likely to be rich in areas susceptible to attack. One important class of phases known to exist in these materials is the molybdates, arising from the reaction of the fission product Mo with the alkali isotopes present. Molybdates appear in the form of crystalline particles, ranging in size up to about 100 μm (*9*), and the crystallites act as hosts for ^{137}Cs and ^{90}Sr, which tend to concentrate there and are liable to be released when the molybdates are attacked. In the case of $CaMoO_4$, the breakdown by this irradiation effect has already been observed in this laboratory (*1*). Corrosion spots of the type shown in Fig. 1 are easily removed by immersion in water. The degradation of the glass should therefore in the first instance manifest itself as an irradiation-enhanced leach rate, particularly of the alkali metals and alkaline earths, as distinct from other nonalkali constituents. Among the tests usually applied to evaluate the performance of proposed nuclear waste glasses, there is usually a determination of the leach rate (*5, 7–9*), and the question arises of why this accelerated leaching of the alkali metals does not appear to have been noticed in earlier investigations.

Table 1. Summary of leach tests.

Source	n (Ci/cm^3)	t (days)	Temperature	Remarks
Hall *et al.* (*5*)	1.7	353	100°C	Glass stored for 1 year before leach test
Merritt (*7*)	0.1	6000	7°C	Leach test extends over 15 years
Laude *et al.* (*8*)	0.1	6000	Ambient	Leach test extends over 40 days
Mendel *et al.* (*9*)	100	6	25°C	Glass initially stored for 6 months; leach test extends over 140 days

To explain this, I would note first that in most publications no separate data are given for irradiated and nonirradiated samples, so that the experiments are intrinsically not able to detect a change in the leach rate due to irradiation. Instead, the investigators are content to demonstrate that under their experimental conditions the rate is sufficiently low for effective immobilization of the radioisotopes. The validity of this assessment for conditions of actual waste storage is discussed in more detail below.

Secondly, it must be remembered that, for breakdown to occur by the mechanism I propose, the glass surface must receive a minimum irradiation dose D. The unfortunately very scant information we have obtained so far on the numerical value of D relates to irradiation with Ar ions of energy about 2 keV, and it shows the minimum D to vary significantly with the composition of the material, ranging from a low of 10^{14} ions per square centimeter for a particularly susceptible soda lime glass to well in excess of 10^{18} ion/cm^2 for some borosilicate glasses. In the absence of more reliable data, let us adopt 10^{16} ion/cm^2 as a representative value and assume that this value also applies to irradiation by the alpha particles from ^{238}Pu, ^{241}Am, or ^{244}Cm isotopes with which test glasses are usually doped to simulate the effect of actual nuclear waste. These alpha particles, with a typical energy of 5 MeV, have a range of about 50 μm, so that only particles originating within that distance from the glass surface can contribute to the activation of catalytic surface sites. For simplicity, I shall assume that all particles emitted down to this depth are effective in doing so. Neglecting cascade effects, the time t required to activate a surface site is then given by

$$t \simeq 6 \times 10^{-14} \frac{D}{n} = \frac{600}{n} \text{ days} \qquad (4)$$

where n is the specific activity of the glass in curies per cubic centimeter, and the value of 1×10^{16} ion/cm^2 has been introduced for D.

Table 1 shows the necessary activation times calculated from Eq. 4 for the specific sample activities used in four representative investigations. The total irradiation times are such that delivery of a full activation D can only be assumed to occur with any degree of confidence in the experiments of Mendel *et al.* (*9*). These investigators are also the only ones to furnish data for both irradiated and nonirradiated samples, thus making a comparison possible, and by a fortunate coincidence their leach rates are expressed in terms of the release of an alkali, namely, K. The results show unambiguously a radiation-induced doubling of the leach rate, but, since even this accelerated rate was deemed acceptable, Mendel *et al.* appear to have dismissed the effect as of little practical significance.

This assessment was based on measurements made at 25°C and may well need to be revised for a temperature of several hundred degrees Celsius caused by self-heating in the massive waste glass blocks during the first 100 years of storage (*3*). The degradation process I propose is known to be speeded up significantly by an increase in temperature (*2*), apparently through the associated marked increase in the diffusion rate of the alkali metals in glass. As Majkova and Trnovcova have shown (*10*), the increase in the diffusion rate is so rapid that at the initial storage temperature we would expect the degradation of the material to occur at a rate exceeding that observed at room temperature by four to six orders of magnitude. Because of this, I believe that other leach rate determinations would also lead to a severe underestimate when applied to practical storage conditions. Devitrification, phase separation, and similar indices of waste glass performance are normally measured at high temperature, albeit on nonradioactive samples, but leaching is generally investigated by immersing the sample either at ambient temperature or at a temperature not exceeding the boiling point of water. The mechanism that I propose does not require immersion; it proceeds rapidly with H_2O in the vapor phase, and readily detectable reaction rates are achieved at room temperature with partial pressures of H_2O well below 1 torr. I would therefore expect very severe attack on a glass storage block surface kept at a high temperature and exposed to the atmosphere, even if the relative humidity is low.

From the foregoing, it is apparent that breakdown according to the mechanism I propose is likely to have escaped detection in earlier work (i) because in most cases the time between formation of the radioactive glass and the leach rate determination was too short for a full activation dose to have been delivered and (ii) because the samples were exposed to H_2O at temperatures much lower than expected under actual conditions of waste storage and thus too low to reveal the full magnitude of the effect.

At this stage, we have very few data on D and we lack knowledge of the factors that control D and the rate constant of the breakdown reaction sequence. In order to gauge reliably the importance of this degradation mechanism in connection with nuclear waste storage and to minimize its effect by suitable formulation of the glass, it will be necessary to understand how these parameters depend on the composition of the material. Here a difficulty arises from the fact that this composition itself will change with time when, through nuclear transformation, ^{137}Cs and ^{90}Sr decay within a few centuries to Ba and Zr, respectively. Composition changes of this kind could be locally magnified since these isotopes tend to concentrate in host phases, which then also become regions of particularly intense self-irradiation. It would seem prudent to investigate these and related problems fully before we embark on the irreversible step of large-scale storage of nuclear waste in vitreous materials.

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Long-Range Atmospheric Transport of Soil Dust from Asia to the Tropical North Pacific: Temporal Variability

Abstract. *The concentration of airborne soil dust at Enewetak Atoll (11°N, 162°E) in April 1979 was 2.3 micrograms per cubic meter but decreased steadily to 0.02 microgram per cubic meter over the next 5 months. The spring dust is probably derived from China; its deposition rate (~ 0.3 millimeter per 1000 years) suggests that it may be a significant contributor to the deep-sea sediments of the North Pacific.*

The areal distribution of certain mineral components such as quartz and illite in the sediments of the North Pacific suggests that wind may be the primary transport mechanism for these materials from the continents. The greatest concentrations of these minerals are found in Pacific sediments at mid-latitudes (30°N to 40°N) beneath the prevailing westerly winds. A continental origin for the quartz fraction of both North Pacific sediments and Hawaiian soils is also inferred from oxygen isotope studies (*1*). The source for this eolian (wind-borne) material has been assumed to be the arid regions of central and eastern Asia—the Takla Makan, Gobi, and Ordos deserts and the regions where loess is deposited south of the Gobi and Ordos deserts.

There are few data on dust in the atmosphere over the North Pacific. High concentrations (up to 60 μg m^{-3}) of dust have been measured over Japan (*2*). This material, generally yellowish, light brown, or red in color, and called Kosa in Japan, is observed most frequently in the spring, when large-scale dust storms occur in northern China and Mongolia. A mean atmospheric dust concentration of 0.16 μg m^{-3} was reported for the equatorial mid-Pacific from filter samples collected aboard the D.V. *Glomar Challenger* in November and December 1973 (*3*). In another ship-sampling program, a mean dust concentration of 2.1 μg m^{-3} was measured in the South China and Philippine seas in April 1975, and a concentration of 1.2 μg m^{-3} was observed in the eastern and central North Pacific between 26°N and 28°N in April and May 1975 (*3*). Rahn *et al.* have concluded that long-range transport of Asian desert dust may contribute to the formation of haze layers commonly found in the North American arctic (*4*).

No earlier study of dust over the Pacific that we know of has extended over a sufficiently long time to permit the determination of the seasonal variability of dust transport and how it might be related to meteorological and climatological factors. We present here the results of a mineral dust investigation that extended over a period of 5 months, from April through August 1979, on Bokandretok Island, Enewetak Atoll, Marshall Islands, as a part of the SEAREX (Sea/Air Exchange) program. This site, at 11°20′N, 162° 20′E, is located in the northeast trade-wind regime and is approximately 5000 km southeast of Asia and 8000 km west-southwest of North America. Samples of atmospheric particulate matter were collected from a tower 20 m high erected on the windward shore of the island. We used double Whatman 41 filters (20 by 25 cm), each of which has a collection efficiency of $\geq$ 90 percent for particles with radii $\geq$ 0.2 μm at the flow rate used. Filters were mounted in plastic holders within a plastic rain shelter. We collected size-separated particle samples by using a Sierra high-volume cascade impactor operating at ~ 68 m^{-3} hour^{-1}. Particles were deposited on Whatman 41 filters mounted on the five stages of the cascade impactor, and then the airstream was passed through a final Whatman 41 filter. Collection was stopped automatically when the surface wind direction was not from the open sea, when the wind speed dropped below 5 knots (9.3 km hour^{-1}), or when the count of condensation nuclei was above 750 particles per cubic centimeter. The sampling duration was generally 1 week for each filter pair or cascade impactor sample.

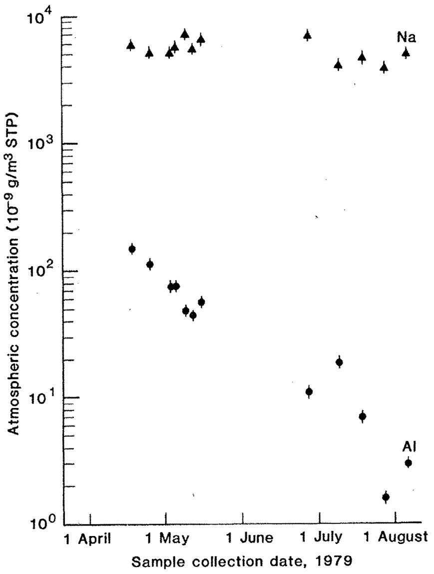

Fig. 1. Atmospheric concentrations of Na and Al at Enewetak Atoll. *STP*, standard temperature and pressure.

The atmospheric concentration of Al was used as an indicator of continental dust in these samples. Atmospheric Al is commonly used as a reference for aerosols produced from soil and crustal weathering processes because of the high aluminosilicate content of these aerosols. Support for the use of Al as a dust indicator in the Enewetak marine aerosol is derived from the Fe/Al, Sc/Al, and Mn/Al ratios in this aerosol, which are very similar to mean crustal ratios. Atmospheric Na at Enewetak is used as a reference for ocean-derived aerosols, which are produced by the bursting of wave-produced bubbles at the sea surface. Samples were analyzed for Al and Na by instrumental neutron activation analysis at the Rhode Island Nuclear Science Center reactor ($\phi_{\text{thermal}} = 4 \times 10^{12}$ neutron cm^{-2} sec^{-1}).

Figure 1 presents the results of the analyses of the atmospheric samples for Na and Al. The atmospheric Na concentration remained quite constant during

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