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Retention of Ion-Implanted-Xenon in Olivine: Dependence on Implantation Dose

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Abstract: The diffusion of Xe in olivine, a major mineral in both meteorites and lunar samples, was studied. Xe ions were implanted at 200 keV into single-crystal synthetic-forsterite targets and the depth profiles were measured by alpha particle backscattering before and after annealing for 1 hour at temperatures up to 1500°C. The fraction of implanted Xe retained following annealing was strongly dependent on the implantation dose. Maximum retention of 100% occurred for an implantion dose of 3×10^{15} Xe ions/cm^2. Retention was less at lower doses, with $\geq 50\%$ loss at 1×10^{14} Xe ions/cm^2. Taking the diffusion coefficient at this dose as a lower limit, the minimum activation energy necessary for Xe retention in a 10 μm layer for 10^7 years was calculated as a function of metamorphic temperature.

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Introduction

The diffusion properties of Xe in meteoritic minerals are important in the interpretation of ^{244}Pu/Xe and ^{129}Xe chronologies of events in the early solar system. In general, these interpretations assume a well-defined "time or temperature of Xe retention", before which Xe is quantitatively lost, and after which Xe is quantitatively retained. An improved understanding of the Xe isotopic data in terms of realistic thermal histories awaits identification of the mineralogical sites of the radiogenic Xe as well as determination of its diffusion coefficients. A number of efforts have attempted to identify the mineralogical sites (e.g., Lewis et al., 1975; Alaerts et al., 1979; Zaikowski, 1980; Rison et al., 1980; Jones and Burnett, 1979). This study deals with the diffusion properties of Xe. We have previously reported measurements of the diffusion of ion-implanted Xe in feldspar (Melcher et al., 1981). We report here new measurements of Xe implanted into olivine.

In our previous studies of feldspar, Xe ions were implanted at 200 keV to doses ranging from 3×10^{14} ions/cm^2 to 10^{17} ions/cm^2. Depth profiles were measured before and after annealing at 900 or 1000°C. The fraction of implanted Xe retained following annealing was strongly dependent on implantation dose. Maximum retention of 100% occurred for an implantation dose of 3×10^{15} ions/cm^2. Retention was less at both lower and higher doses. The Xe retention was unaffected by two-step anneals (750 and 1000°C) or by implanting either Ar or He in addition to the Xe. Helium was implanted to a dose comparable to that expected in a typical solar wind exposure time. Due to the complex dependence of the Xe diffusion on implantation dose, no attempt was made to extrapolate from the laboratory experiments to the much lower concentrations of radiogenic Xe in meteorites or solar-wind-implanted Xe in lunar materials.

Experimental Procedures

The experimental procedure consisted basically of four steps. (i) A target was first implanted with a known dose of Xe ions. (ii) The depth profile of the implanted Xe was analyzed by means of backscattering spectrometry of alpha particles (see Chu et al., 1978). (iii) The target was then annealed, typically for one hour at temperatures up to 1500°C, and (iv) the Xe depth profile was measured again. The basic idea is to observe broadening of the implanted profile due to thermal diffusion. This method has been used previously by a number of workers to study the diffusion of implanted ions primarily in Be, Al, and Si (see, for example, Sippel, 1959; Myers et al., 1974; Fontell et al., 1973; Ohkawa et al., 1974). Our previous study appears to be the only other attempt to apply the backscattering technique to the diffusion of implanted ions in a mineral.

The Xe implantations were performed at an energy of 200 keV with a 400 keV ion accelerator. The beam current density was kept below 3 $\mu A/cm^2$ to avoid heating of the targets. The targets were coupled to the target holder via a thermally conducting grease and remained at room temperature or slightly below during implantation due to radiation to a cooled shield in the target chamber. The pressure in the target chamber was $\leq 10^{-7}$ torr. Values of the bombardment doses were obtained by current integration and are estimated to be accurate within ± 20%. Spatially uniform implantations were obtained by scanning the beam across the target. The bombardment doses ranged from 1×10^{14} to 3×10^{15} ions/cm^2. The xenon concentrations calculated from the backscattering spectra agree with the implantation doses measured by beam integration during implantation within 30%.

The depth profiles of the implanted Xe were determined by Rutherford backscattering of alpha particles. Alpha particles with energies in the range of 1 to 2 MeV are directed at the target and a small fraction of these are scattered elastically by the various nuclides in the taget. Those particles backscattered at some large angle with respect to the incident beam (typically 170°) are detected and counted. The energy of a detected (backscattered) particle is a function of the mass of the nuclide from which is was scattered. Alpha particles which are scattered by heavy nuclei lose a smaller fraction of their incident energy than those particles scattered by light nuclei. The energy of a detected particle is further reduced by the energy it loses in passing through a finite thickness of the target before and after being scattered. Thus, the energy spectrum of backscattered particles can provide information on both the masses of the elements present in a target and their distribution with depth.

A typical backscattering spectrum of an olivine target implanted with Xe is shown in Fig. 1. The major elements present in the target (O, Mg, Si) produce a series of steps. The high energy edge of each step corresponds to alpha particles scattered by atoms of that element located at the surface of the target. Alpha particles scattered by atoms deeper in the target lose additional energy before reaching the detector. The strong increase in counting rate with decreasing energy for a uniformly distributed element, e.g., O in Fig. 1, reflects the increase in the scattering cross section with decreasing energy. The implanted Xe atoms, on the other hand, are not evenly distributed but have a roughly Gaussian depth distribution at a mean depth of ≈ 560 Å. Therefore the Xe signal consists of a Gaussian peak rather than a step.

The incident alpha particle beam (1.0 MeV) was normal to the target surface. The backscattered particles were detected by a silicon surface barrier detector located at 170° with respect to the incident beam. The dose of alpha particles to the target during the analysis is typically 10^{14} -

10^{15} cm^{-2}. The energy resolution of the system is ≤ 20 keV (FWHM), primarily due to the energy resolution of the detector. This corresponds to a depth resolution of ≤ 260 Å (FWHM) for 1.0 MeV alpha particles at normal incidence. The positions of the peaks are reproducible to within ± 40 Å.

The energy scales of the Xe spectra (Figs. 2-5) were converted to depth scales using the surface energy approximation (Chu et al., 1978, Chapter 3).

$$X = \frac{\Delta E}{N}\left[\frac{\epsilon(E_0)K}{\cos\theta_1} + \frac{\epsilon(KE_0)}{\cos\theta_2}\right]^{-1}$$

ΔE is the difference between the energy of an alpha particle which has scattered from a Xe atom at the surface of the target and the energy of one that has scattered from a Xe atom at depth x. N is the atomic density of olivine. K is the ratio of the final to the incident energy when an alpha particle scatters from a Xe atom. $\epsilon(E_0)$ is the stopping cross section for alpha particles of incident energy E_0 in olivine and $\epsilon(KE_0)$ is the stopping cross section for alpha particle of energy KE_o (i.e., after scattering). $\epsilon(E)/N$ is the stopping power, dE/dx, at energy E. θ_1 and θ_2 are the angles between the target normal and the direction of the incident beam and the direction of the scattered particle, respectively. This formula yields a depth conversion scale of 98 eV/Å for 1.0 MeV alpha particles and $\theta_1 = 0^{\circ}$.

After measurement of the implanted depth profiles, targets were annealed at temperatures ranging from 800°C to 500°C. Anneals at ≤ 1000°C were carried out in a vacuum furnace at a pressure of ~ 2×10^{-6} torr. For anneals at ≥ 1100°C, the samples were sealed in Pt capsules and annealed in air.

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All targets were in the form of thick slabs (∼ 2 x 4 x 8mm) which were cut from a single crystal of synthetic forsterite ($Mg_2 SiO_4$). After grinding and polishing, the slabs were annealed for 1 hr. at 1000°C before implantation.

Results

The obvious complication to our technique is the effect of radiation damage produced during implantation, as exemplified by our previous results for implantations into feldspar (Melcher et al., 1981). Consequently our efforts have again focused on studying the effects of varying implantation doses. Targets were implanted with Xe doses ranging from 1×10^{14} to 3×10^{15} ions/cm^2. Table 1 summarizes the implantation doses and annealing temperatures which were investigated.

One sample was implanted with 3×10^{15} Xe ions/cm^2 and annealed for 1 hr. at 800, 900, 1000, and 1100°C. The Xe depth profile was measured after each anneal and was found to be identical to the unannealed profile. At an annealing temperature of 1100°C, the target showed a tendency to acquire Zn contamination from an unknwon source. Consequently, a fresh surface was then prepared for further measurements. However, Zn contamination was encountered to varying degrees in all high temperature (1400 to 1500°) anneals despite the use of two different furnaces and a variety of encapsulation methods. Fig. 2 shows the Xe depth profiles of a second implantation of 3×10^{15} cm^{-2} before and after annealing the target at 1400°C. The target had previously been annealed at 1100, 1200, and 1300°C. There is no loss of Xe and the post-anneal profile is actually somewhat narrower than the pre-anneal profile. This narrowing is apparently due to the use of a higher resolution detector for the post-anneal measurement and probably does not reflect movement of Xe. However, the formation of bubbles could have a similar effect and this phenomenon cannot be totally ruled out. This target was subsequently annealed at 1500°C with no change in the Xe profile.

Targets were implanted with 1×10^{15} and 3×10^{14} Xe ions/cm^2 and also annealed at 800, 900, 1000, and 1100°C for 1 hr. Again no change was observed in the Xe profiles after any of these anneals. Fresh surfaces were prepared after the 1100°C anneals and the targets were reimplanted with the same doses. Figs. 3 and 4 show profiles before and after annealing at 1400°C. In each case, the post-anneal profile shows $\sim$ 10% Xe loss and some movement of Xe toward the surface. Also note the increased Zn background following these high temperature anneals ($\sim$ 100 counts at $\lesssim$ 0.8 MeV).

A final target was implanted with 1×10^{14} Xe ions/cm^2 and annealed at 1400°C. The Xe depth profiles before and after annealing are shown in Fig. 5. Due to the relatively large amount of contamination picked up during the anneal, quantitative analysis of this measurement is difficult. However, there appears to be at least 50% loss of Xe at this implantation dose.

Fig. 6 summarizes the fraction of implanted-Xe retained following a 1400°C anneal as a function of implantation dose. Also shown are some of our earlier data on feldspar (Melcher et al., 1981). Overall, olivine is far more retentive than feldspar. In each case, maximum retention of 100% occurs for an implantation dose of 3×10^{15} Xe ions/cm^2 and retention is less at lower doses. In light of the very different crystal structures of olivine and feldspar, the possibility that this behavior might be common to all silicate minerals must be considered.

Discussion

The strong dependence of Xe retention on implantation dose is similar to that previously observed in feldspar. Diffusion of the implanted Xe may potentially be affected by a number of factors including radiation damage, bubble formation, creation of radiation-damage amorphous layers by the implantation and subsequent recrystallization during annealing, and creation of radiation-damage traps. For a detailed discussion see Melcher et al., (1981). Rather than attempt to fully explain the dose-dependent behavior of the implanted Xe, we will consider here the lowest-dose implantation as a limiting case.

We interpret the data at 1×10^{14} Xe ions/cm^2 to indicate movement of Xe of > 500 Å. This leads to a diffusion coefficient of $D > 7 \times 10^{-15}$ cm^2/sec at 1400°C. If Xe retention does not increase at even lower doses, i.e. if the observed trend does not reverse, then this number may be taken as a lower limit for the diffusion of naturally occurring Xe in olivine. The activation energy Q required for Xe retention may then be calculated as a function of annealing temperature for a given time scale. For retention of Xe in a 10 μm layer over a period of 10^7 years, a diffusion coefficient of $D < 3 \times 10^{-21}$ cm^2/sec is needed. Fig. 7 shows the activation energy necessary to produce this diffusion coefficient as a function of temperature. The curve is calculated from

$$\frac{D}{D_o} = \exp\left[- Q/RT + Q/RT_o\right]$$

where $D = 3 \times 10^{-21}$ cm^2/sec, $D_o = 7 \times 10^{-15}$ cm^2/sec, $T_o = 1673$°K, and $R = .002$ kcal/mole/°K. For combinations of activation energy and metamorphic temperature which fall in the shaded region of the plot, Xe will be lost by thermal diffusion on a time scale of 10^7 years. The unshaded portion of the plot represents values of Q and T for which Xe <u>may</u> be retained. However, a combination of Q and T which falls in the unshaded region does not guarantee Xe retention since the curve which divides the regions is only a lower limit for Q at a given T.

From this plot one sees that at a metamorphic temperature of 800°C, an activation energy of $\gtrsim$ 90 kcal/mole would be needed for Xe retention. Although the activation energy for Xe diffusion in olivine has not been measured and cannot be obtained from the present data, this number may be compared to measured values for Ar diffusion in various minerals. These values are typically in the range 30-60 kcal/mole/°K although a few higher values have been reported (see Hanson, 1971; Everden et al., 1960; Giletti, 1973). Sorption mechanisms between Xe and various substances including carbon chromite, and magnetite have been investigated by Yang et al. (1982) and Yang and Anders (1982a,b). However, it is not clear that the small desorption enthalpies which they measure are related to the diffusion of implanted ions. Consequently a requirement of $Q \gtrsim 90$ kcal/mole/°K for Xe diffusion in olivine is uncomfortably high although perhaps not totally unreasonable. For a more reasonable value of say 50 kcal/mole/°K, our data imply Xe loss for metamorphic temperatures in excess of 500°C for 10^7 years.

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Figure Captions

Fig. 1. Backscattering spectrum of 1.0 MeV alpha particles striking a Xe-implanted olivine target at normal incidence. Stoichiometric elements in the target (O, Mg, Si) result in step-like signals; the high energy edge of each step is indicated corresponding to scattering by an atom of that element on the surface. The implanted Xe distribution results in a Gaussian peak located ~ 45 keV below the energy of alpha particles scattered from Xe atoms at the surface of the target (indicated). The energy distribution of counts in the Xe peak can be directly scaled to a Xe depth distribution.

Fig. 2. Xe energy (depth) profile from backscattering of 1.0 MeV alpha particles at normal incidence. The spectra were taken before and after annealing for 1 hr. at 1400°C. The implantation dose was 3×10^{15} Xe ions/cm^2.

Fig. 3. Xe energy (depth) profile from backscattering of 1.0 MeV alpha particles at normal incidence. The implantation dose was 1×10^{15} ions/cm^2. The increase in background below 0.8 MeV is due to Zn contamination, apparently uniformly distributed over at least 1000 A°. The origin of this contamination and mechanism of incorporation is not known.

Fig. 4. Xe energy (depth) profile from backscattering of 1.0 MeV alpha particles at normal incidence. The implantation dose was 3×10^{14} ions/cm^2.

Fig. 5. Xe energy (depth) profile of a target implanted to 1×10^{14} Xe ions/cm^2. This sample shows a large amount of Zn contamination ($E < 0.8$ MeV) as well as a heavy element impurity ($A \sim 240$) corresponding to an edge at about 0.93 MeV.

Fig. 6. Fraction of implanted Xe retained in olivine and feldspar targets as a function of dose after annealing at 1400°C for olivine and 1000°C for feldspar (Melcher et al., 1981). The 10^{16} ions/cm^2 feldspar target was annealed at 900°C.

Fig. 7. Minimum activation energy required for retention of Xe in olivine for 10^7 years vs. temperature.

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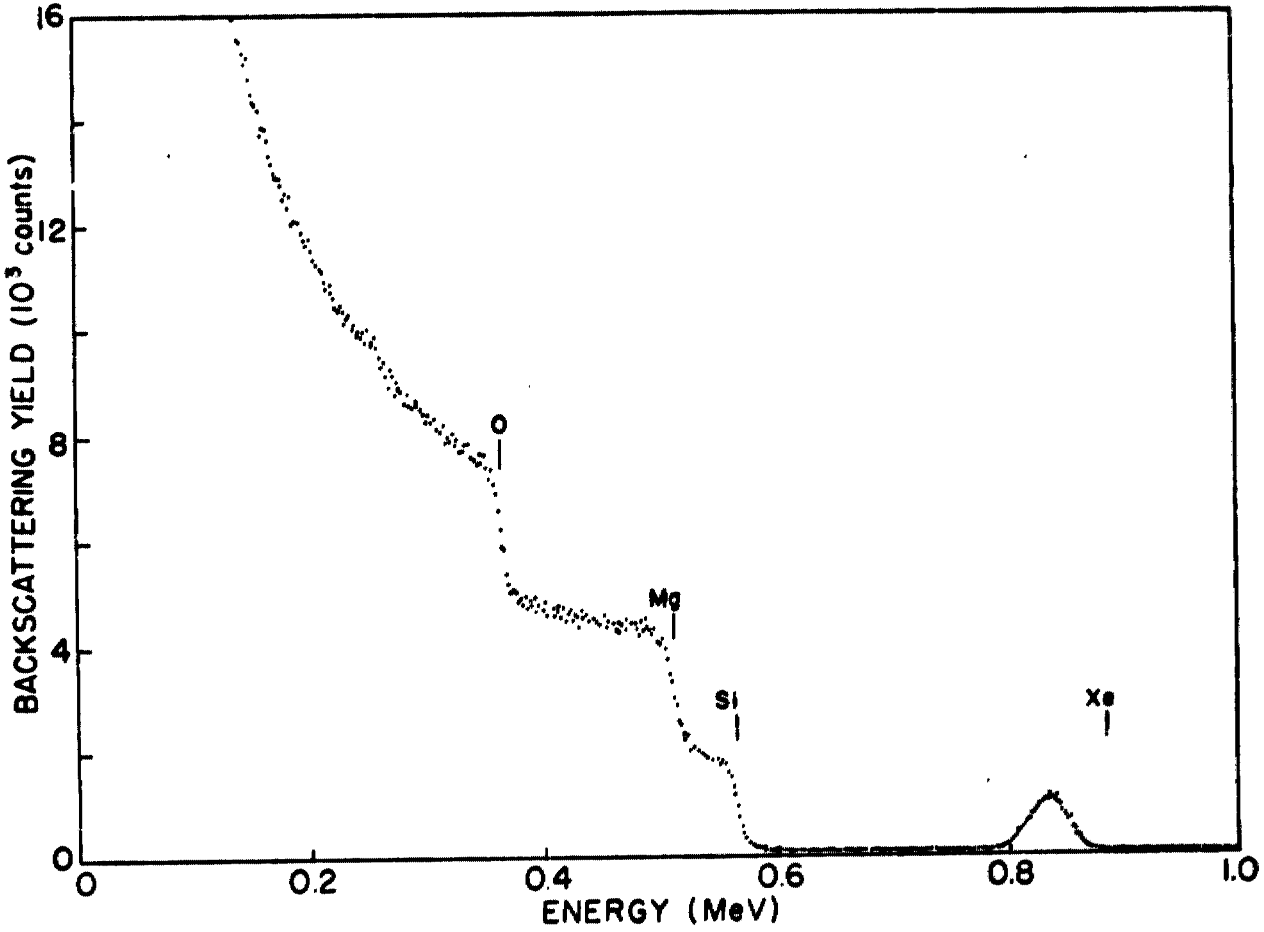
Table 1

Implantation doses and annealing temperatures.

Implantation dose (Xe ions/cm^2)	Annealing temperature (°C)	Xe retained after anneal (%)
1×10^{14}	1400	50
3×10^{14}	800→900→1000→1100	100
	1400	90
1×10^{15}	800→900→1000→1100	100
	1400	90
3×10^{15}	800→900→1000→1100	100
	1100→1200→1300→1400→1500	100


BACKSCATTERING YIELD (10^3 counts)
16
12
8
4
0
0
0.2
0.4
0.6
0.8
1.0
ENERGY (MeV)
O
Mg
Si
Xe

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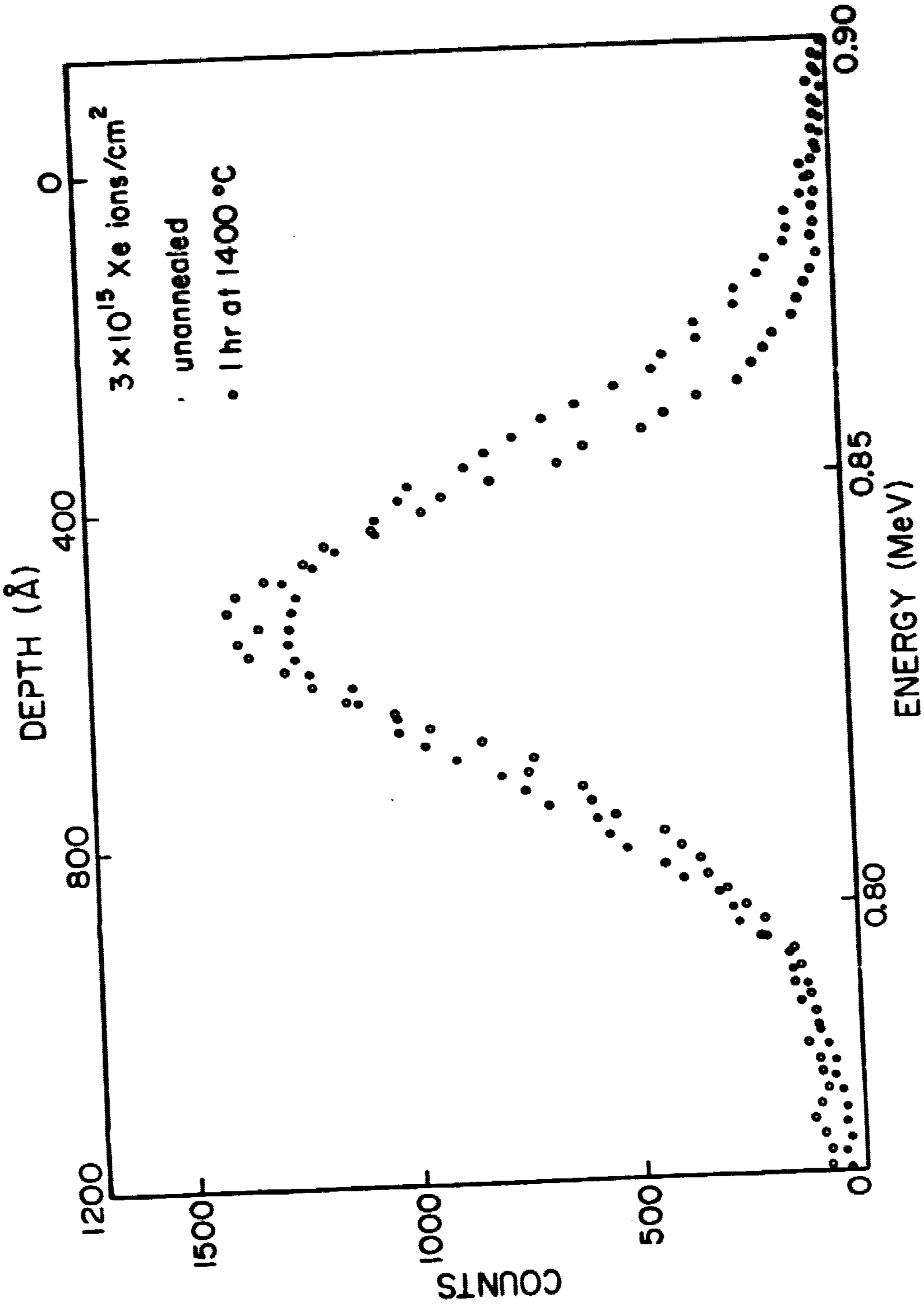
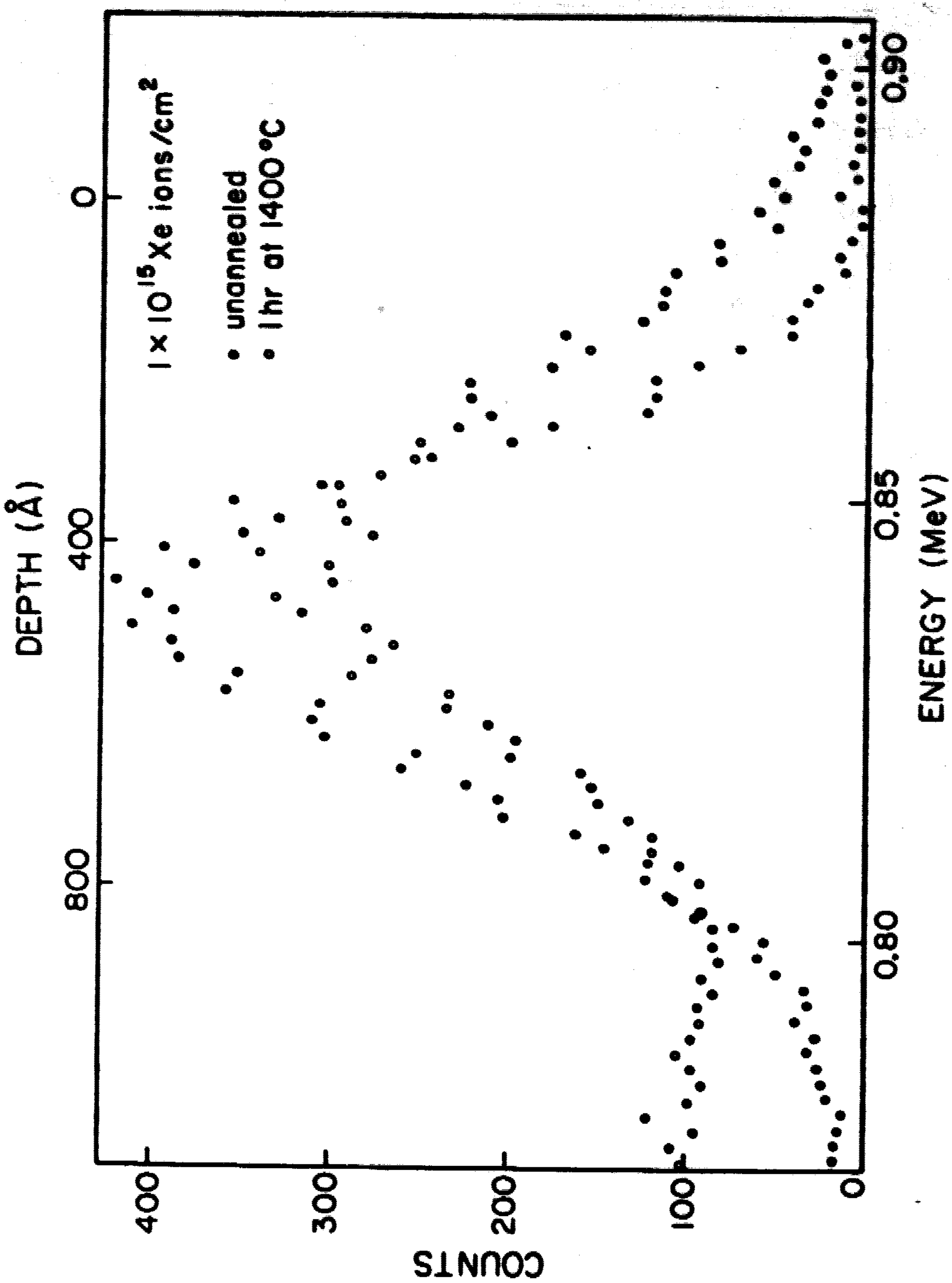
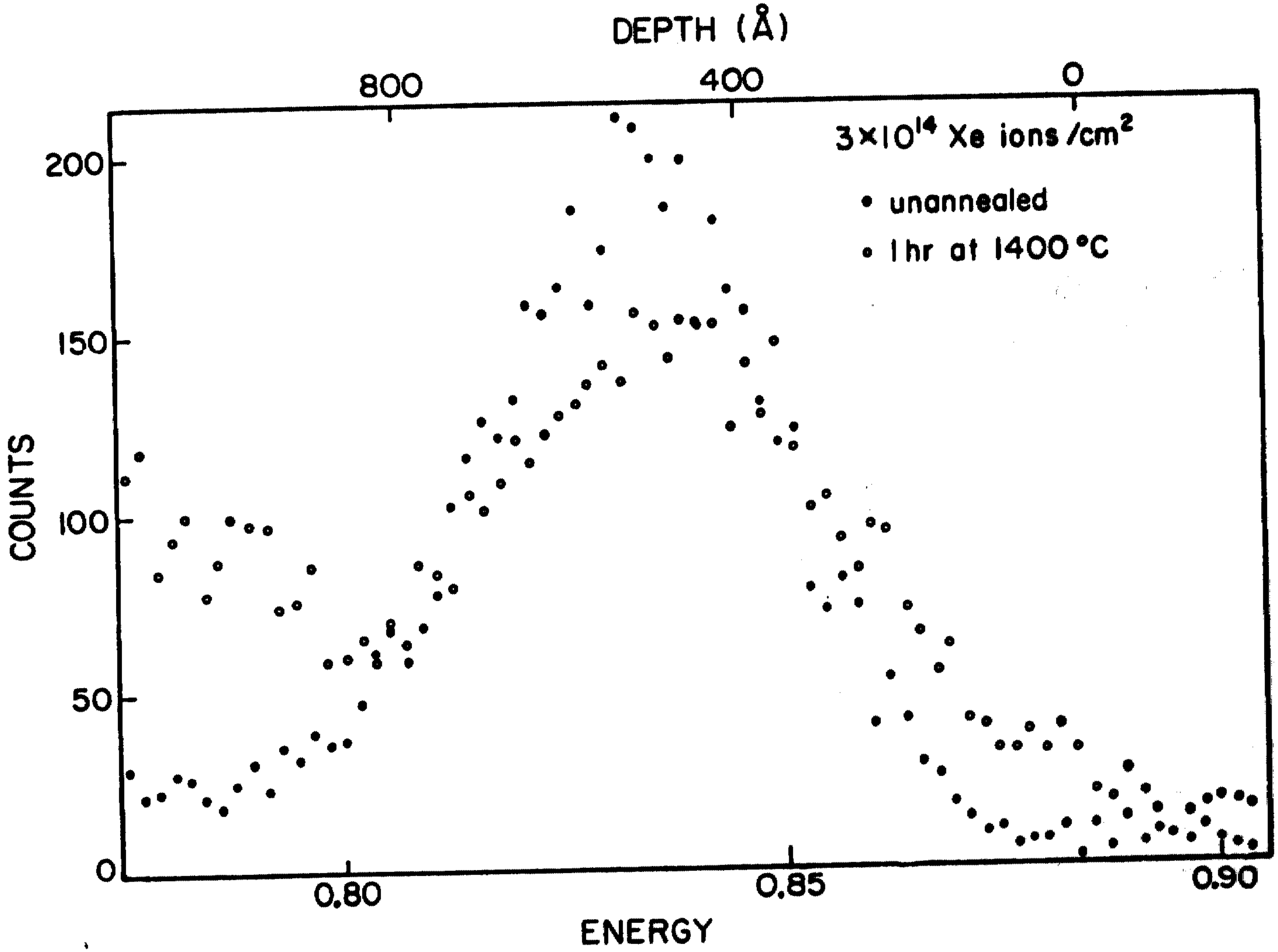



DEPTH (Å)
0
400
800
1 × 10^{15} Xe ions/cm^2
• unannealed
• 1hr at 1400°C
COUNTS
0
100
200
300
400
ENERGY (MeV)
0.80
0.85
0.90


DEPTH (Å)
800
400
0
3×10^{14} Xe ions/cm^2
● unannealed
○ 1hr at 1400 °C
COUNTS
200
150
100
50
0
0.80
0.85
0.90
ENERGY

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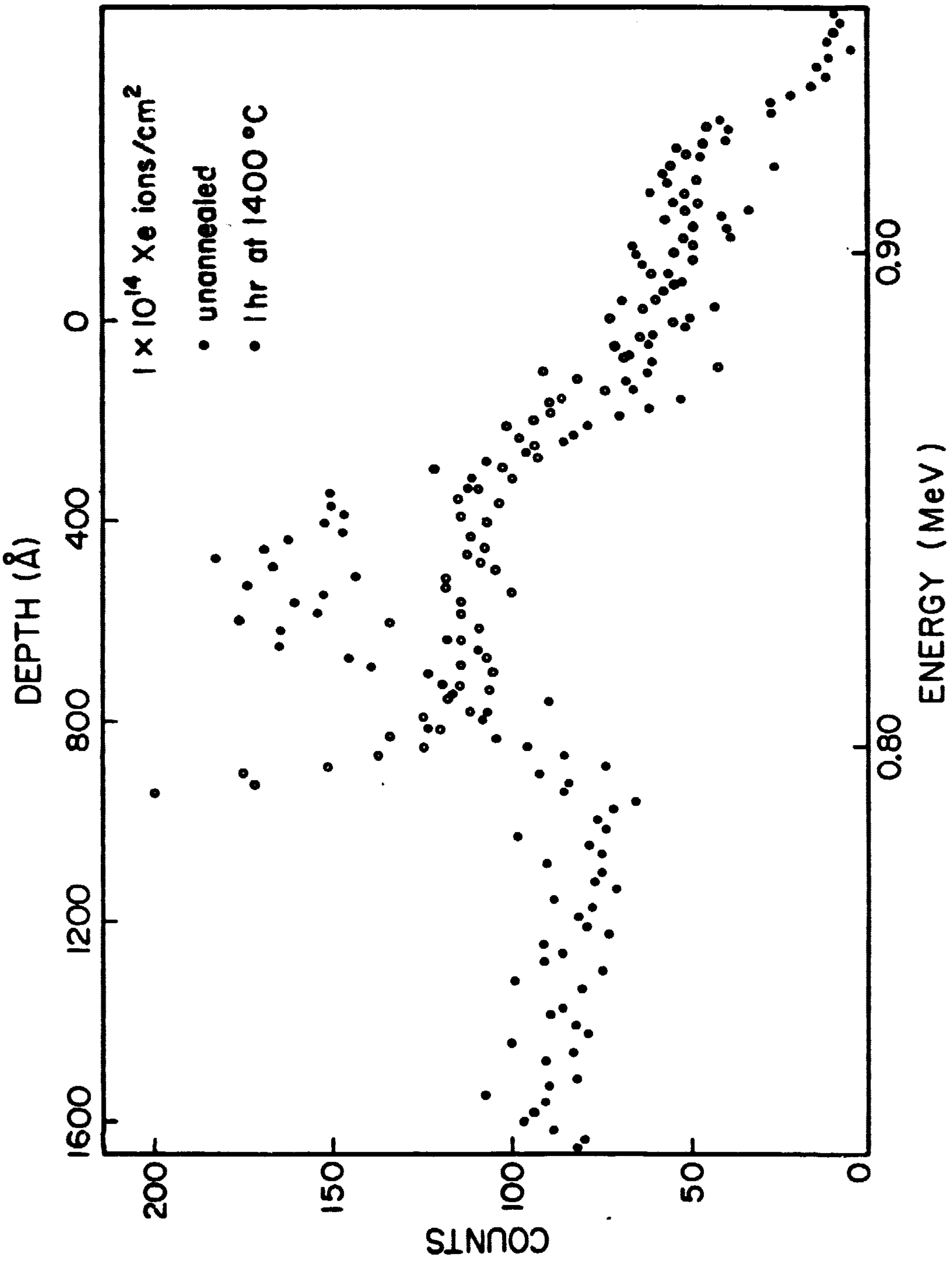

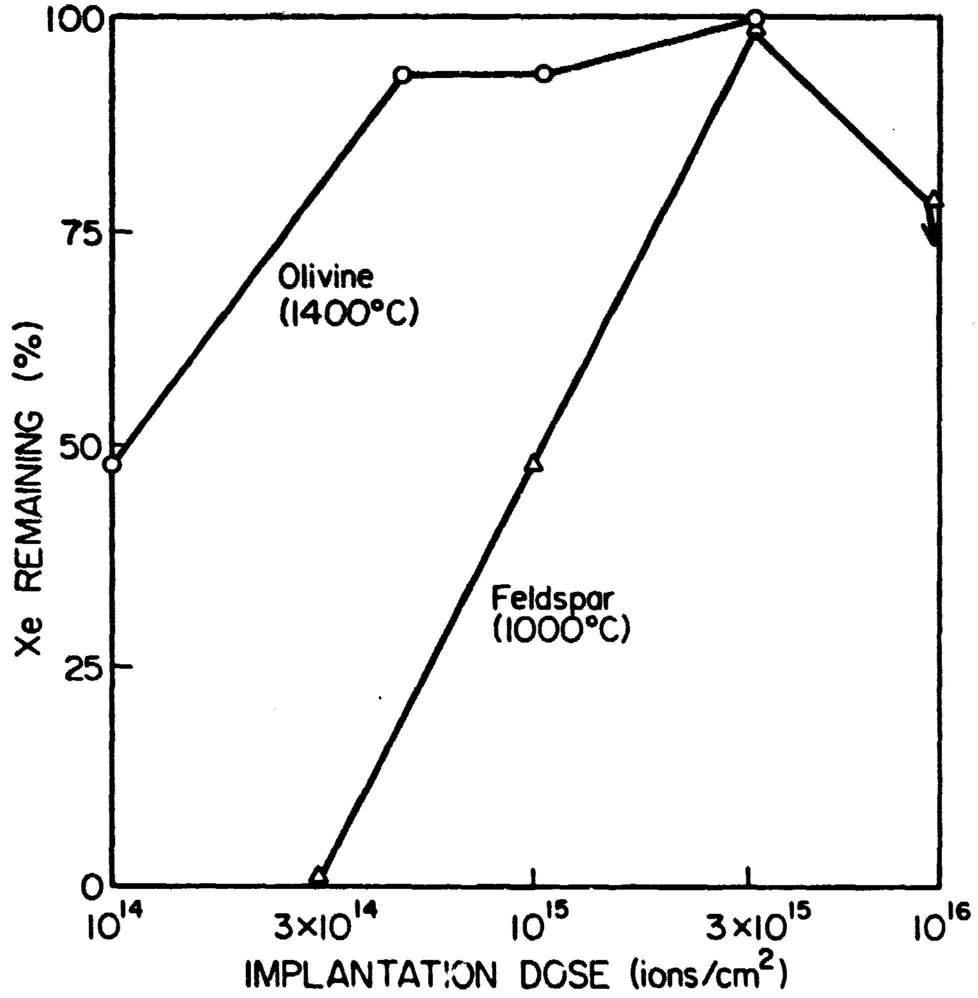
100
75
50
25
0
Xe REMAINING (%)
Olivine
(1400°C)
Feldspar
(1000°C)
10^{14}
3×10^{14}
10^{15}
3×10^{15}
10^{16}
IMPLANTATION DOSE (ions/cm^2)

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