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SUMMARY: In this work, lead was ion implanted into a variety of minerals to doses of order 10^{15} ions/cm². These implanted samples were then annealed at a variety of temperatures for varying times. The resulting lead concentration profiles were then determined using Rutherford backscattering spectrometry. These results were then modeled to determine diffusion coefficients.

Detailed results are given in the attached report.

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THE USE OF ION BEAM TECHNIQUES TO CHARACTERIZE LEAD
DIFFUSION IN MINERALS

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Abstract

The characterization of diffusion of lead and other trace elements in certain mineral phases has great significance in reconstructing the thermal history of the earth's crust. Such studies permit better interpretation of "ages" obtained from isotopic dating.

This study uses ion implantation to introduce lead into the minerals apatite and zircon. Diffusion profiles are obtained using Rutherford backscattering (RBS) and the results fit with a model to determine D. Results for apatite over the temperature range 600 - 900°C show agreement with earlier results obtained traditional geologic techniques. This suggests that radiation damage induced by ion implantation has little effect on diffusion in this case.

This approach is both simple and useful in studying diffusion over a temperature range of geologic interest without inordinate annealing times.

Introduction

Uranium-lead dating has long been an important tool in geochronology [1]. Minerals commonly used in this technique are zircon, apatite, monazite, allanite, and sphene. These accessory minerals concentrate rare earth elements and are principal hosts for U while tending to reject Pb. Hence, the lead contained in these minerals is predominantly from radioactive decay, which makes them the best candidates for dating igneous and metamorphic rocks.

During episodes of crustal fusion, radiogenic isotopes and other trace elements from various mineral phases are redistributed throughout the melt. Mineral clocks are "reset" upon cooling and recrystallization. However, zircon and apatite have been shown to be highly insoluble under some melting conditions [2,3,4]. There is also evidence that this is the case in monazite as well [5]. Unmelted crystals entrained in a melt fraction contain radiogenic components characteristic of their source region [6]. This "inherited lead" provides information about this source region as well as circumstances of the melting event.

Detailed thermal histories may be reconstructed through the observation of diffusion gradients of lead isotope ratios in individual crystals [7,8]. Whether a mineral grain retains information about its source depends on the length of the thermal event, the effective radius of the crystal, and the diffusion coefficient of the element of interest in the mineral [9].

Experimental Methods

Both Rutherford Backscattering (RBS) and ion implantation have been used to study trace-element diffusion in minerals. RBS was used to measure Sr diffusion in diopside [10,11]. Misra and Vankatasubramanian [12] investigated Sr diffusion in feldspars using ion implantation. However, these two techniques have not been used together in a single geologic diffusion study. In the present work, the advantages of both are exploited. RBS permits the measurement of small diffusion coefficients with relatively short annealing times. This allows for the measurement of diffusion at temperatures of geologic interest rather than attempting to extrapolate from higher temperatures. Ion implantation avoids errors in measurement due to hold-up of the diffusant near the sample surface and incomplete removal of material remaining on the surface after annealing. It also provides a way to introduce measurable amounts of the diffusant into the mineral lattice. This is especially important since minerals such as zircon tend to exclude Pb from their lattices and significant amounts may not enter with conventional surface exposure to a Pb-enriched environment.

Sample Preparation

The apatite used in this investigation is a natural mineral. It is from Durango, Mexico and was obtained from Ward's Natural Science Establishment, Inc. The SiO_2 is amorphous and in the form of polished slides.

The apatite was cut parallel to the c-axis with a low-speed saw. The cut surfaces were polished to $0.3\text{ }\mu\text{m Al}_2\text{O}_3$ and ultrasonically cleaned to remove residual grit and material. No preparation was necessary for the silica other than cutting it into small squares. Samples were implanted with a beam of 100 KeV Pb^+ ions produced from a granular PbS source. The nominal dose was 10^{15} ions/cm². Backscattering analyses of 14 separate implants of Pb into the amorphous SiO_2 result in a mean dose of 1.25×10^{15} ions/cm² with a range of $\pm 25\%$. The implanted mineral samples had comparable variations. Because of this inconsistency, a sample from each implant was left unannealed in order to determine both implant dose and width.

The samples were then placed in quartz boats and annealed in air in a quartz tube furnace.

Analysis

RBS with $^4\text{He}^+$ ions was used to obtain profiles. A beam energy of 2.0 MeV was used for the SiO_2 samples. For the minerals, 3.0 MeV ions produced better spectra because of the improved resolution in the high mass region of interest. The minerals have small (up to about 1%) concentrations of rare earth elements which may interfere with the observation of lead. Fig. 1 shows an expanded region of a backscatter spectrum of an implanted unannealed piece of apatite containing the lead peak and the rare earth edge. To avoid this interference, a background spectrum is taken from the same mineral and subtracted from the data. The silica has no high-mass components so this step was not necessary. Diffusion profiles were derived from the spectra

using a simple computer subprogram. Stopping powers for the minerals were calculated by using analytical polynomial expressions for elemental stopping powers [13] and the application of the Bragg rule.

The profiles were fit with a model to determine the diffusion coefficient, D . The model assumes an initial Gaussian distribution of Pb [14]:

$$C(x,0) = \frac{N_{\text{imp}}}{\sqrt{(2\pi)\Delta R}} \exp\left[-\frac{(x - R)^2}{2\Delta R}\right]$$

where: $C(x,0)$ = initial ion concentration

N_{imp} = implanted ion dose

ΔR = range straggling

R = ion range

We consider one dimensional diffusion governed by Fick's second law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

C = concentration of diffusant
 D = diffusion coefficient

The boundary conditions assumed in this case are:

The concentration of diffusant goes to zero at the sample surface, $C(0,t) = 0$

The medium is infinite in the positive x direction

The general solution in this case is:

$$C(x,t) = \frac{1}{\sqrt{(4\pi Dt)}} \int_0^\infty C(x') \left\{ \exp\left[-\frac{(x' - x)^2}{4Dt}\right] - \exp\left[-\frac{(x' + x)^2}{4Dt}\right] \right\} dx'$$

Substituting in $C(x,0)$ for $C(x')$:

$$C(x,t) = \frac{N_{imp}/(2\sqrt{(2\pi)\Delta R})}{\sqrt{1 + \frac{2Dt}{\Delta R^2}}} \left\{ \exp\left[-\frac{(x-R)^2}{2\Delta R^2 + 4Dt}\right] \left[1 + \operatorname{erf}\left[\frac{\frac{R\sqrt{(4Dt)}}{\sqrt{(2)\Delta R}} + \frac{x\sqrt{2\Delta R}}{\sqrt{(4Dt)}}}{\sqrt{(2\Delta R^2 + 4Dt)}}\right] \right] \right. \\ \left. - \exp\left[-\frac{(x+R)^2}{2\Delta R^2 + 4Dt}\right] \left[1 + \operatorname{erf}\left[\frac{\frac{R\sqrt{(4Dt)}}{\sqrt{(2)\Delta R}} - \frac{x\sqrt{2\Delta R}}{\sqrt{(4Dt)}}}{\sqrt{(2\Delta R^2 + 4Dt)}}\right] \right] \right\}$$

This analytical expression is used in a nonlinear fitting routine with R , ΔR , N_{imp} , and D as variable parameters.

Fitting was first done on unannealed implanted samples to get dose, R , and ΔR . The ΔR in this case is a term combining both range straggling and resolution of the system for backscattering. The parameters R and ΔR are fixed when fitting profiles of annealed samples to find D . Better fits were obtained when the dose was permitted to vary by up to 20%. Fits to R for silica and the minerals were found to agree well with those calculated in the ion implantation simulation program TRIM. However, ΔR was much broader than predicted. When contributions from detector resolution and Bohr straggle are added in quadrature to the predicted ΔR , the result agrees with the values of ΔR obtained in fitting the implanted unannealed profiles.

Results and Discussion

SiO_2

Work was begun with amorphous SiO_2 . Because of its simple composition and lack of high-mass components, the lead diffusion

profiles were readily observed. A series of isothermal anneals at 800°C for times ranging from 15 minutes to 48 hours resulted in a D value of $2.5 \times 10^{-16} (\pm 0.4)$ cm²/sec. Some of these profiles are shown in Fig. 2. A set of short (1 hr to 15 min) anneals were performed for temperatures from 700 - 1100°C. A plot of ln(D) vs. 1/T (Fig. 3) yielded a straight line from which an activation energy of 280 kJ/mol (67 kcal/mol) and frequency factor of 1.6×10^{-2} cm²/sec were determined. The model fit the data well except at some peak maxima, where it tended to undershoot the data.

Apatite

Because the presence of Ce substituting for some Ca in the apatite lattice causes interfering background in the RBS spectra, the dynamic range over which diffusion measurements may be made for this mineral is limited. Despite this, a series of measurements for temperatures ranging from 600 - 900°C were made. A set of representative profiles is shown in Fig. 4. These were compared with an earlier study at higher temperature of lead diffusion in apatite by Watson et al. [8]. These authors annealed Durango apatite crystals in a Pb-enriched synthetic silicate "melt" saturated in apatite. Diffusion profiles were measured with an electron microprobe, yielding an activation energy of 290 kJ/mol (70 kcal/mol) and frequency factor of 0.035 cm²/sec. However, these measurements were made for temperatures from 1300 - 900°C, so there is only one point of overlap with the present study. These points agree within error, and the lower temperature data falls along a line that can be extrapolated up to the higher

temperature data (Fig. 5). A least-squares fit to lower-temperature data in this study yields an activation energy of 225 kJ/mol (54 kcal/mol) and frequency factor of $8.6 \times 10^{-5} \text{ cm}^2/\text{sec}$.

Since each set of measurements uses completely different methods for both introduction of diffusant and measurement of profiles, this level of agreement confirms that the ion implantation-RBS technique can be valuable in determining D at or near temperatures of geologic interest. The data also suggest that radiation damage resulting from implantation is not a significant problem. If it were, either enhanced diffusion facilitated by defects or non-Fickian profile shapes resulting from defect trapping would be observed. It is also improbable that the data would agree with the measurements of Watson et al. This is further supported by RBS and TEM studies of lead-implanted crystalline oxides and ceramic materials [15,16]. Calcium and strontium titanates implanted with lead developed an amorphous layer which crystallized epitaxially within a few minutes and incorporated Pb into the lattice when annealed in air at 500°C. Higher temperature anneals would likely produce this effect much faster. Apatite, a phosphate mineral with large amounts of calcium, may behave similarly and can accept Pb at Ca sites under certain circumstances [17]. This may not be the case for minerals more reluctant to accept Pb (e.g. zircon).

Conclusion

Measuring diffusion coefficients in minerals using ion implantation to introduce the diffusant and RBS to measure

profiles appears to be a promising technique. Its advantages include the capability of measuring small values of D , ease of introduction of a variety of diffusants, and the elimination of problems associated with surface introduction of diffusant such as incomplete removal after annealing. Limitations of the technique include restricted dynamic range for measurements because of high-mass components in natural minerals (e.g. rare earths). The question of the effects on diffusion of radiation damage due to ion implantation has not yet been completely addressed for all minerals of interest and may present problems in certain cases. Work is currently in progress on characterizing Pb diffusion in zircon and monazite.

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Captions for Figures

Figure 1. Expanded region of RBS spectrum of Pb-implanted apatite, showing the lead peak and interfering rare-earth edge.

Figure 2. A series of profiles from isothermal anneals of Pb-implanted SiO_2 at 800°C . Symbols represent the diffusion data, lines are fits to the data with the D values indicated.

Figure 3. Diffusivity values for Pb in SiO_2 plotted on an Arrhenius diagram. The line drawn through the data represents a least-squares fit with activation energy of 67 kcal/mol and frequency factor of $1.6 \times 10^{-2} \text{ cm}^2/\text{sec}$.

Figure 4. Diffusion profiles for Pb in apatite at three different temperatures. Symbols represent data, lines are best fits to data.

Figure 5. Arrhenius diagram for Pb diffusion in apatite comparing data from this study with the work of Watson et al (1985). The line through the data represents a least-squares fit with activation energy of 54 kcal/mol and frequency factor of $8.6 \times 10^{-5} \text{ cm}^2/\text{sec}$.

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