Pb diffusion in zircon

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Abstract

Diffusion of Pb was characterized in natural and synthetic zircon under a range of conditions. In most experiments, mixtures of Pb sulfate and ground zircon were used as the sources of diffusant, with Pb depth profiles measured with Rutherford Backscattering Spectrometry (RBS). As complement to these "in-diffusion" experiments, "out-diffusion" experiments were run on both synthetic Pb-doped and natural zircon with relatively high Pb concentrations, and analyzed with either electron microprobe or RBS.

Over the temperature range 1000–1500°C, the following Arrhenius relation was obtained:

$$D = 1.1 \times 10^{-1} \exp\left(-550 \pm 30\,\mathrm{kJ\,mol^{-1}}/RT\right)\,\mathrm{m^2\,s^{-1}}$$

Results for diffusion in natural and synthetic zircon were quite similar, as are those for in- and out-diffusion. Pb diffusion does not appear to be strongly influenced by pressure, crystallographic orientation, or the presence of water.

The slow diffusion rate for Pb indicates that Pb isotope ratios will not be altered by volume diffusion in crystalline zircon under most geologic conditions, a finding consistent with the frequent observation of inheritance and preservation of multistage histories in zircon. Most Pb loss in zircon, then, is likely a consequence of recrystallization or Pb transport in zircons with severe radiation damage (although the latter can be effective only for vast annealing times at very low temperatures).

Mean closure temperatures, calculated from the diffusion parameters, are in excess of 900°C for zircons of typical size, a result in consonance with field-based estimates of closure temperatures. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Because of the importance of U–Th–Pb isotopic dating of zircon in interpreting crustal events, it is necessary to understand the kinetic behavior of these elements in the zircon lattice in order to attain a greater insight into thermal histories. We have in previous work (Cherniak et al., 1997b) investigated diffusion rates of U and Th, as well as the REE (Cherniak et al., 1997a) and oxygen (Watson and Cherniak, 1997), and now report here our findings on Pb diffusion in zircon.

Since many factors have the potential to influence diffusion rates, we investigate the effects of changes

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in several parameters on Pb diffusion, among them crystallographic orientation, zircon composition, the presence of hydrous species, and pressure. In the set of experiments outlined below, we also consider cases of out- and in-diffusion, the effect of concentrations of Pb somewhat higher than natural Pb abundances, and explore the possibility that radiogenic Pb in natural zircon may be displaced from normal lattice sites as consequence of the multistage decay process and thus could diffuse in a different manner than Pb introduced into zircon by other means. The consistency of our findings over this range of conditions will serve to demonstrate that broad application of our results to zircon in natural systems is justified.

2. Experimental procedures

2.1. In-diffusion experiments

2.1.1. Zircon synthesis, source and sample preparation

The synthetic zircons used in this study were grown from a Pb-silicate or Li carbonate–molybdate flux. The latter flux method followed the procedure of Suzuki et al. (1992) using a flux composed of Li_2CO_3 and MoO_3. Following synthesis, the zircons were readily extracted from the flux material remaining in the crucible. They were placed in dilute HCl for a few hours to dissolve any residual flux, and then ultrasonically cleaned in baths of distilled water and ethanol.

The other synthetic zircons were grown from a PbO-rich silicate melt, using procedures and melt compositions similar to those outlined in Watson et al. (1997). Zircon crystals grown from these PbO–SiO_2–ZrO_2 melts incorporate little Pb (< 1 ppm; Watson et al., 1997). However, when phosphorus ($\sim$ several wt.% P_2O_5) is included in the melt, Pb concentrations in the resulting zircons are orders of magnitude higher (~ 1000 ppm; Watson et al., 1997); crystals grown in this melt were used in one of our Pb out-diffusion experiments (OZPb-4; Table 1), to be described below. Following synthesis, zircons were separated from surrounding glass by dissolving

the Pb-silicate glass in dilute HF. The P and Pb contents of these doped zircons are very uniform (Watson et al., 1997) when examined with backscattered electron (BSE) imaging and analyzed with the electron microprobe.

Synthetic zircons with relatively large growth faces were selected for in-diffusion anneals, and underwent no further surface preparation. Because of the crystal habit, the largest crystal faces are parallel to *c*, so all of the diffusion measurements on the synthetic zircons are for transport normal to *c*. In order to investigate whether differences in trace-element compositions or defect concentrations influence Pb diffusion in zircon, experiments were also run on a natural zircon from the Mud Tank carbonatite. Oriented crystal specimens (cut either parallel or normal to *c*, also permitting assessment of the degree of anisotropy in Pb diffusion) were cut into slabs a few millimeters on a side and about 0.5-mm thick and polished to 0.05-μm gamma alumina. Polished samples were then annealed at 1300°C for 3 days in order to repair any surface damage that might be a consequence of cold-working (e.g., Reddy and Cooper, 1982).

Single crystal and powder XRD analyses of synthetic zircons grown in the Pb-rich silicate melt without P, others grown in a molybdate flux, a natural specimen from the Mud Tank carbonatite, and another natural specimen from an unknown locality, revealed only very small and inconsequential differences in lattice parameters and unit cell volumes (J.M. Hanchar and P.C. Burns, in preparation).

The source of diffusant consisted of a mixture of $PbSO_4$ and finely ground zircon. Synthetic zircon was used in the source for experiments with synthetic zircon, and ground Mud Tank zircon was used in the natural zircon experiments to discourage minor element exchange (primarily of Hf) during diffusion anneals. While this was taken as precaution, it is probably not absolutely necessary given that $D_{Pb} \gg D_{Hf}$ in zircon (Cherniak et al., 1997b). The source constituents were mixed, placed in silica glass capsules, sealed under vacuum, annealed for a few days at 1070°C, and then re-ground.

Powdered or ground materials have been employed as sources of diffusant in many of our studies (e.g., Cherniak and Watson, 1992, 1994; Cherniak et al., 1997a,b; Watson and Cherniak, 1997), and have

Table 1
Pb diffusion in zircon

	T (°C)	Time (s)	D (m^2 s^{-1})	log D	$+/-$	Pressure
Synthetic zircon						
grown in Li_2CO_3/MoO_3 flux, in-diffusion:						
ZZPb-18	1000	1.24×10^7	6.84×10^{-24}	-23.17	0.26	1 atm
ZZPb-17	1050	4.32×10^6	2.59×10^{-23}	-22.59	0.32	1 atm
DZ-3	1100	2.59×10^5	3.04×10^{-22}	-21.52	0.28	10 kb, 'dry'
ZZPb-16	1100	1.09×10^6	9.05×10^{-23}	-22.04	0.26	1 atm
ZZPb-5	1150	2.23×10^5	4.47×10^{-22}	-21.35	0.25	1 atm
DZ-5a	1150	4.12×10^5	4.22×10^{-22}	-21.37	0.28	10 kb, 'wet'
ZZPb-6	1200	3.24×10^4	4.68×10^{-21}	-20.33	0.24	1 atm
ZZPb-11	1200	1.30×10^5	2.57×10^{-21}	-20.56	0.17	1 atm
DZ-4a	1200	2.38×10^5	4.47×10^{-21}	-20.35	0.16	10 kb, 'dry'
ZZPb-10	1200	2.92×10^5	2.98×10^{-21}	-20.53	0.10	1 atm
ZZPb-8	1250	7.20×10^3	3.21×10^{-20}	-19.49	0.23	1 atm
ZZPb-13	1250	2.70×10^4	1.54×10^{-20}	-19.81	0.13	1 atm
ZZPb-21	1250	7.38×10^4	1.40×10^{-20}	-19.85	0.13	1 atm
ZZPb-12	1302	7.80×10^3	1.07×10^{-19}	-18.97	0.18	1 atm
zircon grown in Li_2CO_3/MoO_3 flux, out-diffusion 'reversal' experiment:						
OZPb-1	1250	1.69×10^5	2.53×10^{-20}	-19.60	0.28	1 atm
zircon grown in Pb silicate melt, in-diffusion:						
ZZPb-14	1250	2.52×10^4	1.42×10^{-20}	-19.85	0.14	1 atm
zircon grown in Pb silicate melt with P, out-diffusion:						
OZPb-4	1500	4.14×10^5	3.80×10^{-18}	-17.42	0.50	1 atm
Natural Zircon						
Mud tank Carbonatite, in-diffusion:						
cut $\parallel c$:						
ZZPb-15a	1251	2.16×10^4	1.77×10^{-20}	-19.75	0.14	1 atm
cut $\perp c$:						
ZZPb-15c	1251	2.16×10^4	2.21×10^{-20}	-19.66	0.12	1 atm
Sri Lanka, out-diffusion:						
OZPb-2	1250	1.69×10^5	2.63×10^{-20}	-19.58	0.66	1 atm
OZPb-3	1470	9.18×10^5	3.00×10^{-18}	-17.52	0.50	1 atm

yielded diffusivities comparable to those obtained through techniques introducing diffusants through other means (e.g., Cherniak and Watson, 1992, 1994; Giletti and Casserly, 1994; Cherniak and Ryerson, 1993; Watson et al., 1985; Moore et al., 1998; Derry et al., 1981). The numerous point contacts of the source powders (and the sink materials described in later sections) provide essentially continuous surface coverage given the experimental geometry and the relative rapidity of grain boundary and surface diffusion (e.g., Gjostein, 1973; Tannhauser, 1956).

2.1.2. One-atmosphere experiments

Experiments were run at 1 atm by sealing zircon and source under vacuum in silica glass capsules.

Prepared capsules were then annealed in vertical tube furnaces at temperatures ranging from 1000°C to 1300°C and times ranging from a few hours to several months (Table 1). Experiments under 1100°C were run in Kanthal-wound tube furnaces, with temperature monitored by chromel–alumel (type K) thermocouples; the remainder were run in furnaces with MoSi$_2$ heating elements and temperatures monitored with Pt–Pt10%Rh (type S) thermocouples. In both cases, temperature uncertainties were about ± 2°C.

A "zero-time" anneal was also performed, to assess the likelihood of non-diffusional uptake of Pb during the heat-up and quench phases of the anneal, and to explore the possibility of other difficulties

with the experimental approach. For the "zero time" run, a sample capsule was prepared as described above for 1-atm experiments, using a synthetic zircon grown in the Li_2CO_3/MoO_3 flux. The capsule was then brought up to run temperature (1200°C) and immediately quenched.

2.1.3. High-pressure experiments

The high-pressure experiments were run in a piston-cylinder apparatus using pressure-sealing Pt liners inserted into 3-mm diameter holes in oxidized Ni cylinders (see Watson and Lupulescu (1993)). Temperature was monitored and controlled with type D (W25Re75-W3Re97) thermocouples to within 2°C. The overall temperature uncertainty in these runs is believed to be ± 10°C. Experiments were run at temperatures from 1100°C to 1200°C at 1.0 GPa (Table 1).

The Pb sulfate/zircon source employed in the 1-atm experiments was also used in these high-pressure experiments. For "wet" experiments, designed to investigate the effect of hydrous species on Pb diffusion in zircon, the $PbSO_4$/zircon source was mixed with finely ground zirconia and hydroxyapatite.

2.1.4. Out-diffusion and "reversal" experiments

In addition to these "in-diffusion" experiments, a few types of "out-diffusion" experiments were run. For the first, in a sense a "reversal" experiment, a synthetic zircon (grown in the Li_2CO_3/MoO_3 flux) was annealed with the $PbSO_4$ source in a silica glass capsule for 60 h at 1300°C. The sample was removed from the source, cleaned ultrasonically in baths of dilute HCl, distilled water, and ethanol and dried. The Pb uptake profile was measured with Rutherford Backscattering Spectroscopy (RBS). The sample was then annealed in a Pt capsule surrounded by synthetic (Pb-free) zircon, which served as a sink for the Pb. The Pb distribution was again profiled with RBS, and a diffusion coefficient extracted from the Pb profile "relaxed" from its initial form by the second anneal.

A second type of out-diffusion experiment was done with a natural zircon from Sri Lanka with relatively high Pb content. Fragments of the zircon were polished to 0.05-μm gamma alumina, and annealed overnight at 900°C in air in an open Pt

capsule order to repair surface damage that might be a consequence of the polishing process. The specimens were then annealed at higher temperatures (one at 1250°C, another at 1470°C) in Pt capsules surrounded by finely powdered synthetic zircon as a sink for Pb. A third type of out-diffusion experiment was run using Pb doped zircons grown in a PbO–SiO_2–ZrO_2–P_2O_5 melt (Watson et al., 1997). The zircons were annealed in Pt capsules at 1500°C, again surrounded by finely ground synthetic (undoped) zircon. For the latter two types of out-diffusion experiments, Pb profiles of the highest-temperature experiments (i.e., 1470°C and 1500°C) were measured with an electron microprobe; that for the lower temperature experiment was measured with RBS.

2.2. RBS and nuclear reaction analysis (NRA)

RBS has been used in many of our diffusion studies (e.g., Cherniak and Watson, 1992, 1994; Cherniak, 1995), and the experimental and analytical approach used here is similar to that taken in our previous work. Analyses typically employed $^4He^+$ beams of energies of either 2 or 3 MeV. Spectra were converted to Pb concentration profiles using procedures outlined in publications cited above.

In order to obtain information about the substitutional processes and means of charge compensation involved in Pb exchange in zircon, the RBS measurements on in-diffusion experiments were supplemented with NRA measurements of sulfur. Given the composition of the source used in in-diffusion experiments, it is possible that sulfur in a hexavalent charge state provides charge balance for the exchange of Pb^{+2} for Zr^{+4} in the zircon lattice (i.e., $Pb^{+2} + S^{+6} \rightarrow Zr^{+4} + Si^{+4}$). Although sulfur is in general readily detectable with RBS, the presence of high background (mainly due to helium ion backscattering from the zirconium of the zircon matrix) severely limits detection of low levels of S. NRA, given its isotope selectivity, eliminates this background interference and permits determination of S to concentration levels (down to less than 100 ppm) unattainable from the zircon RBS spectra.

Sulfur concentrations were investigated with the $^{32}S(\alpha,p)^{35}Cl$ reaction (Soltani-Farshi et al., 1996), using the 6.90-MeV resonance, with incident beam

of doubly charged helium. Protons produced in the reaction were detected with a solid state surface barrier detector. A Mylar foil absorber of 32-μm thickness was placed in front of the detector to stop the elastically scattered alpha particles but permit the protons to pass through. Measurements of S on a number of the zircon samples show no sulfur above detection limits of about 50 (atomic) ppm, given the collected charge delivered to the sample, background levels, and the cross-section and solid angle of the detector employed.

2.3. Electron microprobe analyses

The electron microprobe analyses were made with the JEOL 733 Superprobe at RPI, using an accelerating voltage of 25 kV, a sample current of $\sim$ 100 nA, and an apparent spot diameter of $\sim$ 2 μm. Lead sulfide served as the Pb standard for calibration at the $L_{\alpha 1}$ X-ray peak position. Counts were collected for up to 15 min at each analysis point on zircon specimens in order to obtain acceptable X-ray count uncertainties (the standard deviations were 5–11% relative at each analysis spot).

Depth profiles were obtained on cross-sectioned zircons by step traverses across the grain, done at an angle of 30° with respect to the zircon surface in order to include more analyses per profile and improve resolution. Profiles (consisting of steps of 1-μm increment) were then "compressed" by a factor of two (i.e., by multiplying by 0.5, the sine of the 30° angle) to obtain the actual depth in the zircon. There is some point-to-point overlap because the excitation volume is on order of 3 μm, which introduces error into the apparent profile shape, but the fits and uncertainties assigned to determined diffusion coefficients incorporate these factors.

2.4. Extracting diffusion coefficients from Pb concentration profiles

The RBS and electron microprobe profiles measured following diffusion anneals were fit with models to determine the diffusion coefficients (D). In-diffusion is modeled as simple one-dimensional, concentration independent diffusion in a semi-infinite medium with a source reservoir maintained at constant concentration (i.e., a complementary error func-

tion solution). The rationale for the use of this model has been discussed elsewhere (e.g., Cherniak and Watson, 1992; 1994; Cherniak, 1993). Diffusivities are evaluated by plotting the inverse of the error function (i.e., erf^{-1} $((C_o - C(x,t))/C_o)$) vs. depth (x) in the sample. A straight line of slope $(4Dt)^{-1/2}$ will result if the data satisfy the conditions of the model. C_o, the surface concentration of diffusant, is determined by iteratively varying its value until the intercept of the line converges on zero. In Fig. 1, typical in-diffusion profiles and their inversions through the error function are shown. The uncertainties in concentration and depth from each data point (mainly derived from counting statistics in the for-
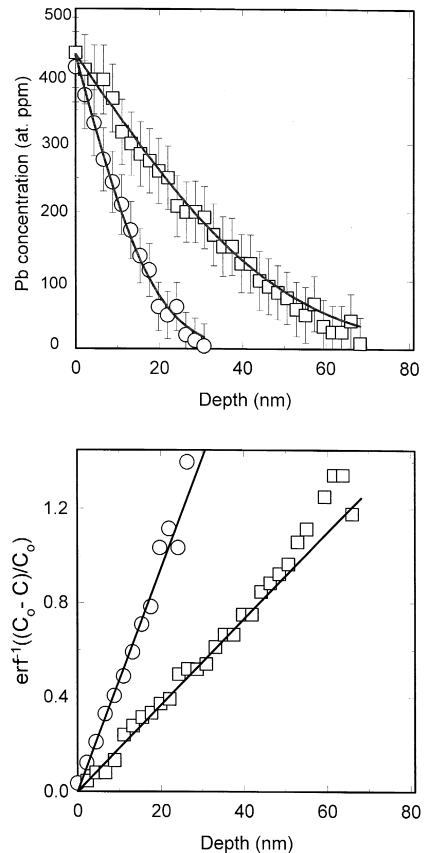

Fig. 1. Typical diffusion profiles for Pb in-diffusion experiments. Profiles were measured by RBS. (a) The diffusion data are plotted with complementary error function curves. (b) The data are inverted through the error function. Slopes of lines are equal to $(4Dt)^{-1/2}$.

mer and detector resolution and energy spread of the analyzing ion beam in the latter) were used to evaluate the uncertainties in the diffusivities determined from the fits to the model.

Pb concentration as a function of depth x and anneal time in the out-diffusion "reversal" experiment can be described by the integral

$$
\begin{aligned}
C(x,t_2) \\
= \frac{1}{\sqrt{4\pi D_2 t_2}} \int_0^\infty \mathrm{erf}c\left(\frac{x}{\sqrt{4D_1 t_1}}\right) \\
\times \left[e^{-(x-x')^2/4D_2 t_2} - e^{-(x+x')^2/4D_2 t_2} \right] \mathrm{d}x', \quad (1)
\end{aligned}
$$

a solution to the diffusion equation where the initial distribution of the diffusant is a complementary error function (determined by the duration and temperature of the in-diffusion anneal), and the surface concentration (for the out-diffusion) is fixed at zero. The subscripts 1 and 2 denote the diffusion coefficients and anneal durations for the experimental conditions of in-diffusion and out-diffusion, respectively. Since the amount of diffusant remaining after a given time t is

$$
M_\mathrm{r} = \int_0^\infty C(x,t)\mathrm{d}x, \qquad (2)
$$

it becomes a relatively straightforward task, either by solving the integrals analytically or (as in this case) numerically, to extract both the relaxed profile shape and the amount of diffusant lost as a function of $D_2 t_2$. The out-diffusion coefficient was extracted by measuring the integrated amount of Pb remaining and taking the ratio of this to the initial integrated Pb following the in-diffusion anneal. With knowledge of the duration of the out-diffusion anneal, a diffusivity can then be calculated. Uncertainties in diffusion coefficients were obtained from the uncertainties in Pb concentrations both before and after the out-diffusion anneal (largely a function of counting statistics in RBS spectra yields) and uncertainties in depth determination (a function of RBS detector resolution and energy spread of the analyzing beam). A further check on the reasonableness of D calculated in this manner was performed by generating a profile using this value and comparing it with the measured Pb profile, to establish whether the data conform well to the diffusion model. The shape of the Pb profile is consistent with the model, and area-calculated D consistent with this finding.

The Pb diffusivity for the out-diffusion experiment in the natural (Sri Lanka) zircon run at 1250°C was determined by comparing the integrated Pb concentration (extracted from an RBS analysis of the sample) with the Pb concentration of a piece of the same specimen exposed to the same pre-treatment (polishing and 900°C anneal), but no diffusion anneal. In this experimental configuration, we have a semi-infinite medium, with an initial concentration of diffusant C_1, and surrounding medium with Pb concentration essentially fixed at zero. In this case, M_t, the amount of diffusant that has left the sample after time t, is defined as (e.g., Crank, 1975):

$$
M_t = 2 C_1 \sqrt{\frac{Dt}{\pi}}, \qquad (3)
$$

so it is straightforward to determine the amount of diffusant present following the anneal and extract a diffusivity if the initial concentration is known, as it is in our experiment. Uncertainties in determination of D include the factors cited above, along with the contributions to uncertainty in Pb concentrations due to the interfering signals from Hf, U and other heavy elements in the RBS spectra.

Diffusivities for the high-temperature out-diffusion experiments analyzed by electron microprobe were determined by fitting the Pb profiles with error function curves, taking into consideration the uncertainties associated with each point in the profiles. In this case, uncertainties in diffusion profiles were largely a function of counting statistics in the electron microprobe analyses and the extent of the activation volume for each analysis. With initial and boundary conditions noted in the previous paragraph, the solution to the diffusion equation for the Sri Lanka zircon experiment is

$$
C(x,t) = C_1 \mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right), \qquad (4)
$$

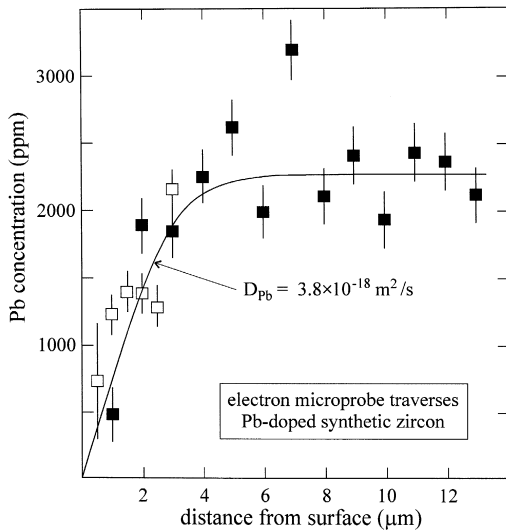where C_1 is the initial concentration of Pb in the zircon.

Fig. 2. Pb diffusion profile for out-diffusion from a synthetic Pb doped zircon. Profile was measured by electron microprobe analysis. The different symbols represent separate traverses of the sample. The curve is a fit to the data with the model outlined in the text.

For the experiment run with the synthetic Pb-doped zircon grown from a melt containing Pb and P, the data were fit with both the solution for one-dimensional diffusion (Eq. 4) and that for diffusion in a sphere, since the zircons were relatively small (~ 50 μm) in comparison to the length of diffusion profiles (> 5 μm). The solution of the diffusion equation for a sphere, given appropriate boundary and initial conditions is (Crank, 1975):

$$C(r,t) = \frac{2 C_1 a}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \sin \frac{n \pi r}{a}$$

$$\times \exp(-D n^2 \pi^2 t / a^2), \qquad (5)$$

where C_1 is again the initial concentration of Pb in the zircon, a is the radius of the sphere, and r is the radial distance in the sphere. Fits to the data with both models yielded indistinguishable results. The Pb diffusion profile and fit of the one-dimensional diffusion model to the data is shown in Fig. 2.

3. Results

The results for Pb diffusion in zircon are presented in Table 1 and plotted in Figs. 3–5. A least-squares linear fit to the in-diffusion data (Fig. 3) yields an activation energy for diffusion of 550 ± 30 kJ mol^{-1} (131 ± 7 kcal mol^{-1}) and pre-exponential factor 1.1×10^{-1} m^2 s^{-1} ($\log D_o = -0.962 \pm 1.074$). A time-series of anneals run at 1200°C (Fig. 4a) indicates that Pb diffusion is independent of time for durations differing by a factor of 9. Further, Pb diffusion appears to be little influenced by pressure (Fig. 4a and d), or the presence of hydrous species in the system (Fig. 4d). The latter finding is in contrast to the diffusion behavior of oxygen in zircon. When hydrous species are present, oxygen diffuses more rapidly and with a lower activation energy for diffusion than under dry conditions (Watson and Cherniak, 1997).

The compositional variations between the two types of synthetic zircon, and the natural zircons, also seem to produce little difference in Pb diffusion rates (Fig. 4b and c). Little anisotropy in Pb diffusion in zircon appears to exist, as diffusion coeffi-
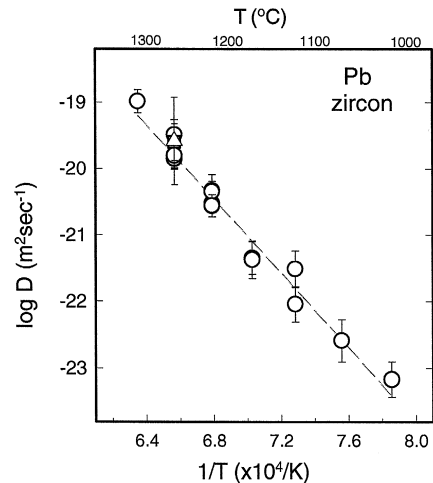

Fig. 3. Arrhenius plot of Pb diffusion in zircon. Plotted are in-diffusion experiments on synthetic and natural (Mud Tank) zircon. The line is a least-squares fit to the data. Arrhenius parameters extracted from the fit are: activation energy 550 kJ mol^{-1}, and pre-exponential factor 1.1×10^{-1} m^2 s^{-1}.

cients in specimens of Mud Tank zircon cut parallel and perpendicular to c agree within experimental uncertainty (Fig. 4b).

The time series cited above provides one means by which we can affirm that what we are measuring is in fact volume diffusion; the "zero time" experi-

ment offers another. The lack of a significant amount of Pb uptake or near-surface exchange in the "zero time" run (not plotted) suggests that rapid surface reaction during the initial stages of the anneal does not contribute substantially to observed Pb profiles in the diffusion experiments.

The out-diffusion "reversal" experiment on synthetic zircon yields a diffusion coefficient that agrees within uncertainty with that of the in-diffusion experiments at 1250°C (Fig. 4c), adding further support to the contention that we are measuring volume diffusion. We cannot characterize Pb out-diffusion accurately in most natural zircons because signals from Hf and U interfere the RBS analyses of Pb (and Pb concentrations are relatively low in most zircons). However, we did investigate Pb out-diffusion in a natural zircon with relatively high Pb content from Sri Lanka, analyzing experiments run at 1250°C and 1470°C with RBS and electron microprobe, respectively. Interpretation of the RBS spectra was simplified by the assumption, supported by experimental evidence (Cherniak et al., 1997b) that $D_{Pb} \gg D_U$, D_{Hf}. Given the relatively small number of counts in the RBS spectra produced by Pb and the limited depth range over which the Pb signal could be followed due to the presence of Hf, uncertainties in the measurement of D were rather large (roughly two-thirds of a log unit). Nevertheless, this determi-
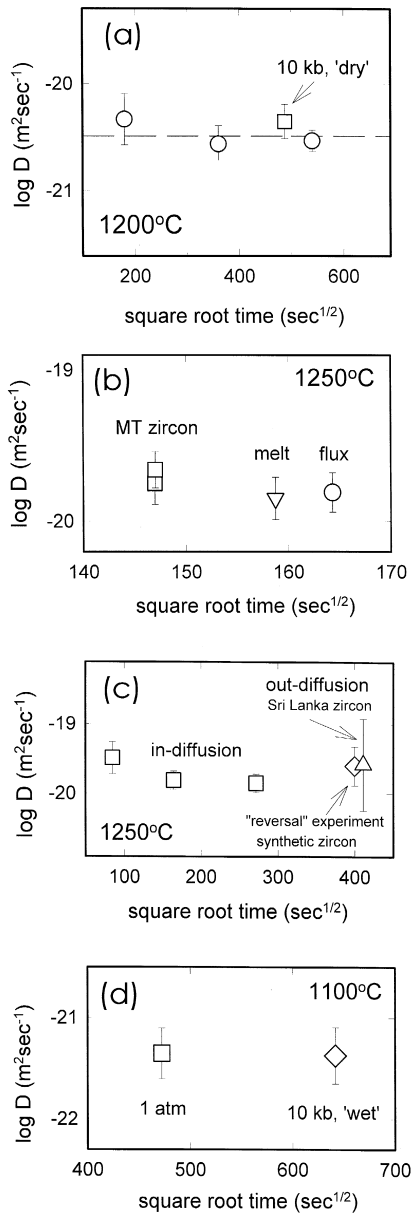

Fig. 4. Time series for Pb diffusion anneals, and consideration of the influences of various factors on Pb diffusion. (a) Time series at 1200°C. diffusivities at constant temperature are generally quite similar for anneal times differing by a factor of 9. In addition, diffusion coefficients for experiments run at 1 atm agree within uncertainty with that for an experiment run at 10 kb, suggesting little influence of pressure on Pb diffusion in zircon. (b) Comparison of Pb diffusion for synthetic zircons grown in lithium carbonate–molybdenum oxide flux and in Pb silicate melt, and a natural zircon from the Mud Tank Carbonatite. Zircons, regardless of origin or means of synthesis, have similar Pb diffusion rates. Further, measurements on the Mud Tank zircon indicate little anisotropy of Pb diffusion. (c) In-diffusion vs. out-diffusion. Diffusion coefficients for in-diffusion in synthetic zircon are comparable to that for Pb out-diffusion from a natural (Sri Lanka) zircon, and a "reversal" experiment (described in text) on a synthetic zircon. (d) "Wet" vs. dry diffusion. Diffusion rates at 1100°C for experiments at 1 atm and at 10 kb in the presence of water agree within experimental uncertainty, and indicate that the presence of hydrous species has little influence on Pb diffusion in zircon.
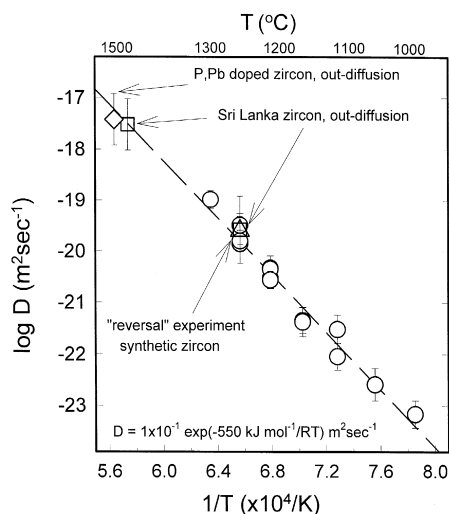
Fig. 5. Arrhenius plot of diffusivities from out-diffusion experiments on natural (Sri Lanka) zircon and zircon grown from Pb silicate melt doped with phosphorus, and "reversal" experiment on a synthetic zircon described in the text. Also plotted for comparison is Arrhenius line determined from the in-diffusion data plotted in Fig. 3, extrapolated to 1500°C, illustrating the consistency between these data sets.

nation of D is entirely consistent with our other measurements of Pb diffusion at this temperature, and, even with the large uncertainty taken into account, is still significantly smaller than the finding of Lee et al. (1997), in which a similar experimental protocol (i.e., out-diffusion of Pb from a natural zircon into a Pb-poor medium) was adopted.

The 1470°C experiment on the Sri Lanka zircon, and the out-diffusion experiment on the Pb doped synthetic zircon (at 1500°C), are also consistent with our lower-temperature results, as they lie on an up-temperature extrapolation of the Arrhenius line determined from the out-diffusion data gathered at temperatures 1000–1300°C (Fig. 5). A "global" fit to all the data yields an activation energy of 545 ± 25 kJ mol^{-1} (130 ± 6 kcal mol^{-1}) and pre-exponential factor of 7.8×10^{-2} m^2 s^{-1} ($\log D_o = -1.110 \pm 0.875$), for temperatures spanning 500°C and diffusivities ranging over 6 orders of magnitude.

The substitutional processes involved in Pb exchange in experiments using the PbSO$_4$ source were investigated though complementary RBS and NRA measurements of Pb and sulfur. While sulfur has

been reported in chemical analyses of zircon (e.g., Speer, 1982), it is not clear whether it is ubiquitous or might play some charge compensating role. Conceivably, Pb could be charge compensated in substituting for Zr through a substitution of S (in the hexavalent state) for Si, i.e., $Pb^{+2} + S^{+6} \rightarrow Zr^{+4} + Si^{+4}$. However, our NRA findings suggest that this substitution is not a significant facilitator of Pb exchange in zircon. It seems likely that divalent Pb is charge compensated by oxygen defects (O$^-$ centers), as can be the case for the REEs in zircon (Cherniak et al., 1997a). Diffusion of oxygen, even under dry conditions (Watson and Cherniak, 1997), is also faster than diffusion of Pb in zircon (Fig. 7), so movement of Pb would then be expected to be the rate-limiting factor in Pb transport. This is also consistent with the agreement of diffusivities from the in- and out-diffusion experiments for both natural and synthetic zircon. If a coupled mechanism were operant for in-diffusion, it is possible that diffusion would be rate-limited by sulfur if in the hexavalent state, since cations of high charge have been found to diffuse quite slowly in zircon (Cherniak et al., 1997b). Rates of out- and in-diffusion, if governed by different mechanisms, would then not necessarily be expected to agree unless diffusion of Pb was the rate-limiting process in exchange.

4. Measurements of Pb diffusion in zircon — a brief summary

Efforts have been made for some time to quantify and characterize Pb diffusion in zircon, in deference to its significance in interpreting Pb isotopic signatures and refining understanding of thermal histories. As is evident from the summary of data plotted in Fig. 6a, there is relatively little agreement between determinations of Pb diffusion rates, and values span a remarkably broad range (more than 10 orders of magnitude) in measured D. Many of these Pb diffusion studies have been considered in detail by Lee (1993); only brief discussion and summary are offered here.

The experiments of Shestakov (1969, 1972) and Magomedov (1970) relied upon bulk release methods, with the zircon crystals heated and the amount
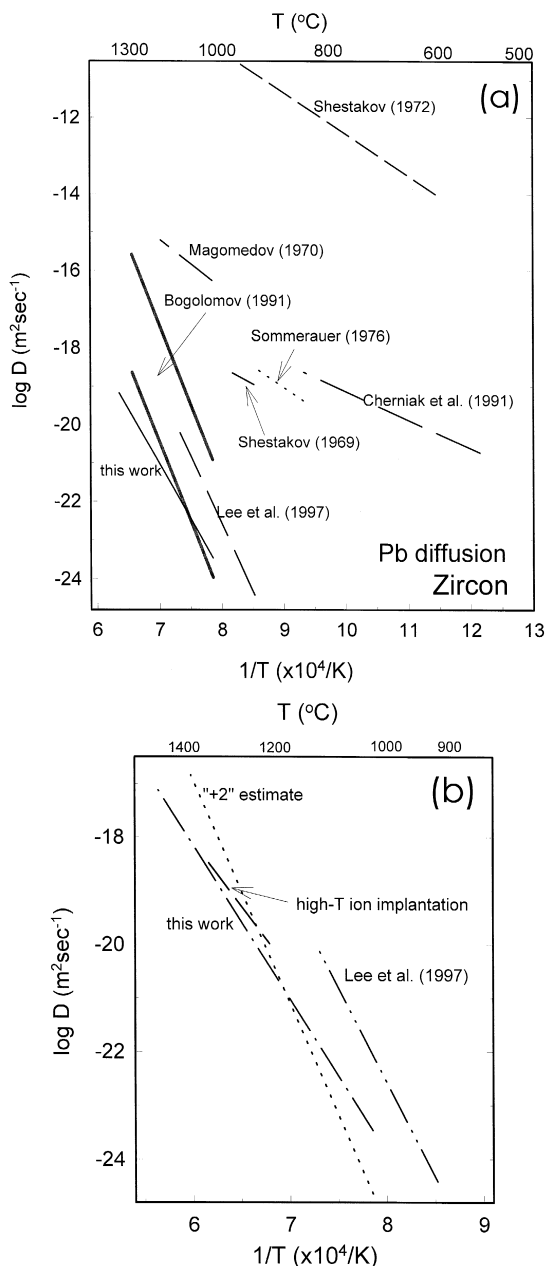
Fig. 6. (a) Summary of measurements of Pb diffusion in zircon. Sources for data are noted on the graph. (b) Expanded region of Fig. 6a, showing the results of the present study and that of Lee et al. (1997). Also plotted for comparison are the (unpublished) results of Cherniak et al. using high-temperature ion implantation to introduce Pb, described in the text, and the theoretical prediction of Pb diffusion rates in zircon from Cherniak et al. (1997b).

of Pb released recorded as a function of time. Such measurements are plagued by several difficulties, among them the presence of cracks, cleavage surfaces, dislocations and other features that might provide shortcut pathways for Pb transport, and the departure of real mineral surfaces from the model's assumption of ideal smooth surfaces, which would increase available surface area for exchange. In these studies, Pb release did not obey a typical volume diffusion relationship, indicating the possibility of grain-boundary diffusion, and suggesting that surface volatilization as well as Pb migration might be a factor influencing Pb release patterns.

Sommerauer (1976) heated both crystalline and metamict zircons with PbO powder, and obtained an upper-limit estimate of Pb diffusion in the crystalline zircon based on an electron microprobe profile (or lack thereof, as Pb penetration was found to be less than 1 μm for an anneal of 2 days at 840°C). It is not surprising that an appreciable profile was not detected, since penetration distances would be < 1 Å for these time–temperature conditions given our diffusion parameters.

The thermal evaporation experiments of Bogolomov (1991), which yield quite high activation energies (790–1180 kJ mol^{-1}) likely involved decomposition of zircon to ZrO_2 + SiO_2 during heating, as suggested by the work of Chapman and Roddick (1994). Pb loss in this case is not governed by simple volume diffusion but is instead controlled by the decomposition process and movement of the reaction front.

There are relatively few studies of Pb diffusion in zircon in which analytical techniques with superior depth resolution have been employed. Cherniak et al. (1991) implanted Pb ions into natural zircon and annealed the implanted samples under a range of time–temperature conditions, and measured resultant profiles with RBS. The process of ion implantation, however, produced significant amounts of damage of the zircon crystal lattice, leading to elevated transport rates for Pb, and a low activation energy for diffusion (142 kJ mol^{-1}). Interestingly, implantation of Pb at energies in the range of those used by Cherniak et al. (1991) creates damage comparable to that produced by alpha-recoil events in the decay of U to Pb in natural zircon (e.g., Headley et al., 1982; Petit et al., 1987), so their results, as the authors then

noted, provide a determination of Pb transport rates in zircons that have experienced significant radiation damage.

Lee et al. (1997) measured out-diffusion of Pb (as well as U and Th) in a natural zircon from Sri Lanka with SIMS. They obtained an activation energy of 675 kJ mol^{-1} and pre-exponential factor of 3.9×10^5 m^2 s^{-1}. In the temperature range over which their study overlaps with the present work (1000–1100°C), diffusivities determined by Lee et al. (1997) are more than an order of magnitude faster; the variance approaches 2 orders of magnitude at 1100°C (Fig. 6b). The reasons for this discrepancy are unclear. The diffusion rates for U and Th measured by Lee et al. (1997) are 4 orders of magnitude larger than those of Cherniak et al. (1997b). Lee et al. (1997) contend that this difference may be a consequence of the fact that their experiments were run on natural zircons and measured out-diffusion and those of Cherniak et al. (1997b) were run with synthetic zircons and measured in-diffusion, but this explanation seems unconvincing for several reasons. Both the present work and that of Cherniak et al. (1997a) on REE diffusion in zircon indicate that there exists no appreciable difference in cation diffusion rates in synthetic zircons and natural zircon with little radiation damage. Variations in minor and trace element compositions, and differences in defect concentrations as consequence of different growth conditions of the natural and synthetic zircons, appear to exert little influence on cation diffusion. The small amounts of radiation damage present in the Sri Lanka zircon (which, as Lee et al. (1997) note, exhibits "excellent crystallinity") should be annealed out readily, as the reported α-dose for the zircon (4.8×10^{14} decays/mg) is well within the Stage I regime of damage accumulation (zircon with $< 3 \times 10^{15}$ α-decays/mg; Murakami et al. (1991)). Therefore, radiation damage in this case should not greatly affect Pb transport. Furthermore, our out-diffusion experiments, using a zircon similar to that used by Lee et al. (1997) as well as a generally comparable experimental approach, yield diffusivities consistent with the rest of our measurements rather than the faster diffusion rates measured by Lee et al. (1997). The medium employed as sink for the diffusant is (other than the analytical techniques used to measure Pb distributions) the salient difference between our out-diffusion experiments and those of Lee et al. (1997). The material constituting the reservoir surrounding the sample in our experiment, ground zircon, is quite refractory and was unreactive with the zircon specimen. NaCl exhibits quite different attributes. It is not unreasonable to conjecture, although Lee et al. (1997) failed to clearly and adequately address the possibility in their paper, that reaction of the zircon surface with the molten salt reservoir might produce near-surface (non-diffusional) Pb loss, since it has been noted elsewhere that NaCl solutions may enhance Pb loss through "chemical leaching" (e.g., Lee, 1993).

Other elements of the Lee et al. (1997) study are problematic. The authors did not offer sufficiently strong evidence that what they were measuring was indeed volume diffusion of Pb. They mentioned two key "tests" undertaken to confirm the occurrence of volume diffusion. The first is the independence of diffusion coefficient on the duration of the diffusion anneal. While the time series is a well-established test, anneal times must differ by an amount such that diffusion profiles are significantly different in length. Since diffusion distance scales as the square root of time, a difference in anneal times of a factor of 4 (which would result in length scales differing by a factor of 2) is generally considered a minimum variance for this test. Anneal times at a given temperature differ by at most a factor of 1.8 in the Lee et al. (1997) study. The second "test" mentioned by Lee et al. (1997), that of Arrhenian behavior (i.e., linear dependence of $\log D$ on $1/T$), is not definitive, as the Arrhenius relation is empirical and kinetic processes other than volume diffusion might also exhibit some form of linear dependence in $1/T$. Furthermore, profiles at the lowest temperature (900°C) are extremely short (only a few nanometers, given the durations of the diffusion anneals and reported diffusion coefficients) and thus carry much greater uncertainty in SIMS analysis than the authors suggest.

Our measurements yield comparable diffusivities at a given temperature for a wide range of conditions, and consistent diffusivities over a broad temperature span with a variety of experimental approaches and two different analytical techniques. This lends strong support to the conclusion that several factors that might have been heretofore suspected of affecting Pb diffusion in zircon, among

them out-diffusion vs. in-diffusion, the presence of concentrations of Pb somewhat higher than natural Pb abundances, and the possibility that radiogenic Pb may not occupy lattice sites due to displacement as consequence of the multistage decay process and thus could diffuse in a different manner than Pb in our experiments with the $PbSO_4$ source, do not seem to exert significant influence.

Further support for the reasonableness of our Pb diffusion findings comes from a set of high-temperature ion implantation experiments (Cherniak et al., unpublished data) on synthetic zircon and a theoretical prediction of Pb diffusion rates (Cherniak et al., 1997b) These are shown in Fig. 6b. The ion implantation experiments were conducted in a manner similar to that outlined by Cherniak et al. (1991). In those experiments, zircon was implanted with Pb ions, and the initial Pb distributions depth-profiled with RBS. The samples were then annealed and subsequent depth profiles were fit with a model to determine diffusion coefficients based on the spreading of the initial implanted Pb distributions. The high-temperature implantation study cited here differs from the experiments of Cherniak et al. (1991) in that implantation took place with samples mounted on a heated stage (held at 800°C), rather than at room temperature as in the earlier work. Heating the sample during implantation permits radiation damage produced by the implantation to anneal out rather than accumulating as rapidly as it would during implantation at room temperature, so ion doses required to induce amorphization of the material increase with increasing temperature of implantation. At temperatures of 800°C, zircon will resist amorphization even for relatively high implant doses of heavy ions (e.g., Wang and Ewing, 1992; Weber et al., 1994). For the heated-stage experiments, synthetic zircons were implanted with Pb^+ ions with an energy of 250 keV. Implant doses were 1×10^{15} Pb ions/cm^2 (a similar dose to that used in the Cherniak et al. (1991) experiments). Over the temperature range 1200–1350°C, we obtain from these diffusion data an activation energy of 456 ± 109 kJ mol^{-1} (10926 kcal mol^{-1}) and pre-exponential factor 1.6×10^{-4} m^2 s^{-1} ($\log D_o = -3.80 \pm 3.69$). While these data extend over a fairly short range in $1/T$ and carry a relatively large amount of uncertainty, they are consistent with the remainder of our Pb diffusion

measurements reported here, despite a very different means of introducing Pb into the zircons.

The theoretical prediction, based on observed trends for diffusion of trivalent and tetravalent cations in zircon, was reported by Cherniak et al. (1997b), and is discussed in Section 5.

5. Cation diffusion in zircon — a consideration of some trends

There now exists a body of data for diffusion of various cations and anions in zircon (Fig. 7). Certain systematic behaviors have been observed (Cherniak et al., 1997a,b) among trivalent and tetravalent cations. For cations of a given charge, diffusivities increase with decreasing ionic radius. The rare earths, for example, exhibit marked variation in diffusion rates from the light to heavy REE, with diffusion coefficients of Lu and La expected to differ by roughly 2 orders of magnitude. Among tetravalent
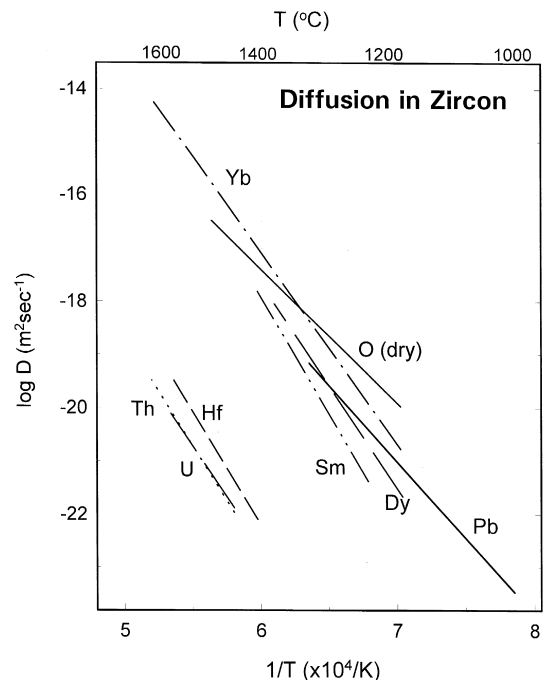

Fig. 7. Summary of diffusion data for various cations and anions in zircon. Sources for data: Yb, Dy, Sm — Cherniak et al. (1997a); Hf, U, Th — Cherniak et al. (1997b); Oxygen — Watson and Cherniak (1997); Pb — this study.

cations, Hf diffuses more rapidly than U or Th, but these differences are not as pronounced as those found between trivalent cations. The influence of cation charge is also great; the (trivalent) REEs diffuse 3–5 orders of magnitude faster than tetravalent cations in zircon. Pb likely exists in the divalent state in these experiments, and in zircons in nature as well, since Pb is stable in the $+4$ valence state at elevated temperatures only under conditions of very high fO_2 (e.g., Otto, 1966; Watson et al., 1997). At the same time, the ionic radius of Pb^{+2} is quite large (1.29 Å in eightfold coordination; Shannon (1976)). If the above trends broadly obtain for cations in zircon, it appears that these two factors, i.e., lower charge tending to increase diffusion rates and larger ionic radius tending to reduce them, provide competing influences.

Based on the trends observed for diffusion of tetravalent and trivalent cations noted above, Cherniak et al. (1997b) made an estimate of Pb diffusion rates in zircon. This is shown in Fig. 6b. The degree of agreement of this estimate with our measured diffusivities may be entirely fortuitous. On the other hand, it may suggest that there is at least some value in attempts to develop predictive models for diffusion coefficients based on ion charge, size, and (perhaps) crystal–chemical properties.

6. Pb diffusion in other minerals

There now also have been measurements made of Pb diffusion in a range of minerals, including those of other accessory minerals employed in U–Pb geochronometry. These are plotted in Fig. 8. It is evident from this compilation that diffusion of Pb in zircon is quite slow with respect to other minerals for which Pb diffusion data exist. [Monazite is the nearest, but the reported activation energy for diffusion is much lower than that of zircon (by about a factor of 4), so diffusion rates of Pb in monazite will be considerably higher than those in zircon under most geologic conditions.] This is consistent with the observation that zircon is considerably more resistant to thermal disturbance than other accessory minerals (e.g., Mezger and Krogstad, 1997; Mezger et al., 1991, 1989). The high activation energy and low diffusivity of Pb in zircon are also in agreement with
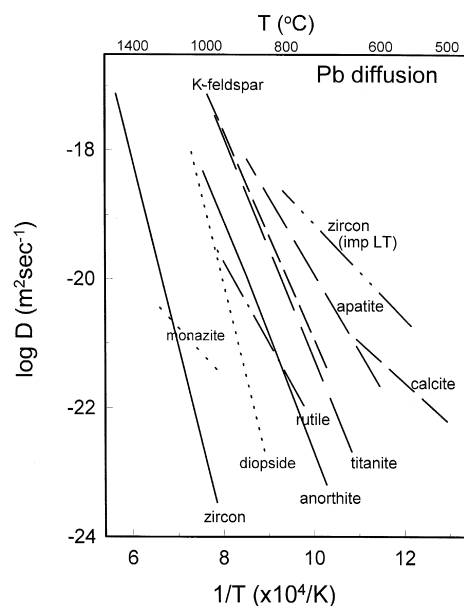

Fig. 8. Pb diffusion data for various minerals. Pb diffuses most slowly in zircon among minerals for which diffusion data exist. Sources for data: anorthite, K-feldspar — Cherniak (1995); apatite, zircon (imp. LT) — Cherniak et al. (1991); calcite — Cherniak (1997); diopside — Cherniak (1998a); monazite — Smith and Giletti (1997); rutile — Cherniak (1998b); titanite — Cherniak (1993).

observed trends of negative correlations of diffusion rates at metamorphic temperatures and activation energy for diffusion with mineral ionic porosities (Dahl, 1997).

7. Closure temperatures

Dodson's (1973) classic construct of closure temperature is now quite familiar, and frequently appears in the form

$$T_c = \frac{E_a/R}{\ln\left(\dfrac{ART_c^2 D_o/a^2}{E_a dT/dt}\right)}, \qquad (6)$$

where E_a and D_o are the activation energy and pre-exponential factors for diffusion of the relevant species, dT/dt is the cooling rate, a is the effective diffusion radius, and A is a geometric factor. The derivation of the above expression rests on several

assumptions (Dodson, 1973, 1986); among these is the condition that the initial homogeneous composition of the mineral grain attained at peak temperature T_o is sufficiently removed from the composition (at all points) of the quenched grain. This assumption, which makes T_c independent of T_o, is, as Ganguly et al. (1998) note, not satisfied for slowly diffusing species such as the REEs in garnet and various cations in pyroxene. Given that diffusion of Pb in zircon is much slower than any of these, this condition is not satisfied for zircon either, nor can it even be assumed that homogeneity is achieved at a peak metamorphic temperatures. However, when the dependence of T_c on T_o is taken into account in calculating closure temperatures, the deviations of these T_c values from conventional closure temperatures calculated using Eq. 6 above are smaller with increasing peak temperature (T_o) and slower cooling rate (Ganguly et al., 1998). The geometric factor, A, in Dodson's expression of mean closure temperature above, is equal to $\exp(G)$, where G is the value of the closure function, $G(x)$, spatially averaged over the crystal. In deriving the expression for $G(x)$, and ultimately A, the dimensionless parameter M [where M is defined as $D(T_o)RT^2/(E_a a^2 dT/dt)$], is much greater than 1 (Dodson, 1986). For larger values of M, G will increase, thus A will be smaller than the value of 55 [i.e., $\exp(4.0066)$] one obtains when the condition of $M \gg 1$ is met. As the factor A increases, mean closure temperatures will be decreased.

As noted above, closure temperatures calculated using Eq. 6 are mean values, as closure temperature varies with distance from the crystal surface. However, except for a very narrow outermost layer, closure temperatures will not differ from the mean by more than a few tens of degrees for cooling rates between 1 and 10°C/Ma and grain sizes up to a few millimeters. For example, for 100-µm radius grains, mean T_c is about 10°C higher than that for a point 10 m from the surface; T_c for the grain center will be about 40°C higher than the mean value. A point 1 µm from the surface, however, will have a T_c 80–90°C lower than the mean.

It should be clear from the above brief discussion that closure temperature is dependent on many factors. Nonetheless, we can use the simplified expression above to make broad comparisons of closure of Pb in various accessory minerals, and to consider closure temperature values calculated from our diffusion parameters in light of the estimates made of closure temperatures for Pb in zircon in field-based investigations.

In Fig. 9, we plot closure temperature for various accessory minerals as function of effective diffusion radius, using the "traditional" Dodson equation (i.e., Eq. 6). We plot curves calculated using both the usual geometric factor for spherical geometry (i.e., $A = 55$). Closure temperatures for Pb in zircon are quite high, considerably in excess of those for other accessory minerals. For example, the closure temperature for Pb in a zircon of 100-µm effective diffusion radius for a cooling rate of 10°C/Ma is 991°C. Evidence in field based studies of the high closure temperature (in excess of 950–1000°C) for Pb in zircon has long been found (e.g., Black et al., 1986; Claoué-Long et al., 1991; Williams, 1992). Higher
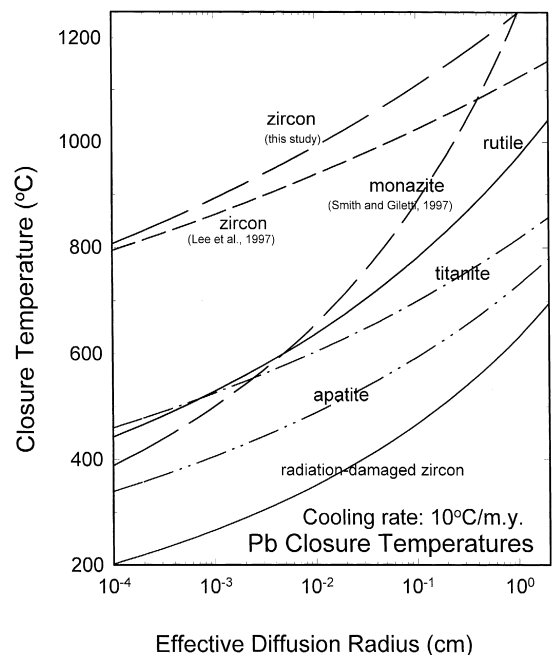

Fig. 9. Closure temperatures for Pb in accessory minerals as function of effective diffusion radius for a cooling rate of 10°C per million years. Calculations were made employing the standard expression of Dodson (Eq. (6)). Sources for diffusion data for closure temperature calculations are included in the caption for Fig. 7. Also plotted for comparison are closure temperatures calculated using the diffusion data of Lee et al. (1997).

closure temperatures for zircon in comparison to other accessory minerals are evidenced by various studies (e.g., McLelland et al., 1988; Mezger et al., 1991; Chiarenzelli and McLelland, 1993; Hölzl et al., 1994) that have observed that monazite and titanite from high grade metamorphic terranes yield U–Pb ages younger than zircons from the same samples, or other samples experiencing the same geologic history. Given the same cooling rate and effective diffusion radii (i.e., 10°C/Ma and 100 μm), calculated closure temperatures for monazite and titanite are 335°C and 385°C lower, respectively, than that of zircon.

8. The preservation of Pb zoning in zircon

Sharp compositional zoning in zircon is often observed, as the slow diffusivities characteristic of most elements in zircon can influence both the likelihood of formation of such zoning (e.g., Watson and Liang, 1995) and its preservation under a broad range of geologic conditions (Watson and Cherniak, 1997; Cherniak et al., 1997a,b). Both sector zoning and igneous growth or "oscillatory" zoning have been reported in various zircon populations, with zoning down to micron and sub-micron scales (e.g., Hanchar and Miller, 1993; Halden et al., 1993; Wayne et al., 1992). Species for which zoning is most commonly noted are the high-Z elements incorporated into zircon in relatively high abundance (Hf, and to lesser extent, U), with zoning observable in BSE images, and the REE (most notably Dy), whose emissions often dominate the visible in cathodoluminescence (CL) spectra (e.g., Marfunin, 1979; Mariano, 1989).

While zoning in Pb generally cannot be observed by these means because of its low abundance and the fact that its electronic structure militates against its being a CL activator in zircon, marked variations in Pb isotopes across individual grains, representing different stages (and ages) of zircon growth, have been detected in ion probe analyses (e.g., Hanchar and Rudnick, 1995), and discordance in many cases has been attributed to "mixing" as consequence of combining isotope information from distinct regions into a single analysis.

Given the slow diffusion rates of Pb in crystalline zircon under most geologic conditions, distinct zones,

even on relatively fine scales, will quite often be preserved. This can be illustrated by a simple model. Zones in a zircon are modeled as plane sheets of thickness l; adjacent planes have different concentrations of diffusant. Only diffusion normal to the planar interface is considered. Two different (and somewhat arbitrary) criteria for alteration of zones are evaluated: (i) "blurring" of zones, defined by a compositional change of 10% one-tenth of the way into the zone; and (ii) "disappearance" of zones, defined by a compositional change of 10% in the zone's center. The dimensionless parameter Dt/l^2 is equal to 1.8×10^{-3} for condition (i), and 3.3×10^{-2} for condition (ii). Fig. 10 shows curves constraining the time–temperature conditions under which Pb zoning of various dimensions will be retained given the above criteria. For example, 10-μm scale zones would resist obliteration at 750°C over times greater than the age of the earth; even at 900°C, zones of this dimension would endure for a few million years.

Although the diffusion rates of Pb in zircon do not differ greatly from those of the REE over the investigated temperature range (Fig. 7), the differences in activation energy for diffusion (550 kJ mol^{-1} for Pb vs. 690–840 kJ mol^{-1} for the REE) result in significant differences in diffusion rates at most temperatures of geologic interest. For example, at 800°C, diffusion rates of Dy and Pb will differ by more than 2 orders of magnitude, with diffusion distances (which scale as the square root of D) differing by a factor of ~ 20. Differences become even more pronounced with decreasing temperature. Hence, the preservation of REE zoning observable with CL spectroscopy does not guarantee preservation of Pb isotope signatures on the same scale, as can be seen from the set of curves for Dy zoning also plotted in Fig. 10. Preservation of BSE-observable zoning in Hf or U offers even less evidence for simultaneous preservation of Pb zoning, as diffusion of the tetravalent cations is considerably slower than that of the REE (Cherniak et al., 1997b).

It should be made clear, however, that these diffusion data apply strictly to crystalline zircon. Diffusion may be significantly enhanced in severely radiation-damaged zircon (e.g., Cherniak et al., 1991), thus permitting the obliteration of zoning under much less extreme thermal conditions. Further discussion of the influence of radiation damage, and
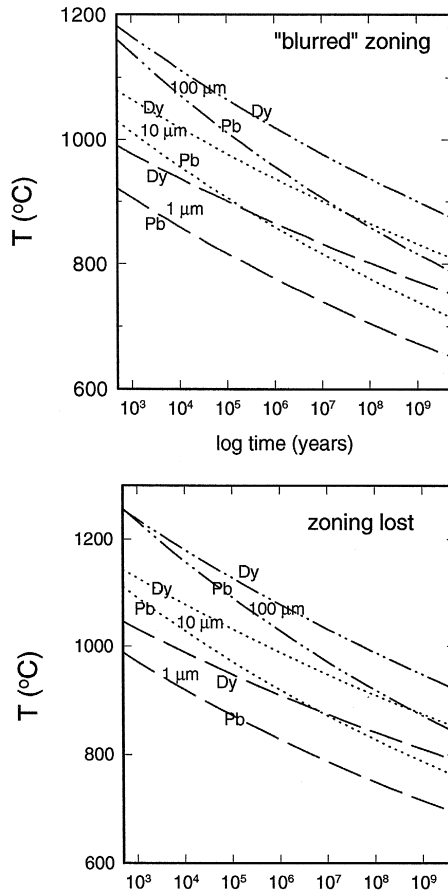
Fig. 10. Preservation of Pb and Dy zoning in zircon. Curves represent maximum time–temperature conditions under which 1, 10 and 100 μm zoning in these elements will be preserved in zircon. For conditions above the upper curves in each group, well-defined zoning will be lost. For conditions above the lower curves, zones will be "blurred" but still retain initial composition in zone centers.

zircon at geologically reasonable temperatures due to volume diffusion. Fig. 11 illustrates this point. The curves represent the percent of Pb loss for zircons of 10- and 100-μm radii when subjected to various time–temperature conditions. Zircons of 10-μm radius would lose only about 1% of their Pb if residing at 750°C for times on order of the age of the earth. Zircons exposed to upper mantle temperatures for extended periods of time would, however, experience significant Pb loss through diffusion, although not always complete resetting, as suggested by stud-
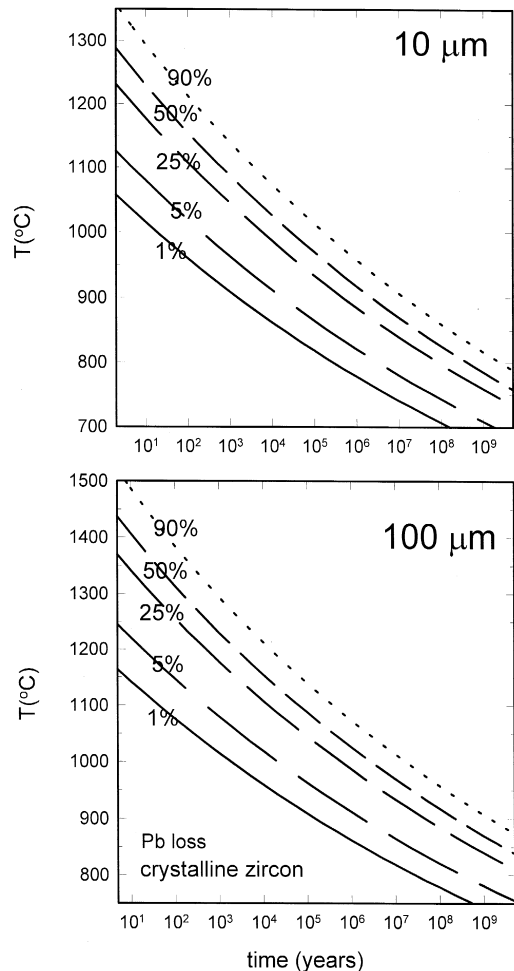

Fig. 11. Conditions for diffusional Pb loss in crystalline zircon for zircons of effective radii of 10 and 100 μm. Curves represent time–temperature conditions under which zircon will lose the indicated fraction of total Pb.

other factors, on Pb transport will be taken up in a subsequent section.

9. Pb loss

Discordant U–Pb ages are on occasion attributed, generically, to "Pb loss." The findings reported here indicate that Pb diffusion in crystalline zircon is remarkably slow, thus it is highly unlikely that significant amounts of Pb will be lost from crystalline

ies of kimberlitic zircons (Scharer et al, 1992; Mezger and Krogstad, 1997).

Pb loss due to diffusion is more likely in metamict zircons, since Pb diffusion has been found to be much more rapid in zircon that has been severely radiation-damaged (Cherniak et al., 1991). Radiation damage, however, takes significant amounts of time to accumulate because of the natural annealing that occurs on geologic timescales (e.g., Lumpkin and Ewing, 1988; Meldrum et al. 1998). The annealing process is such that zircons residing at temperatures above a "critical amorphization temperature" will not become metamict. The critical amorphization temperature is a weak function of activity, i.e., zircon U content and age (Meldrum et al, 1998). The critical amorphization temperature for zircons with 1000 ppm U is about 360°C, and only about 20°C higher for zircons with as much as 10,000 ppm (i.e., 1%) uranium; it varies as a function of zircon age by less than a degree per billion years for a given U content. Zircons exposed to temperatures below the critical amorphization temperature can accumulate damage, but only over long time scales.

Using the expressions derived by Meldrum et al. (1998), we generate curves defining the range of time–temperature conditions that radiation damage in zircon will accumulate to sufficient degree that the zircon becomes metamict. This curve is plotted in Fig. 12. It can be readily noted that times upward of a billion years at low temperatures are required to induce amorphization, and, as noted above, damage sufficient to cause amorphization will fail to accumulate at elevated temperatures. Also plotted against this curve are curves indicating the degree of diffusional Pb loss for metamict zircon. The diffusion data of Cherniak et al. (1991) are used here, since the zircons are considered severely radiation-damaged under these circumstances. Added complexities, such as the possibility that Pb transport rates may change with differing degrees of radiation damage, and the two-stage annealing kinetics of zircon (e.g., Weber et al., 1994; Meldrum et al., 1998) were not considered in this simple model. In severely radiation-damaged zircon, in contrast to crystalline zircon, significant amounts of diffusional Pb loss are possible, even at relatively low temperatures given the enhanced transport rates in the damaged material. Complete resetting of Pb isotopes
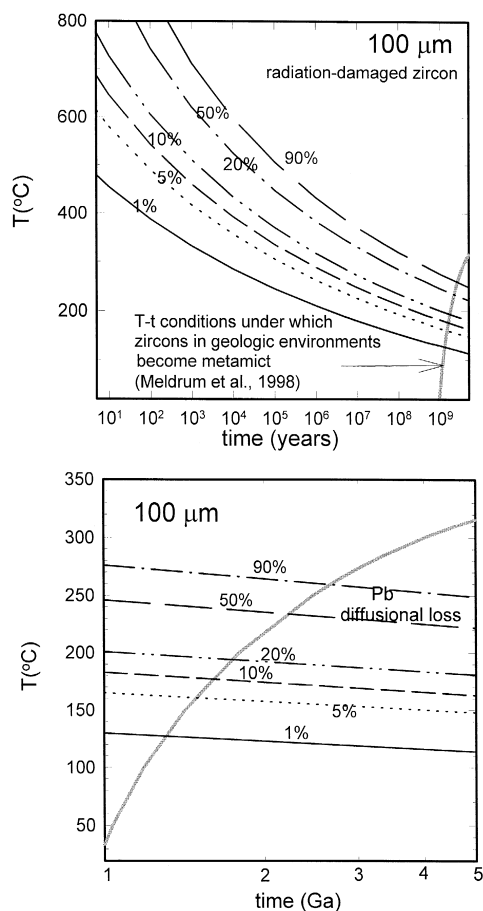

Fig. 12. Conditions for diffusional Pb loss in metamict zircon. Curves represent time–temperature conditions under which a zircon of 100 μm radius will lose the indicated fraction of Pb. These are generated using the diffusion data of Cherniak et al. (1991) for radiation-damaged zircon. Also plotted is a curve indicating time–temperature conditions under zircon with 100 ppm U will become metamict, calculated from the expressions in Meldrum et al. (1998). Times in excess of a billion years, even at near-surface temperatures, are necessary in order for the zircon to accumulate sufficient radiation damage to become metamict. Significant Pb loss will be likely only in the region below this curve.

through volume diffusion could also occur if zircon possessing significant amounts of radiation damage (in residing at low temperatures) were rapidly heated, since the zircon structure is slow to recover crystallinity after experiencing radiation damage beyond certain levels (e.g., Weber et al., 1994; Murakami et al., 1991; Weber, 1990), and Pb diffusion would remain relatively rapid.

It has long been argued (e.g., Silver and Deutsch, 1963) that there exists a correlation between U content and discordance, although there are cases (e.g., Schärer and Allègre, 1982) where this relationship does not seem to apply. Recent work (Sanborn et al., 1998; Stern et al., 1998), however, continues to point to the complexity of the phenomenon of "Pb loss" in natural zircon. While some correlation between U content and degree of discordance in mildly discordant ($< 10\%$) zircons studied has been found, suggesting a possible role of enhanced volume diffusion in radiation-damaged zircon, there is often no such correlation in severely discordant zircon, indicating possible influence of other (non-diffusional) processes, such as recrystallization and various fluid-assisted processes, including physical deformation (e.g., Pidgeon et al., 1998; Sinha et al., 1992), that could significantly alter Pb isotope ratios and zircon U contents. The zircon composition itself can be an important factor influencing the probability of recrystallization. Pidgeon et al. (1998) argue that recrystallization (and consequent exclusion of trace elements from the zircon lattice) is more likely in zircon (or regions of zircon) with high trace element concentrations, as the zircon lattice, experiencing strain due to the significant substitution of these other elements, can become metastable upon cooling from magmatic temperatures.

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