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Zircon reaction and stability of the U-Pb isotope system during interaction with carbonate fluid: experimental hydrothermal study

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Abstract The interpretation of metamorphically induced U-Pb isotopic discordance requires a thorough understanding of zircon-fluid interactions. With this aim we have studied the behaviour of metamict and crystalline zircon phases and their U-Pb systems by cathodoluminescence after treatment by 2M Na₂CO₃ solution at T = 200–800 °C and P = 1–5 kbar for 3–14 days, X-ray diffraction, microprobe and isotope dilution analysis. The data indicate that zircon transformation under hydrothermal conditions depends on the experimental conditions and the degree of structural damage. Reconstitution of defective and impurity-enriched zones of metamict zircon (homogenization of impure element concentrations and increase of crystallinity) was observed at 400 °C and P = 1 kbar. Considerable lead and uranium loss occurred under these conditions. As a result of zircon dissolution, newly formed baddeleyite accommodating U from 2M Na₂CO₃ solution and Zr-Na-silicate were recognized. This process intensified with increasing pressure. Study of crystalline zircon indicates that migration of U and Pb took place only during dissolution of zircon at T above 650 °C. In the presence of carbonate-ions essential U and Pb amounts are lost from metamict zircon at a lower P-T than is typical for greenschist facies metamorphism.

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Introduction

Zircon is commonly used as natural U-Pb geochronometer due to α -decay of radioactive U and Th atoms that are captured in the crystalline matrix up to stable Pb atoms. However, radioactive decay damages the zircon structure from the crystalline to the metamict state resulting in increased zircon solubility and mobility of trace elements. Migration of U and Pb may result in discordant U-Pb isotopic ages. The reliable interpretation of isotopic data requires a clear understanding of the processes occurring in zircon under different natural conditions.

In recent years a number of studies have been undertaken regarding the behaviour of zircon under various metamorphic conditions. Experiments on migration of Pb and U isotopes in zircon provide very important information about its behaviour in natural processes.

The first experimental study of interaction of metamict zircon with 2M NaCl solution at T = 500 °C and P = 1 kbar (Pidgeon et al. 1966) showed that within 24 hours the mineral lost about 50% Pb while U was fully retained. Later it was found (Pidgeon et al. 1974) that Pb and U loss in zircon depended on the temperature, composition of the fluid and degree of the mineral metamictization. It was noted that Pb loss increased (up to 80%) and α -activity decreased within the temperature range 350–800 °C during exposure lasting up to 2 months. The greatest Pb loss, α -activity decrease and the highest rates of lattice defect annealing were observed when zircon was treated with 2M HCl. The least aggressive medium was water. Preliminary annealing of zircon reduced Pb and U loss. Interaction of nonmetamict zircon with river water enriched in Ca during 600 hours at T = 180 °C was accompanied by comparative loss of Pb (15%) and U (17%) (Hansen and Friderrichsen 1989).

Kotov et al. (1991) found that U loss during interaction of XRD amorphous zircon with 2M NaCl

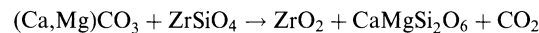
solution at T of 400–600 °C and a P of 1 kbar was much lower than Pb loss.

Sinha et al. (1992) showed that U was lost from crystalline zircon in 2M NaCl solution and 2% HNO₃ solution in conditions similar to amphibolite facies metamorphism (T = 400–600 °C; P = 4–6 kbar). Uranium migration depended more strongly than Pb migration on fluid composition. Using scanning electron microscope data it can be assumed that Pb and U loss can partly be attributed to zircon dissolution. Partial homogenization of chemical zonation and lattice defect annealing was also observed within this temperature range.

All named studies were concerned with stability of U-Pb system in zircons during interaction with acid and neutral solutions.

Although a minor component, CO₂ plays an important role in the Earth's mantle, evidenced by its predominance in volcanic gases and the existence of numerous carbonate-rich deep lavas. Processes of alkaline metasomatism and charnockitization proceeding in conditions of granulite facies metamorphism are connected with these fluids too. So far zircon behaviour and migration of Pb and U in CO₂-rich media has been studied insufficiently. It is supposed that in conditions of CO₂ fluid-induced granulite facies metamorphism zircon dissolution is insignificant (Stahle et al. 1987). Friend and Nutman (1992), who studied the response of U-Pb isotopes to these conditions, concluded that surviving zircon was not modified during this process despite the zircon corrosion and bulk-Zr loss from the granulite facies domain. It was deduced that at a temperature of about 700 °C, at which the CO₂ fluid flux had taken place, there were no radical effects on the U-Pb systematics of the zircons.

Stronger zircon transformation with formation of baddeleyite reaction zones around the zircon grains caused by alkaline metasomatism under mantle conditions according to the reaction:



have been described for kimberlites by Heaman and Le Cheminant (1993).

Because of obvious contradictions in data cited, some further experiments are clearly required. In order to understand the effect of influence of CO₂-rich fluids on the zircon U-Pb isotopic system and to study the dynamics of zircon structure transformation, a series of experiments with metamict and crystalline zircon samples in 2M Na₂CO₃ solution were carried out. As there are two active ions in 2M Na₂CO₃ solution (carbonate-ion and sodium-ion), which can have different effects on Pb and U migration, an additional study of zircon reaction with NaOH and NaCl, respectively, was performed.

Techniques

The experiments were performed in hermetically sealed gold capsules of 3 mm diameter and 50 mm length using hydrothermal

high-pressure equipment with cold seal. An average run contained 10–15 mg of zircon and 50 or 100 mg of solution. Water was used as the pressure medium. The runs were performed at pressures of 1 and 5 kbar with an accuracy ±50 bars and run duration of from 3 to 14 days. Temperature ranged from 200 to 800 °C and was monitored with chromel-alumel thermocouples accurate to ±3 °C. A temperature of 800 °C was reached in less than 0.5 hour. A 2M Na₂CO₃·10H₂O solution was used. After quenching in cold water, the capsules were treated with dilute HCl. On removal from the capsules the samples were twice washed with 5% HCl, then with distilled H₂O.

The samples from the capsules were divided into several parts for X-ray and fission-track investigations, microprobe analysis (EMPA), scanning electron microscope (SEM), cathodoluminescence (CL) and isotopic analysis. The starting samples and run products were not powdered because several of the analytical methods require whole grains.

For polishing, the zircon grains were positioned on a glass plates with a small amount of epoxy resin and were ground by hand with 1–2 µm abrasive, water and detergent up to the middle of the grains. The second and final step was to polish the zircons with the same abrasive on a wool fabric.

The phase composition of both starting material and run products was determined by powder X-ray diffraction (XRD) using a DRON-UM1 diffractometer and standard techniques. The degree of metamictization was assessed visually using diffractograms and by the unit-cell parameters of the sample which were calculated from a set of 6–14 reflections within 20–90° 2Θ_{CoKα}.

The chemical composition of zircon grains and run products was analysed by EMPA using a scanning electron microscope "CamScan" with "LINK AN-10000". Minimum detection limits were approximately 0.1 wt% for the analysed elements. The fine grain structure was studied on the same equipment in backscattering mode and by CL analysis on the microprobe "Camebax" using "LINK AN-10000" and an optical binocular microscope. The fission-track radiography was used to study distribution of U in starting material and run products.

The U-Pb analyses of initial samples and run products followed the method described by Krogh (1973). Part of the treated material, extracted from the capsule, was used for isotopic analyses. All samples were weighted on a micro balance with a precision of ±10 µg. The isotopic measurements were performed on a Finnigan MAT-261 8-collector mass-spectrometer in static mode. The isotopic analysis of Pb was carried out with the aid of silica-gel emitter. The Pb of samples and standards was analysed at T = 1250–1350 °C. Mass fractionation was determined to 0.13 ± 0.03%/amu by 44 measurements of NBS standard SRM 982. Aliquots of NBS standard SRM 983 were analysed over the same period as the samples. Reproducibility of standard SRM 983 analyses (n = 30) in the temperature range 1256–1350 °C is 0.46% for ²⁰⁶Pb/²⁰⁴Pb = 2735, 0.03% for ²⁰⁷Pb/²⁰⁶Pb = 0.071102 and 0.075% for ²⁰⁸Pb/²⁰⁶Pb = 0.013597. Errors of mass-spectrometric analysis are quoted at the 2σ level. The U was analysed as U⁺; U mass fractionation was determined to 0.02 ± 0.05%/amu by 40 measurements of natural U. All samples were spiked with a ²³⁵U/²⁰⁸Pb mixed tracer.

Ratios used in age calculation were corrected by 0.1–0.2 ng of blank Pb and 0.01 ng of blank U. The PBDAT and ISOPLOT programs of Ludwig (1991a, b) were used for calculating U-Pb isotopic ratios and regressions. Correction for common Pb content is based on the Stacey and Kramers model Pb composition (1975) equivalent to the zircon age.

Replicate analyses of the former USSR standard (n = 13) zircon show that measurement of Pb and U concentration has accuracy of 1.2%. Uncertainty in isotopic Pb/U values is 0.5%.

Taking into account the natural heterogeneity of the starting samples, ten isotope analyses of the Pb and U contents for metamict zircon (Table 1) and six for crystalline zircon (Table 2) have been carried out. The reproducibilities of the analyses were ±5.4% and ±4.1% respectively for Pb and U at the 95% confidence limit for the metamict zircon and ±2.5% and ±2.3% for the crystalline material.

Table 1 U and Pb contents in starting metamict zircon (Pb_{rad} radiogenic lead)

No.	Weight, mg	^{238}U , mol/g $\times 10^{-6}$	$^{206}\text{Pb}_{rad}$, mol/g $\times 10^{-6}$	$^{207}\text{Pb}_{rad}$, mol/g $\times 10^{-6}$	Measured composition $^{206}\text{Pb}/^{204}\text{Pb}$	Atomic ratios	
						$^{206}\text{Pb}/^{238}\text{U}$	$^{207}\text{Pb}/^{235}\text{U}$
1	1.4	10.3	3.22	0.522	6990	0.3112	6.957
2	1.5	9.80	3.18	0.515	5900	0.3245	7.249
3	1.4	9.89	3.33	0.528	4810	0.3370	7.784
4	5.2	9.65	3.10	0.502	5600	0.3217	7.179
5	0.4	9.22	3.01	0.494	3690	0.3265	7.394
6	1.7	10.6	3.47	0.561	2935	0.3261	7.282
7	4.8	10.4	3.71	0.541	5800	0.3598	8.176
8	2.5	9.86	3.13	0.630	2125	0.3176	6.300
9	3.2	10.3	3.26	0.520	1140	0.3178	6.989
10	5.0	11.3	3.74	0.583	1830	0.3305	7.096
Weighted average		10.1	3.31	0.530		0.3237	7.240
2 σ		± 1.2 (12%)	10.5 (15%)	± 0.056 (11%)		± 0.015 (4.7%)	± 1 (14%)
95% Confidence limit		0.42 (4.1%)	0.18 (5.4%)	0.022 (4.1%)		0.0059 (1.8%)	0.36 (4.9%)

Table 2 U and Pb contents in starting crystalline zircon

No.	Weight, mg	^{238}U , mol/g $\times 10^{-7}$	$^{206}\text{Pb}_{rad}$, mol/g $\times 10^{-7}$	$^{207}\text{Pb}_{rad}$, mol/g $\times 10^{-7}$	Measured composition $^{206}\text{Pb}/^{204}\text{Pb}$	Atomic ratios	
						$^{206}\text{Pb}/^{238}\text{U}$	$^{207}\text{Pb}/^{235}\text{U}$
1	4.28	4.32	1.66	0.233	5855	0.3838	7.430
2	3.56	4.07	1.56	0.220	8885	0.3819	7.431
3	6.40	4.12	1.57	0.221	14140	0.3801	7.409
4	6.54	4.24	1.61	0.228	19630	0.3805	7.439
5	8.23	4.22	1.60	0.227	20640	0.3806	7.417
6	9.58	4.27	1.63	0.230	14335	0.3812	7.438
Weighted average		4.21	1.60	0.227		0.3813	7.428
2 σ		± 0.18 (4.3%)	± 0.075 (4.7%)	± 0.01 (4.5%)		± 0.0018 (0.48%)	± 0.024 (0.32%)
95% Confidence limit		0.097 (2.3%)	0.004 (2.5%)	0.0055 (2.4%)		0.0012 (0.32%)	0.013 (0.17%)

The difference in measured ratio $^{206}\text{Pb}/^{204}\text{Pb}$ for the starting sample (Tables 1, 2) and treated material may be explained by Pb infection during hydrothermal experiments from gold capsules. Therefore blank contributions were about 2% except for runs 5, 9–12, and 19^b in which the blank rises up to 8% (Table 6). All values of radiogenic ^{206}Pb absolute contents are presented taking into consideration this blank value. The errors of ^{238}U , ^{206}Pb , ^{207}Pb contents of treated samples are quoted at the 20 level.

Sample description

A metamict zircon (sample 9A) was selected from the late Archaean quartz-plagioclase-biotite metasomatite rock of the Uroszero area, Central Karelia. The sample is represented by dark brown opaque short prismatic grains with lustrous surface. The back-scattering image of a typical grain is shown on Fig. 1A. The zircon is heterogeneous. According CL imaging the zircon grains have two main components: (1) the primary matrix; (2) the tongue-like alteration zones developed over the primary zircon which extend from the outer part towards the grain interiors and cut original magmatic zoning. The CL images of 140 metamict zircon grains show that the alteration zones comprise from 25 to 75% of the grain volume. The EMPA shows that the primary matrix contains fewer impurities than alteration zones and that the Fe and U concentration increases and Si decreases towards the grain centre, which probably reflects the initial distribution. Alteration zones of zircon contain a great quantity of impurities: U, Ti, Ca, Mg, Fe,

Mn, Hf, K, Na (Table 3) with the usual decrease towards the central part.

The sample of 100–150 μm size fraction with high concentrations of ^{238}U (10.1×10^{-6} mol/g) and $^{206}\text{Pb}_{rad}$ (3.31×10^{-6} mol/g) and insignificant amount of ^{204}Pb (Table 1) was used for future experiments. The less altered grains have relatively homogeneous distribution of U that can be estimated visually by fission-track radiography (Fig. 1B). In order to simplify the presentation of our data we have used Pb and U in the text in place of $^{206}\text{Pb}_{rad}$ and ^{238}U . The absence of X-ray reflections for zircon powder (Fig. 2, a) and of CL images confirm the amorphous nature of the starting zircon and allow us to use it as representative metamict zircon material.

The crystalline sample was a lower Proterozoic zircon 4518-11 derived from enderbite-gneiss in the Sutamsky Block, in the Eastern Aldan Granulite Gneiss Area. The zircon sample consisted of transparent pink pure and optically homogeneous grains of 110–140 μm in length (Fig. 3A). In this sample it was established that about 30% of grains contain older cores with a higher U content which may be observed by CL and fission-track radiography (Fig. 3B). Crystalline zircon grains have intensive CL and protocores with inclusions and thin growth zones have weak CL images. The single measurement by EMPA of U content in the protocore gives 0.3 wt% (Table 3). Intensive, symmetrical reflections on X-ray powder diagram and calculated unit-cell parameters demonstrate a high degree of starting material crystallinity that assigns it to the crystal zircon group (Fig. 2, a', Table 5). The U and Pb contents determined by isotopic dilution are ^{238}U – 4.21×10^{-7} mol/g and $^{206}\text{Pb}_{rad}$ – 1.60×10^{-7} mol/g (Table 2). Applied air abrasion technique confirmed the presence of an older

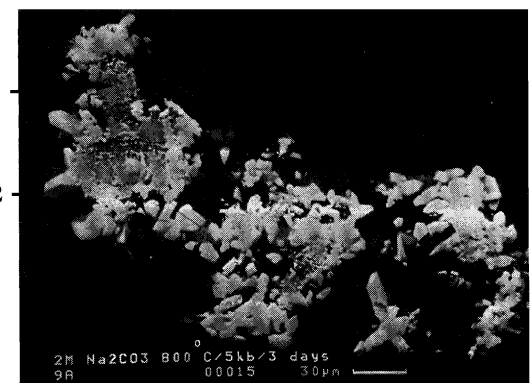
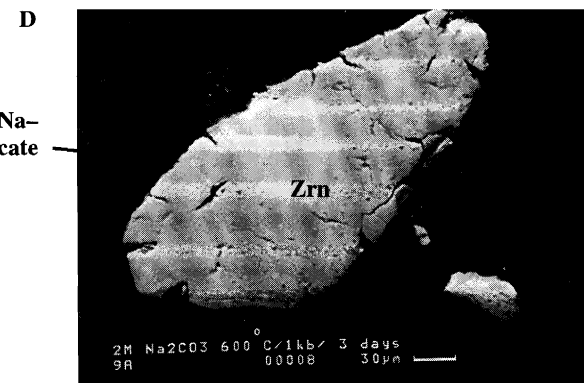
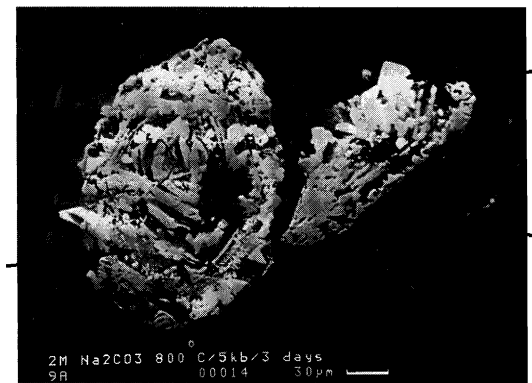
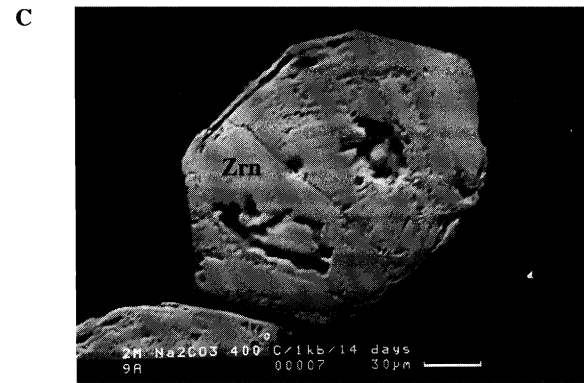
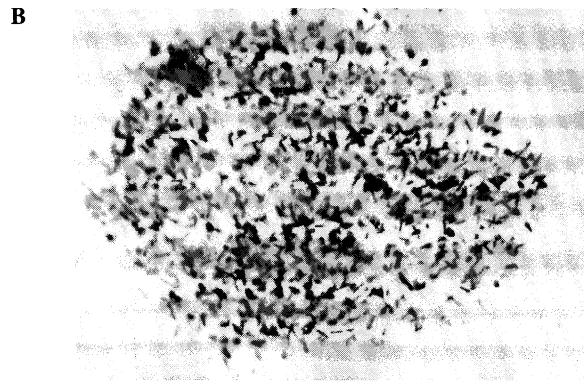
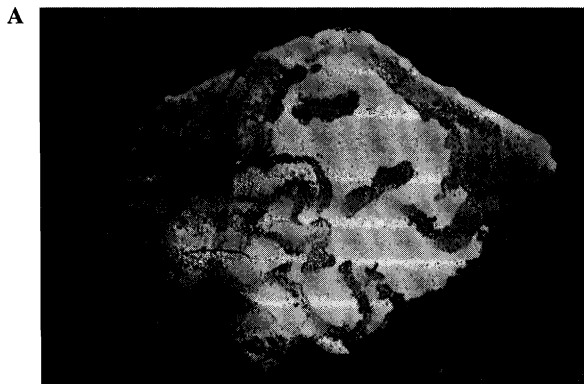


Fig. 1A–H Micrographs of the metamict zircon 9A: **A** The backscattering electron (BSE) image of the starting material, most typical grain: the primary matrix (light) and the altered zones developed over this matrix (dark); **B** Fission tracks demonstrating the relatively even U distribution in grains. **C–G** BSE images of grains after hydrothermal treatment in 2M Na₂CO₃ at the following conditions: **C** 400 °C, 1 kbar, 14 days; **D** 600 °C, 1 kbar, 3 days; **E** 700 °C, 1 kbar, 14 days; **F** 800 °C, 1 kbar, 3 days; **G, H** 800 °C, 5 kbar, 3 days. **C** Initial habit is preserved, recrystallization of the grains with development of growth zones which were not observed in starting grains. **D** Habit alteration; some areas with different chemical composition are revealed (Table 4). Light blocks probably have fewer defects (homogeneous) i.e. highly recrystallized material. **E** Formation of small needle-like Bd 1 crystals and large Bd 2 crystals. **F** Recrystallization of a grain with preserved habit. The homogeneous zircon blocks and fragments in which small Bd 1 crystals are formed replace dissolved zircon matrix. The dark areas are the holes filled with epoxy. **G** The size of the recrystallized (homogeneous grey) zircon areas decreases with the increasing pressure; large Bd 2 crystals (light) are formed along with Bd 1 crystals (**H**)

core enriched in U and Pb and its analytical point on discordia line is situated higher than that of the starting sample (Table 6, Fig. 5B, point 15).

Results

Metamict zircon after treatment by 2M Na₂CO₃

200 °C. Metamict zircon after treatment demonstrated a mixture of variously altered crystals: from originally brown to white brittle sugary grains of starting zircon with the same habit as the original. The analysis of separated brown zircon showed 12% Pb loss and 4% U loss (Table 6, Fig. 4A, point 2a), which resulted in a shift of the representative point on discordia towards the origin (Fig. 4B, point 2a). The material containing a mixture of brown and colourless sugary grains lost 27% Pb and 28% U which did not cause significant changes in the Pb-U ratio (Fig. 4B, point 2b). This indicated that Pb and U

Table 3 Electron microprobe analyses (wt%) of starting metamict (9A) and crystalline (4518-11) zircons before hydrothermal treatment. The total sum including oxygen content is 100 ± 1 wt%;

Grain area	n	Zr	Si	Hf	Fe	Ti	Ca	Mg	Na	U
Starting metamict zircon (9A)										
Primary matrix										
Centre	3	46.6–47.4 47.0	15.7–16.0 15.9	1.2–1.9 1.5	ND–0.2 0.13	ND	ND	ND	ND	0.3–0.6 0.4
Outer part	4	46.0–46.8 46.4	16.0–16.4 16.2	1.4–1.9 1.6	ND–0.1 <0.1	ND–0.1 <0.1	ND	ND–0.1 <0.1	ND–0.1 <0.1	0.1–0.3 0.1 (5)
The alteration zones										
Centre	3	43.3–46.9 45.3	15.3–15.6 15.4	1.3–1.5 1.4	0.3–1.2 0.7	ND–0.1 0.07	0.3–2.0 1.2	ND–0.1 0.03	ND–0.2 0.1	ND
Outer part	9	38.5–46.1 41.9	13.2–17.4 15.4	1.2–2.1 1.7	0.5–3.1 1.5	ND–0.3 0.1	0.7–2.6 1.8	ND–0.3 <0.1	ND–0.5 0.17	ND–2.4 0.6
Starting crystalline zircon (4518–11)										
Centre	2	47.1–48.1 47.6	15.2–15.5 15.3 (5)	1.3–1.9 1.6	ND	ND	ND–0.1 <0.1	ND–0.1 <0.1	ND	ND–0.3 0.1
Outer part	2	48.0–48.6 48.3	15.4	1.1–1.4 1.2 (5)	ND	0.1	ND	ND	ND	ND

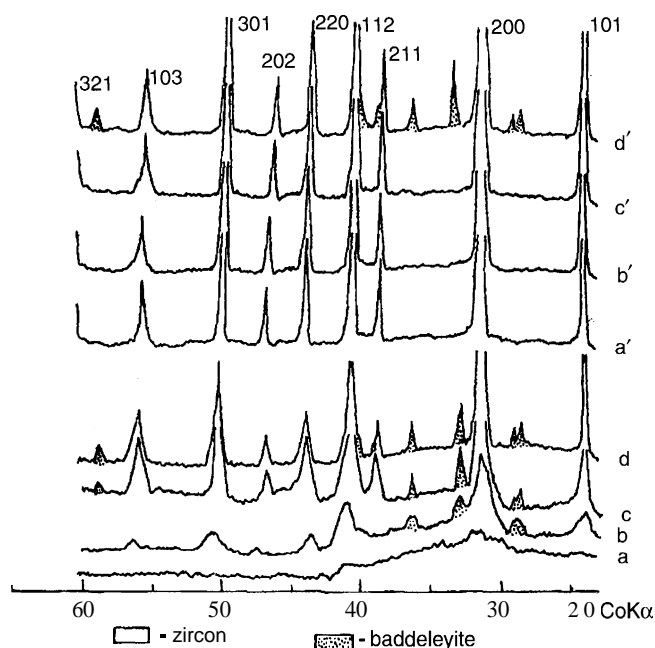


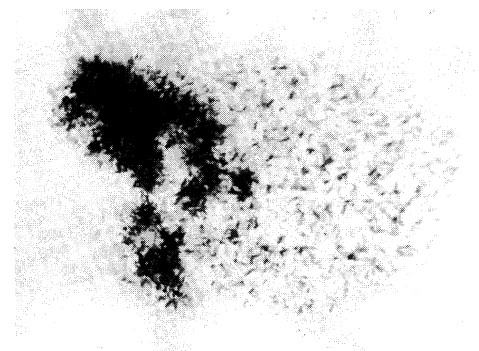
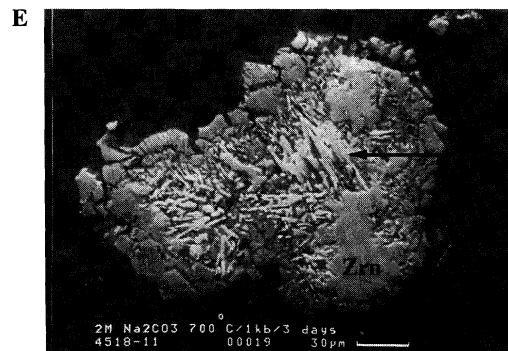
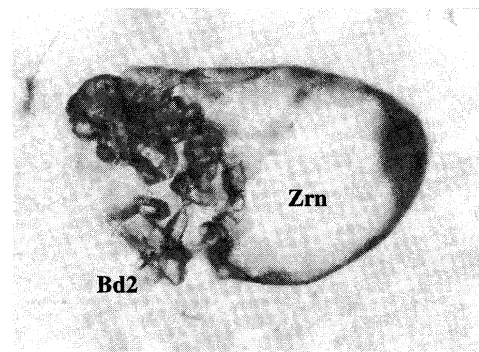
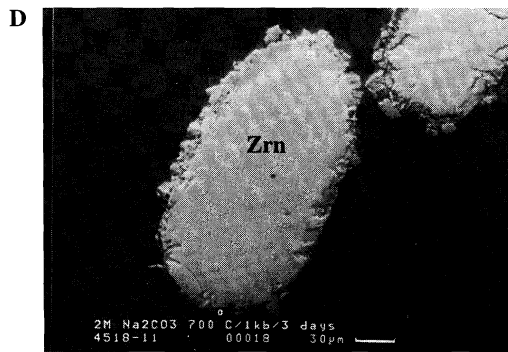
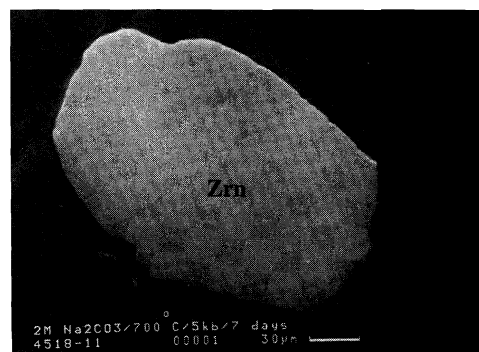
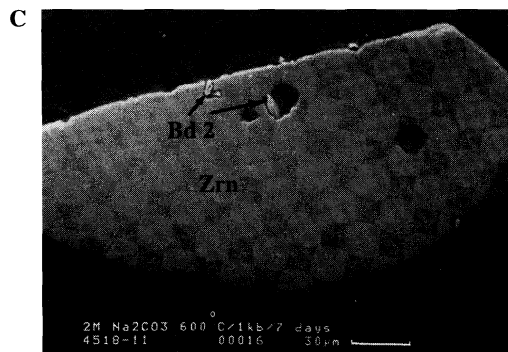
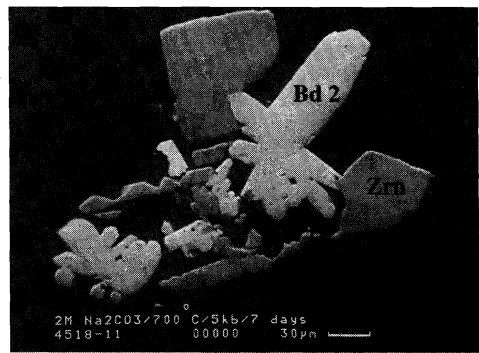
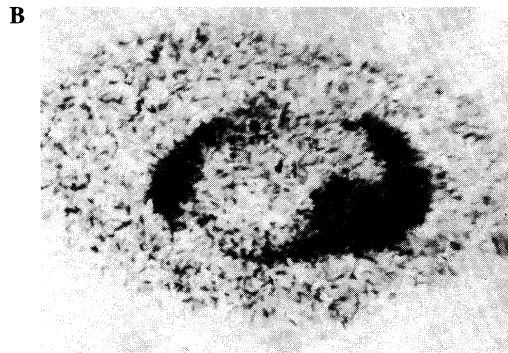
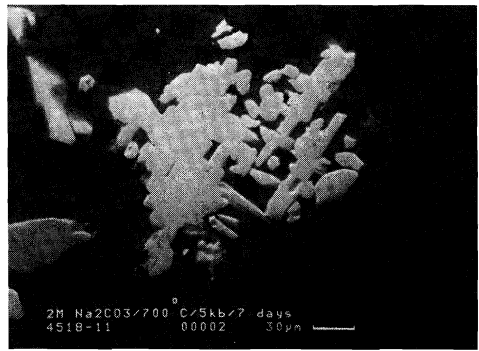
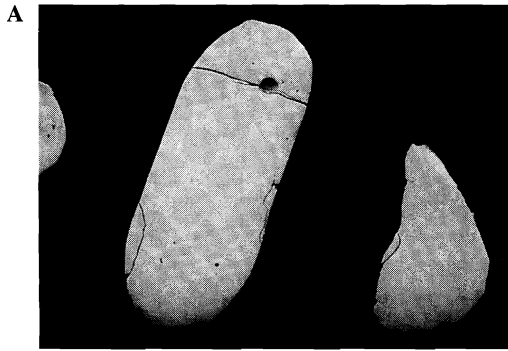
Fig. 2 X-Ray powder patterns for starting (a) and treated metamict (b–d) zircon and for starting (a) and treated crystalline (b'–d') zircon samples (b, b' treatment at 400 °C, c, c' at 600 °C, d, d' at 800 °C)

loss from the white grains was higher than that from the brown grains and U loss was higher than Pb loss.

300 °C. Zircon became uniformly white saccharoidal. The discolouration of the crystals reflected the degree of zircon hydrothermal treatment. The grains had 43% Pb and 35% U in comparison with starting zircon and the respective data point on the discordia showed an upwards shift in relation to the starting material (Table 6, Fig. 4A, B, point 3).

400 °C. A backscattered electron (BSE) image of a treated zircon grain is given in Fig. 1C. Metamict zircon grains showed a considerable increase in CL intensity

n—number of measurements. Primary matrix is the unchanged parts of zircon; the alteration zones are the changed parts of zircon during the metamorphic process (ND not detected)



and change in wave range: the dark CL component became light yellow while the primary blue-green CL changed to brown which signified the beginning of intensive zircon recrystallization.

With the increase of pressure to 5 kbar most of grains became lilac-coloured in CL and more homogeneous. Only the most resistant grains retained their yellow-brown colour of the central zones. Small 1–2 μm baddeleyite crystals with turquoise CL were observed in some grains.

An increase of run duration from 3 to 14 days and pressure from 1 to 5 kbar at the same temperature resulted in a decreased content of element impurities (Table 4) and higher degrees of lattice perfection, which was reflected by an increasing intensity and decreasing line broadening of X-ray diffraction patterns as well as in a decrease in the unit-cell parameters (Table 5, Fig. 2, b).

The Pb concentrations of run products under these conditions did not exceed 9% of that in the starting materials and the U content was correlated to treatment duration and pressure (Table 6). The respective data point was located below the starting point on the concordia diagram (Fig. 4A, B, point 4). With run duration and pressure increasing, the U content in the remaining solid phase was elevated. The representative points shifted on the concordia diagram towards the coordinate origin (Fig. 4B, points 5–7).

600 °C. A BSE image of zircons showed that recrystallization occurred in metamict zircon grains in the form of block shaped domains within the grain (Fig. 1D). Dark blocks were very close in CL to the primary matrix and constituted up to 50% of grains. Light blocks had bright CL which proved total recovery of their crystalline structure. The most unstable grains were fully recrystallized. The unit-cell parameters of zircon became less: $a = 6.601(1)\text{\AA}$; $c = 5.978(2)\text{\AA}$, than those obtained during treatment at T 400 °C (Table 5). Baddeleyite crystals of 1–3 μm with turquoise CL were found on the zircon grain face. The substitution of some entire zircon grains by baddeleyite was observed with increase of pressure to 5 kbar and exposure for 14 days.

Quantitative EMPA showed that non-isomorphous Mg, Fe, and Ca were removed from the zircon. The distribution of impurities and main elements became

more uniform. Sodium saturation of the zircon grains from the Na_2CO_3 solution was observed (Table 4). Sodium contents up to 0.8 wt% in the centre and 9 wt% in outer part of grains were measured. After achieving a Na content of 14–15 wt%, a new phase of Zr-Na-silicate was formed in outlying zones, which had non-coherent boundaries and bright indigo CL.

The 600 °C run products contained 1–5% Pb while the U content depended on pressure and exposure and reached 77 and 150%, respectively, of the starting material (Table 6, Fig. 4A, point 8, 9). The representative points were close to the origin of the concordia diagram (Fig. 4B, points 8, 9).

700 °C. During the 7 day treatment at 1 kbar metamict zircon underwent more intensive phase transformation involving baddeleyite formation. Very fine baddeleyite aggregates, with different degrees of perfection, were found in run products. They ranged from irregularly shaped blocks of tiny particles of 1 μm with a higher portion of impurities and dark turquoise CL (Bd 1) to regular crystals of 10 μm with bright turquoise CL (Bd 2) (Fig. 1E). The chemical compositions of the initial zircon (Si – 15.9 wt%, Zr – 47 wt%) and the zircon matrix residue (Si – 51 wt%, Zr – 13 wt%) near Bd 1 differed considerably. The grains of Bd 1 and Bd 2 contained insignificant amounts of Fe, Ti, Ca, Mg, Na; Bd 1 was enriched in Si in contrast to Bd 2 (Table 4). The U content in run products represented by a baddeleyite and zircon mixture was only 92% of the starting material (Table 6, Fig. 4A, point 10) and no Pb was found. Thus on the concordia diagram the representative point plotted near the origin (Fig. 4B, point 10).

800 °C. After 3 days treatment at 1 kbar, about 50% of starting zircon grains were replaced by baddeleyite (Bd 1 and Bd 2), while other parts of grains retained the recrystallized zircon zones (Fig. 1F). At 5 kbar large regular baddeleyite crystals (Bd 2) grew to 30 μm in length. These crystals formed around the recrystallized fragments of the starting zircon and the aggregate of tiny baddeleyite particles (Bd 1) (Fig. 1G, H).

Quantitative EMPA of the recrystallized zircon zones showed the stoichiometric chemical composition and the very low degrees of impurities which corresponded to samples with high degrees of crystallinity. In contrast baddeleyite crystals Bd 1 and Bd 2 contained some impurities including up to 0.8 wt% U in some spots (Table 4).

The U and Pb content of the large crystals of baddeleyite (Bd 2) was $32.3 \cdot 10^{-6}$ mol/g and $0.088 \cdot 10^{-6}$ mol/g, respectively (Table 6, Fig. 4A, point 13b). The isotope analysis of run products represented by baddeleyite and zircon mixture showed that they contain U from 6.82 to $12.6 \cdot 10^{-6}$ mol/g and Pb from 0.011 to $0.068 \cdot 10^{-6}$ mol/g (Table 6, Fig. 4A, points 11–13a). Their low Pb-U ratios were responsible for the position of the representative points near the origin of the concordia diagram (Fig. 4B, point 11–13b).

←
Fig. 3A–J Micrographs of the crystalline zircon 4518-11. **A** BSE image of starting material, most typical grain; **B** fission tracks demonstrating the U distribution in grain, the core with elevated U concentration. **C–H** BSE images of zircon grains after hydrothermal treatment in 2M Na_2CO_3 at the following conditions: **C** 600 °C, 1 kbar, 7 days; **D, E** 700 °C, 1 kbar, 3 days; **F–J** 700 °C, 5 kbar, 7 days (**I** TEM micrograph; **J** fission tracks). **C** Newly formed Bd 2 crystals; **D, E** the different degrees of alteration of grains at the same experimental conditions: large homogeneous areas of recrystallized zircon, Zr-Na-silicate phase crystals in the outer zones and the needle-like Bd crystals in the inner part. **F, G, H** Zircon crystals completely transformed into baddeleyite (**F**), aggregates of the zircon-baddeleyite mixture (**G**) and completely preserved zircon crystals (**H**). **I** TEM micrograph of zircon with baddeleyite; **J** fission tracks, demonstrating the U concentration in baddeleyite

Table 4 Electron microprobe analyses (wt%) of metamict (9A) and crystalline (4518-11) zircons after hydrothermal treatment (*ND* not detected – <0.1 wt%). *Bd1* is formed on metamict phases of zircon; *Bd2* grows from solution (*Bd*) (baddeleyite)

Grain area	<i>n</i>	Zr	Si	Hf	Fe	Ti	Ca	Mg	Na	U
<i>Meramict sample</i>										
400 °C, 1 kbar, 14 days										
Centre	1	48.6	14.7	1.4	0.2	0.1	0.2	0.2	ND	0.1
Outer part	3	47.7–48.9	14.6–14.7	1.3–1.5	ND–0.2	ND–0.2	0.2	0.14.2	0.1–0.8	ND4.8
		48.2	14.6	1.4	0.1	0.7		0.17	0.47	0.37
600 °C, 1 kbar, 3 days										
Centre	1	48.7	14.7	0.9	0.1	ND	0.1	ND	0.8	0.3
Outer part	1	41.0	13.9	0.8	0.1	ND	0.3	ND	9.3	0.6
Zr-Na-silicate	2	38.2–38.9	11.7	1.1–1.2	0.2–0.3	ND	0.6–0.7	ND–0.3	14.1–15.0	0.2–0.5
		38.6		1.1 (5)	0.2 (5)		0.6 (5)	0.1 (5)	14.6	0.3 (5)
700 °C, 1 kbar, 7 days										
Bd1	1	67.6	2.4	2.1	ND	0.1	ND	0.2	ND	0.4
Bd2	1	71.3	ND	1.7	0.1	0.1	0.2	0.1	0.2	0.5
Matrix near Bd1	1	13.1	51.0	1.4	0.3	0.5	0.1	ND	ND	ND
800 °C, 5 kbars, 3 days										
Bd1	1	66.4	2.2	2.3	0.1	0.5	0.2	0.1	0.2	0.8
Bd2	1	71.0	ND	1.8	0.1	0.1	ND	0.2	ND	0.8
Matrix near Bd1	1	51.1	4.9	1.1	1.7	0.3	4.0	1.4	2.7	1.2
Zircon zone	1	48.2	15.0	1.8	0.2	ND	ND	ND	0.2	ND
<i>Crystalline sample</i>										
400 °C, 1 kbar, 7 days										
Centre	1	48.0	15.4	1.4	ND	0.1	ND	ND	0.2	ND
Outer part	1	49.6	14.6	1.1	ND	ND	ND	0.2	ND	ND
600 °C, 1 kbar, 7 days										
Outer part	2	47.9–48.1	15.1–15.5	0.8–1.5	ND	0.1	ND	ND–0.1	ND–1.1	ND
		48.0	15.3	1.1 (5)				0	0.5 (5)	
Matrix near Bd2	1	46.4	16.3	1.3	ND	ND	0.1	ND	0.4	ND
Bd2	1	68.9	1.1	1.7	ND	0.1	0.2	ND	0.9	ND
700 °C, 1 kbar, 3 days										
Little-changed grain										
Centre	1	49.6	15.0	0.5	ND	ND	ND	ND	ND	0.1
Outer part	2	48.2–48.8	14.6–15.0	1.0–1.2	ND	ND–0.1	0.1	0.24.3	ND–0.6	ND–0.1
		48.5	14.8	1.1		<0.1		0.2 (5)	0.3	<0.1
Zr-Na-silicate	2	31.5–32.3	14.1–15.0	0.6–0.7	ND	ND	ND–0.1	0.1	17.1–19.0	ND–0.3
		31.9	14.6	0.6 (5)			<0.1		18.1	0.1 (5)
Highly changed grain										
Preserved zircon	2	48.9–49.0	14.9	0.8–1.2	ND	ND	ND	0.14.3	ND–0.3	ND–0.4
		48.9 (5)		1.0				0.2	0.1 (5)	0.2
Bd2	1	67.5	3.0	1.3	ND	0.1	ND	ND	0.3	ND
Matrix near Bd2	3	41.6–58.0	7.7–16.8	0.5–1.2	ND	ND	ND–0.2	ND–0.2	1.0–4.3	0.1–0.6
		50.4	12.3	0.9			0.1	0.1	2.5	0.3
700 °C, 5 kbar, 7 days										
Preserved zircon grain										
Centre	1	48.1	15.3	1.4	ND	ND	0.1	ND	ND	0.4
Outer part	2	47.0–47.9	14.9–16.4	1.0–1.4	ND	ND	ND	ND	ND	ND–0.5
		47.5	15.7	1.2						0.2 (5)
Changed zircon grain										
Centre	1	45.8	15.1	1.2	ND	ND	ND	ND	ND	0.5
Outer part	1	47.5	15.5	0.9	ND	ND	ND	0.2	0.2	ND
Bd2	2	70.2–71.2	0.1–0.3	1.9–2.2	ND	ND–0.2	ND–0.1	ND–0.2	ND–0.2	0.2–0.5
		70.7	0.2	2.0 (5)		0.1	<0.1	0.1	0.1	0.3 (5)

Crystalline zircon after treatment by 2M Na₂CO₃

400 °C. At this temperature crystalline zircon grains were somewhat discoloured. No perceptible changes in their lattice and phase composition were found (Fig. 2, b', Table 5). The content of Na captured from solution did not exceed 0.2 wt% (Table 4).

The U and Pb loss were 5 and 3%, respectively (Table 6, Fig. 5A, point 16). The Pb-U ratio is practically unchanged as reflected by the location of the representative point near the starting material on the concordia diagram (Fig. 5B, point 16).

600 °C. After 7 days at 1 kbar needle-shaped baddeleyite (Bd 2) particles with turquoise CL appeared

Table 5 Run products from hydrothermal treatment of zircon in 2M Na₂CO₃ after CL, EMPA and XRD data. The errors are given in parentheses (*Zrn* zircon. *Bd* baddeleyite)

T, °C	P, kbar	Run duration. days	Phase composition	Zircon unit-cell parameters. Å		
				a	c	V
Metamict sample 9A						
Starting conditions						
		3	Zrn	ND		
		14	Zrn + Bd	6.619(2)	5.976(3)	261.8(2)
400		3	Zrn + Bd	6.612(1)	5.983(2)	261.6(2)
		3	Bd + Zrn	—	—	—
	5	14	Zrn + Bd	6.609(1)	5.980(2)	261.2(1)
	1	3	Zrn + Bd + Zr-Na-Si-phase"	6.601(1)	5.978(2)	260.5(2)
600	5	14	Bd + Zrn	—	—	—
700	1	7	Bd + Zrn ^a	ND		
	1	3	Bd	ND		
800	5		Bd + Zrn"	ND		
			Bd	ND		
Crystalline sample 4518-11						
Starting conditions						
400	1	7	Zrn	6.604(1)	5.983(2)	260.9(2)
		14	Zrn	—	—	—
		14	Zrn	6.604(1)	5.980(1)	260.8(1)
600	1	7	Zrn + Bd"	6.604(1)	5.986(2)	261.1(2)
650	1	7	Zrn + Bd	6.604(1)	5.986(1)	261.1(2)
	1	3	Zrn + Bd + Zr-Na-Si-phase ^a	6.605(1)	5.985(2)	261.1(2)
700		7	Zrn + Bd	6.606(1)	5.985(3)	261.2(2)
	5	7	Zrn + Bd	—	—	—
800	1	7	Zrn + Bd	6.606(1)	5.984(2)	261.1(2)

"Phase is not determined by XRD-method due to small amount

in the imperfect parts of zircon (Fig. 3C). According to EMPA, the zircon along the boundary with baddeleyite was depleted in Zr (46.4 wt%) and slightly enriched in Na (0.4 wt%) while baddeleyite contained up to 0.9 wt% Na (Table 4) which indicated active diffusion of atoms in those areas. The Pb and U loss in run products did not exceed 5% (Table 6, Fig. 5A, point 17), and the position of the representative point on the concordia diagram did not change essentially (Fig. 5B, point 17).

At the same time the shift of experimental points (especially 16 and 17) to the right of that representing the starting crystalline zircon was explicable by the dissolution of the rim and enrichment of the whole sample in the older core component.

650 °C. After 7 days of treatment at 1 kbar the zircon grains appeared as white sugary crystals. The SEM study showed enlargement of the baddeleyite crystals. Baddeleyite formation is also confirmed by XRD (Table 5).

The Pb and U content in run products was 78 and 120% respectively of the starting material (Table 6, Fig. 5A, point 18). On the concordia diagram the analytical point moved towards the origin (Fig. 5B, point 18).

700 °C. After 3 days at 1 kbar, in the case of the perfectly crystalline grains the formation of 20–30 µm thick baddeleyite rims were observed on 60% of the zircon grains and, in addition, a Zr-Na-silicate phase overgrew this baddeleyite (Fig. 3D). This location of the Zr-Na-silicate and baddeleyite phases pointed to inter-

action of the exterior zones with the fluid. Fairly uniform recrystallized zircon is observed in the middle of the grains. The grain stability was confirmed by absence of Na in the inner parts (Table 4, little-changed grains).

In zircon grains, where the crystalline lattice was less perfect (structure defects, impurity atoms, etc.), baddeleyite formation involved the whole grain with the appearance of Zr-Na-silicate in the outermost zones (Fig. 3E). The baddeleyite particles of 1–30 µm in length and not more than 2–3 µm in width exhibited a specific needle shape and contained 0.3 wt% Na and up to 0.5% U (EMPA). Zircon grains were divided by hand into central part and brittle rim enriched by baddeleyite and Zr-Na-silicate phase. The U-Pb analysis of outer zones revealed that the Pb/U ratios were lower than those in the starting material (Table 6, Fig. 5A and B, point 19b). This may have led to a highly discordant data point on the concordia presentation. The separated central part with older core had elevated Pb (132%) and U (160%) content in comparison to the starting zircon (Table 6, no. 19a). This fact could be explained by higher Pb and U content in the core of this sample, which was proved by higher Pb and U content in abraded grains of the starting zircon (Table 6, no. 15).

Increase of pressure to 5 kbar results in considerable intensification of the transformation process in zircon grains. The total-sample analysis shows that 30% of the grains have fully converted to large regular baddeleyite crystals 4–100 µm long with bright CL colour (Fig. 3F). About 50% of the grains have retained outer zones of

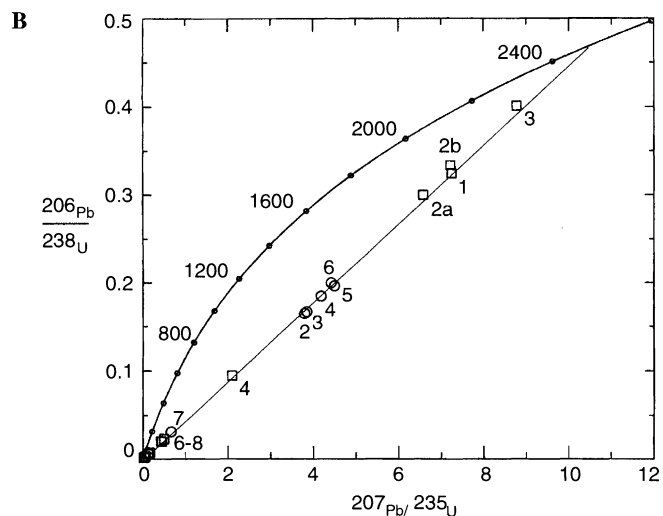
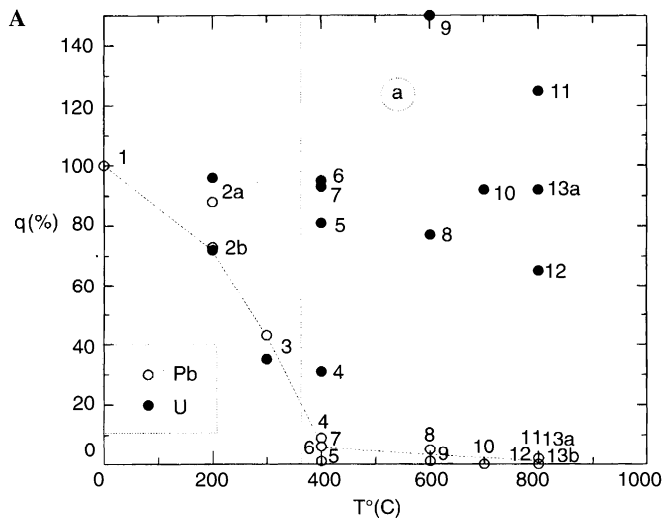


Fig. 4A, B Metamict zircon 9A treated in 2M Na_2CO_3 : **A** (q % contents of Pb and U in run products relative to original sample at various temperatures, a field of baddeleyite formation). Point numbers correspond to fraction numbers in Tables 6 and 7. **B** U-Pb concordia diagram for zircon after hydrothermal treatment. (Boxes results of the interaction of zircon with 2M Na_2CO_3 , Table 6, circles results of the interaction of zircon with 1M Na_2CO_3 , 1M NaOH and 1M NaCl. (Table 7)

more perfect zircon while originally more metamict inner zones have decayed under formation of baddeleyite crystal aggregates (Fig. 3G, I, J). A 20% of the grains were fully preserved (Fig. 3H) and retained their primary U distribution. These grains had bright pink-lilac CL and did not contain any Na (Table 4).

Discussion

In the experiments on reactions of zircon with 2M Na_2CO_3 in solution the most active components are Na^+ , CO_3^{2-} and OH^- . To estimate the influence of these ions upon Pb and U mobility in the metamict zircon, the

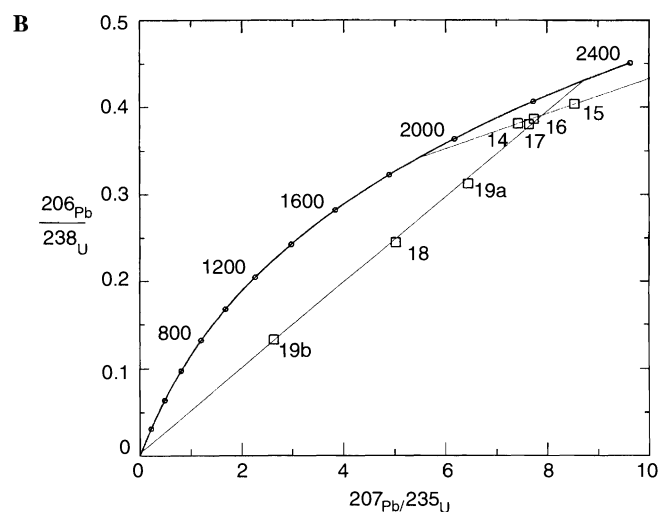
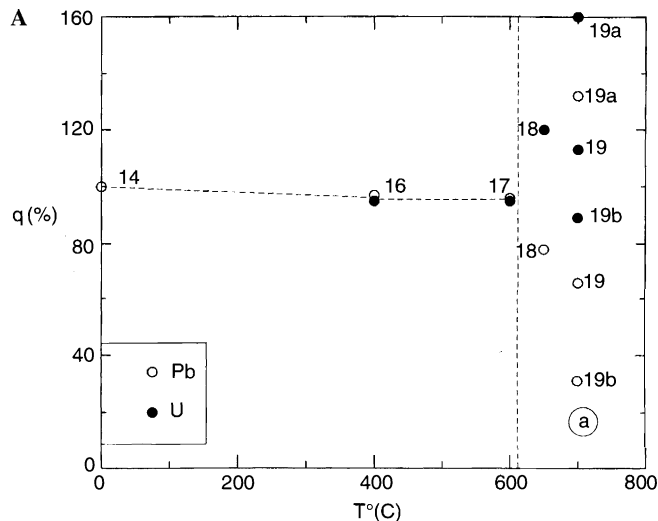


Fig. 5A, B Crystalline zircon 4518-11 treated in 2M Na_2CO_3 : **A** (q % contents of Pb and U in run products relative to original sample at various temperatures, a temperature range for baddeleyite formation). Point numbers correspond to fraction numbers in Table 6. **B** U-Pb concordia diagram for zircon after hydrothermal treatment

experiments at $T = 400\text{ }^\circ\text{C}$, $P = 1\text{ kbar}$, run duration 7 days with the 1M NaOH, 1M NaCl and 1M Na_2CO_3 solutions were carried out.

In 1M NaOH solution lead remains in the solid phase in an amount from 58 to 76%. This fact is explained by zircon dissolution and by formation of Zr-hydroxide, sodium silicate and hard insoluble lead silicate (Polyanskiy 1986). Therefore the analysed solid products may contain some quantity of a newly formed phase of Pb silicate. Unlike Pb, content of U in run products exceeds 100% at the same condition. The excess U content over 100% in run products of zircon with solution at the temperature of $400\text{ }^\circ\text{C}$ is connected with zircon decomposition and formation of $\text{Zr}(\text{OH})_4$, which is dehydrated by heating with baddeleyite formation.

In the experiment with 1M NaCl, Pb and U were lost from the metamict zircon (4 and 8% respectively)

Table 6 U and Pb contents in run products of zircons interaction with 2M Na₂CO₃ solution

No. of fraction	Weight, mg	T, °C	P kbar	t day	²³⁸ U		²⁰⁶ Pb _{rad.}		Measured atomic ratios			Calculated atomic ratios	
					mol/g x 10 ⁻⁶	q ^g , %	mol/g x 10 ⁻⁶	q ^g , %	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁸ Pb	²⁰⁶ Pb/ ²³⁸ U	²⁰⁷ Pb/ ²³⁵ U
Metamict zircon 9A													
1	Starting conditions				10.1		3.31		—		—	0.3237	7.240
2 ^a	1.6	200	1	14	9.69	96	2.91	88	4010	6.184	14.94	0.3005	6.578
2 ^b	5.46	200	1	14	7.26	72	2.42	73	5170	6.281	16.20	0.3336	7.220
3	2.23	300	1	14	3.57	35	1.43	43	3650	6.173	14.88	0.4013	8.784
4	0.7	400	1	3	3.13	31	0.29	9	1270	5.893	13.09	0.0949	2.094
5	3.89	400	5	3	8.20	81	0.018	1	355	5.072	6.438	0.0022	0.049
6	2.27	400	1	14	9.54	95	0.194	6	740	5.890	11.83	0.0203	0.428
7	2.82	400	5	14	9.41	93	0.213	6	1960	5.972	14.09	0.0226	0.502
8	2.4	600	1	3	7.79	77	0.154	5	2690	6.004	15.20	0.0198	0.443
9	0.94	600	5	14	15.1	150	0.036	1	130	4.071	3.383	0.0024	0.049
10	0.88	700	1	7	9.32	92	0.014	0	340	4.860	6.166	0.0020	0.040
11	1.41	800	1	3	12.6	125	0.068	2	210	4.589	4.508	0.0054	0.119
12	1.57	800	1	7	6.82	65	0.011	0	125	4.123	3.303	0.0016	0.031
13 ^c	3.63	800	5	3	9.24	92	0.067	2	2935	6.021	15.20	0.0072	0.161
13 ^d	0.92	800	5	3	32.3	320	0.088	3	1140	5.796	11.88	0.0027	0.061
Crystalline zircon 4518-11													
14	Starting conditions				4.21		1.60		—		—	0.3813	7.428
15	0.49	Starting abraded			4.69	112	1.90	118	2250	6.305	3.940	0.4040	8.544
16	2.35	400	1	7	4.01	95	1.55	97	4760	6.766	4.084	0.3865	7.742
17	4.83	600	1	7	4.01	95	1.53	96	5140	6.753	4.124	0.3803	7.643
18	2.17	650	1	7	5.04	120	1.24	78	795	6.083	3.646	0.2449	5.014
19	3.47	700	1	3	4.76	113	1.06	66	2670	6.687	4.637	0.2219	4.434
19 ^e	0.85	700	1	3	6.77	160	2.11	132	4460	6.566	4.930	0.3121	6.438
19 ^f	1.19	700	1	3	3.75	89	0.50	31	450	5.826	3.464	0.1329	2.624

^a Brown zircon

^b The mixture of brown and white zircons

^c Phase mixture

^d Baddeleyite-2

^e Core of grains

^f Rim of grains

^g q percentage U and Pb in run products, in relation to U and Pb contents in starting zircon sample

(Table 7) and formation of new phases was not observed. The results of the experiments on reaction of metamict zircon with NaCl do not contradict the earlier data reported by Pidgeon et al. (1966, 1974). The position of the analytical points plotted on concordia is indistinguishable, despite the observed differences in Pb and U losses under 1M NaOH and 1M NaCl conditions (Fig. 4B).

In 1M Na₂CO₃ solution the carbonate-ion substitutes for the silicate-ion preventing formation of lead silicates. The main portion of Pb is in the form of carbonate, perhaps co-precipitate with Ca, which according to microprobe analysis occurs in metamict zircon (Table 3). These carbonates are well dissolved by 5% HCl during sample washing, before the decomposition of run products. Perhaps the difference in Pb behaviour in 1M Na₂CO₃ and 1M NaOH explains the different percentage of Pb loss in these solutions: 92 and 24–42% respectively, that is Pb in the presence of carbonate-ions is transferred into the liquid more readily (Tables 6 and 7).

The high U content in run products of metamict zircon with 1M Na₂CO₃ as 2M Na₂CO₃ apparently is explained by the fact that during zircon dissolution the crystallizing baddeleyite captures a great quantity of U from the solution (Table 7).

Consequently, comparison of results of hydrothermal experiments in three solutions demonstrates that disturbance of the U-Pb isotopic system in zircon is more noticeable when carbonate-ions are present (Fig. 4B).

The differences in metamict and crystalline zircon behaviour during interaction with 2M Na₂CO₃ solution are connected mostly with the difference in defectiveness of zircon structure. The transformation of these zircons occurs in different temperature ranges. For example, trace element redistribution in metamict zircon begins at 200 °C and under this condition the essential proportion of Pb and U is dissolved. In the temperature range of 200–300 °C the predominant U loss is observed. These results are confirmed by the well-known fact of U behaviour in carbonate solutions in which U forms soluble complexes with (CO₃)⁻². Such a chemical peculiarity of U causes the shift of the corresponding experimental points relative to the point of starting metamict zircon (Table 6, Fig. 4B, points 2b, 3), upwards along discordia to the upper intercept with the concordia curve. Leaching of Pb and U from unmetamict zircon by spring water (Ca of 161 ppm; pH of 7.3) under hydrothermal conditions also showed removal of 17% of U and 15% of radiogenic Pb (Hansen and Friderichsen 1989).

Recrystallization of metamict zircon begins at 400 °C and is followed by practically full loss of Pb (90%) and the essential U loss also (69%) (Table 6, no. 4). Simultaneously high U baddeleyite formation takes place. But the value of U loss from zircon cannot correctly be calculated because of the presence of these two mineral phases, which are difficult to separate from each other. It should be mentioned too that only a part of the material in the capsule was used for isotope analysis, therefore

Table 7 U and Pb contents in run products of metamict zircon interaction with 1M NaOH and 1M NaCl solutions at $T = 400$ °C, $P = 1$ kbar, 7 days

No. of fraction	Fluid composition	Weight, mg	²³⁸ U mol/g × 10 ⁻⁷	q^a , %	²⁰⁶ Pb _{rad.} mol/g × 10 ⁻⁷		Measured atomic ratios			Calculated atomic ratios		
					q^a , %	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁸ Pb	²⁰⁶ Pb/ ²³⁸ U	²⁰⁷ Pb/ ²³⁵ U		
1	Starting composition (average)	—	101	100	33.1	100	—	—	—	0.3237	7.240	—
2	1M NaOH	1.8	115	114	19.3	58	12035	5.975	22.75	0.1674	3.843	3.763
3	1M NaOH	1.61	155	152	25.1	76	19075	5.942	23.51	0.1626	4.157	4.489
4	1M NaOH	1.46	137	135	24.6	74	22610	5.954	23.24	0.1798	4.489	4.440
5	1M NaOH	1.42	112	111	21.9	66	4000	5.899	18.13	0.1954	4.440	0.642
6	1M NaCl	3.56	93.5	92.0	18.6	56	3360	6.036	16.63	0.1986	—	—
7	1M Na ₂ CO ₃	2.81	96.2	90.0	2.79	8.0	1680	5.956	13.73	0.0290	—	—

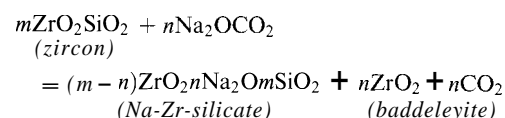
^a q percentage U and Pb in run products, in relation to U and Pb contents in starting zircon sample

the U content also depended on the quantity of baddeleyite in the sample taken. Due to this fact the U contents in run products are observed essentially to be scattered. The increase of pressure and of the run duration at this temperature result in an increase of the U content in run products due to intensification of baddeleyite formation (Table 6, nos. 5–7).

High U contents measured in separated baddeleyite crystals (7000 ppm) is consistent with data reported by Davis (1977). He showed the significantly higher U content of the baddeleyite rim (318 ppm) formed during mantle metasomatic processes in comparison with the zircon megacryst (29 ppm).

While there is no considerable alteration in the crystalline zircon in the temperature range up to 600 °C, when the formation of baddeleyite begins, baddeleyite is mainly formed in structurally more defective central parts of the studied grains: If the central part is well protected by a perfect rim, the grain has high stability. The Na-Zr-Si-phase is formed intensively on metamict zircon at 600 °C and on crystalline at 700 °C.

The formation of baddeleyite and Na-Zr-silicate corresponds to the following reaction:



As our experiments show the main final products – recrystallized zircon and baddeleyite, are formed over a wide temperature range, while Na-Zr-silicate formation is observed at some intermediate temperatures. The latter process decreases at 800 °C, 5 kbar and formation of baddeleyite becomes the main process. It was noted that the formation of baddeleyite occurs by two means: (1) fine grains of Bd 1 form on metamict zircon and in the most defective parts of crystalline zircon; (2) regularly shaped crystals of Bd 2 indicate their growth from solution as a result of the dissolution of the starting zircon. The grains of Bd 2 have low content of trace elements. The residual matrix of zircon is depleted in Zr and rich in Si, Fe, Ca, Mg. While for its crystallization baddeleyite captures U from the solution, inheritance of radiogenic lead was not marked. But such a possibility can not be excluded for Bd 1 because the reaction of its formation takes place in solid phase.

The study of the treated metamict zircon by powder X-ray diffraction shows that practically full lattice recovery occurs at 600 °C, the unit-cell parameters (Table 5) being close to those of samples with a maximum degree of crystallinity such as kimberlite zircons [$a = 6.6043(4)$ Å; $c = 5.9797(5)$ Å] and artificially annealed zircons at high temperature (Fig. 2, c), while recovery of the metamict zircon lattice is established at 870 °C under dry atmospheric conditions (Lipova et al. 1965).

It is necessary to point out that the degree of reconstruction of starting metamict zircon structure in the process of recrystallization is higher than that for the crystalline sample. The crystalline zircon unit-cell

parameters are constant in all experiments including the maximum temperature. This fact allows to suppose that there is no full reconstruction of starting crystalline zircon structure even at 800 °C, unlike the metamict sample. This can be explained by the higher activation energy required for reconstruction of the crystalline zircon lattice in comparison with the defective metamict sample (Makeev and Maslenikov 1997).

The process of new phase formation is intensified at a given temperature with pressure and duration increasing, while Pb and U loss from the zircon depend mostly on the temperature. A considerable portion of U and Pb is preserved in the fragments of crystalline zircon structure despite the transformations, including partial dissolution of its matrix. Moreover, the investigations demonstrate that even crystalline zircon grains belonging to the same generation have a wide range in their degree of structure distortion. For example, EMPA data reveals wholly preserved zircon grains in the run products of the experiment at $T = 700$ °C, $T = 5$ kbar along with ones that have reacted.

Various degrees of zircon U-Pb system disturbance, depending on the lattice defects, are observed under granulite facies metamorphism: from the entire loss of age information (e.g. Baur et al. 1991; Kroner 1995) to the preservation of the magmatic zircon age (e.g. Friend and Nutman 1992). In the latter study it was concluded that despite zircon corrosion and bulk-Zr loss from the granulite facies domain, at the temperature (≈ 700 °C) at which reaction with CO₂ fluid took place, the U-Pb systematics of the surviving zircon were not modified.

The new results lead to some general "rules" for the interpretation of discordia trends in zircons related to effect of CO₂ fluid with accompanied migration of Pb and U and baddeleyite formation. In the case of zircon interaction with CO₂ fluid the lower intercept age would date the metamorphic processes as granulite facies metamorphism. The lower intercept age could also date the mantle metasomatic event resulting in desilicification of mantle zircon xenocrysts (Kresten 1973); likewise the date of contact metamorphism of marbles and associated skarn development resulting in the breakdown of original zircon (detrital?) in dolomite (Kato and Matsubara 1991); and possibly the date of meteorite impact where zircon is affected (El Goresy 1965).

A CL study of metamorphic zircon in order to reveal baddeleyite should precede U-Pb age determination. Correct dating requires both the baddeleyite and the metamorphic zircon rims to be separated for the U-Pb study. Then it is possible to obtain both the zircon age and the age of metamorphism by the baddeleyite dating from the same sample.

Concluding remarks

Analysis of the data shows that in the presence of carbonate-ions and at evaluated P and T conditions the following processes occur in zircon:

1. Zircon recrystallization is accompanied by annealing of lattice defects, averaging of the major and trace element distribution and its partial removal. The degree of lattice recovery of zircons in the course of recrystallization is higher for initially metamict zircons than for crystalline zircons under same conditions.

2. In the course of zircon recrystallization new phases are formed: baddeleyite and Zr-Na-silicate. The intensity of baddeleyite formation depends on the degree of structure defectiveness of the initial grains, on temperature (400–800 °C), pressure and duration of run. During zircon dissolution the newly formed baddeleyite takes the majority of U atoms released into its crystalline structure. The formation of Zr-Na-silicate occurs in the outer zones. This process is most intensive in metamict zircons at 600 °C, 1 kbar, and in crystalline zircons at 700 °C, 1 kbar.

3. The obtained data show that mobility of U and Pb under aforementioned conditions is conditioned by the defectiveness of zircon structure. The ability for U to migrate from metamict zircon is slightly higher than for Pb in the temperature interval of 200–300 °C. At higher temperatures U loss is masked by U-enriched baddeleyite formation. Migration of Pb and U from a crystalline zircon into carbonate solution is effected via the mineral dissolution.

4. In the case where CO₂ fluid affects the age of a distortion of the zircon U-Pb system and baddeleyite is formed, this event is determined by the lower intercept discordia trend with concordia while the upper intercept gives the zircon age.

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