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Interaction of Metamict Zircon with Fluids of Various Composition

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Abstract—Interaction of metamict zircon with solutions of various composition (H_2O, 1 m NaCl + 0.5 m HCl, 1 m NaCl, 1 m $NaHCO_3$, 0.1 m Na_2CO_3, 1 m Na_2CO_3, 2 m Na_2CO_3, and 1 m NaOH) was examined at temperatures of 25–800°C, pressures of 1 and 5 kbar, and exposure times of 3, 7, and 14 days. The choice of fluid compositions was determined by the fact that aqueous, chloride, and carbonate solutions are the principal components of postmagmatic, metamorphic, and metasomatic fluids that can affect zircon in nature. Occurring in contact with these solutions, metamict zircon congruently and incongruently dissolves competing with the sorption of elements, crystallization of newly formed phases, and the restoration of the crystal structure. The intensities of these processes are controlled by the temperature, pressure, exposure time, and the pH and composition of the solution.

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INTRODUCTION

Naturally occurring zircons show traces of their postcrystallization alterations and transformations under the effect of various external and internal factors. A major internal process affecting the crystal structure of zircon is the radioactive decay of U and Th atoms captured during the crystallization of this mineral. The principal external factor inducing the most significant transformations of zircon is thought to be fluid. The complexity of processes occurring in zircon during its interaction with a fluid call for their experimental modeling and studying.

It was previously demonstrated that the interaction of metamict zircon with a hydrothermal fluid is accompanied by the distortion of the U–Th–Pb system of the mineral [1–8].

Pidgeon et al. [3] reported the results of their experiments on zircon interaction with H_2O, 2 M NaCl, and 2 M HCl solutions at temperatures of 350°–800°C. It was noted that fluid strongly affects the U–Pb system of zircon. An increase in the intensity of hydrothermal action on metamict zircon results in an increase in the Pb losses, a decrease in the α activity, and the partial restoration of the crystal structure. These researchers also presented data on the treatment of metamict zircon with solutions enriched in ^{235}U and ^{208}Pb, when zircon preferably accommodated U with respect to Pb.

Geisler et al. [7, 8] demonstrated that much Si, U, Th, and Pb is lost when metamict zircon interacts with 2 M $AlCl_3$ and, particularly, 1 M HCl–$CaCl_2$ solutions at a low temperature (175°C), and the surface of the zircon crystals is overgrown by reaction rims up to a few micrometers thick. No recrystallization of metamict zircon was observed at this temperature. Metamict zircon is partly dissolved at 350–650°C and exchanges its cations with the solution. The zircon itself thereby shows traces of recrystallization and the development of newly formed rims around its crystals. These rims are similar to those observed around naturally occurring zircons. The authors proposed a diffusion model of filtration type, which was based on the assumption that pathways for the fluid filtering through the crystal are its domains with lower atomic density, which are located between crystalline and metamict domains of this mineral.

The results of these experiments confirm the possibility of episodic Pb and U losses from zircons. The values of these losses depend on the metamictness of the zircons, composition of the solutions, temperature, pressure, and the duration of the hydrothermal experiments.

Our research was centered on studying the behavior of major and trace elements in zircon during its interactions with fluids of various composition and pH at elevated temperatures and varied duration of the experiments. These relations should be analyzed to adequately understand the behavior of zircon and its U–Pb system when this mineral occurs in contact with postmagmatic, metamorphic, and metasomatic fluids, as well as to accurately interpret isotopic age data.

Our research was carried out using zircon from Late Archean quartz–plagioclase–biotite metasomatic rock collected in the vicinity of Urosozero Lake in central Karelia. The zircon crystals were dark brown, nontransparent, short prismatic, with glossy faces. The absence of diffraction reflections and cathodoluminescence indicates that this zircon was metamict [9].

EXPERIMENTAL

The experimental modeling with the use of metamict zircon was conducted at two laboratories: at St. Petersburg State University and the Institute of Experimental Mineralogy, Russian Academy of Sciences. In the experiments conducted at the laboratory of St. Petersburg State University, zircon interacted with H_2O and 2 m NaCl within a temperature range of 300–600°C and 1 kbar pressure, and exposures of 3 days. The experiments carried out at the laboratory of the Institute of Experimental Mineralogy were focused on studying the dissolution of Pb and U depending on temperature (within the range of 200–800°C) in carbonate solution, at a pressure of 1 kbar, and exposures of 3, 7, and 14 days. In another series of experiments at the Institute of Experimental Mineralogy, we examined the dependence of Pb and U dissolution depending on pH at a temperature of 400°C and an experimental exposure of 7 days. The pH was varied from 1.9 to 9.8 by using solutions of various composition and concentration: 1 m NaCl + 0.5 m HCl, H_2O, 1 m NaCl, 1 m $NaHCO_3$, 0.1 m Na_2CO_3, 1 m Na_2CO_3, 2 m Na_2CO_3, and 1 m NaOH. The procedures related to the extractions of the solid phase from ampoules after the experiments and the subsequent processing of the material are described in detail in [5, 9].

In order to study the dependence of the dissolution Pb and U of zircon during its interaction with solutions within a broader temperature range (200–800°C), a set of experiments was conducted in Teflon microautoclaves at 200°C and a pressure of 0.01 kbar.

Heterogeneities in the structure of zircon crystals and the distribution of Si, Zr, Hf, U, and Pb along selected profiles were examined on a Jeol JXA 8600S raster electron microscope coupled with X-ray microprobe at a laboratory of St. Petersburg State University. The mineral was examined in back-scattered electrons with the use of three types of contrasts. The quickest and the most informative method applicable to the solution of our problems proved to be the analysis of zircon images in compositional contrast, which turned out to be sensitive to even insignificant compositional variations.

The concentrations of major and minor elements were measured with both wave- and energy-dispersive detectors (TAP, PET, and LIF). The sample current ranged from 5×10^{-8} to 1.4×10^{-7} A, and the counting time was 5–10 s when Si and Zr concentrations were measured and 10–40 s when concentrations of minor elements were analyzed. Back-scattered electron images of original zircon grains were obtained on an ABT-55 scanning electron microscope at the Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences.

Zircons were dissolved and Pb and U were extracted in compliance with the method [10] at the Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences. The laboratory blank did not exceed 0.1 ng for Pb and 0.01 ng for U. The isotopic measurements of U and Pb were conducted on a MAT-261 mass spectrometer. The errors of the measured Pb/U isotopic ratios were within 0.5% (2σ), and ^{206}Pb, ^{208}Pb, and ^{238}U concentrations in zircon fractions were assumed equal to 5.4 and 4.1%, respectively, at a 95% confidence level because of uneven U and Pb distributions in crystals (see [5]). All calculations were conducted by Ludwig's programs [11, 12].

RESULTS

Electron Microscopy

Original zircon crystals. Figure 1a shows a BSE image of a typical zircon crystal. The grain has a heterogeneous inner structure, whose principal elements are a pale primary matrix and darker zones of metasomatically altered mineral, which developed from the peripheries of the grain inward and cut across its primary zoning.

H_2O, 400°C, 1 kbar, 7 days. The interaction of zircon with H_2O more clearly revealed the heterogeneous inner structure of the original zircon: a pale primary matrix and darker zones of altered zircon, which developed from the peripheries of the zircon grain toward its core and cut across the primary zoning of the grain (Fig. 1b). No zircon dissolution were detected.

1 m NaCl, 400°C, 1 kbar, 7 days. BSE images clearly demonstrate the heterogeneous structure of the grain: a paler primary matrix, darker zones of metasomatically altered zircon, and an outer zone. Structural heterogeneities and cracks are accentuated by weak zircon dissolution (Fig. 1c).

1 m NaCl + 0.5 m HCl, 400°C, 1 kbar, 7 days. In acidic solution, zircon is dissolved along single metamict zones, particularly those in the outer parts of the grain. This highlights the heterogeneity of the inner structure of the crystal (Fig. 1d).

1 m Na_2CO_3, 400°C, 1 kbar, 7 days. When zircon interacts with fluids containing carbonate components, the degree of zircon dissolution increases with increasing concentration of carbonates in the solution, as is seen in BSE images (Figs. 1e, 1f).

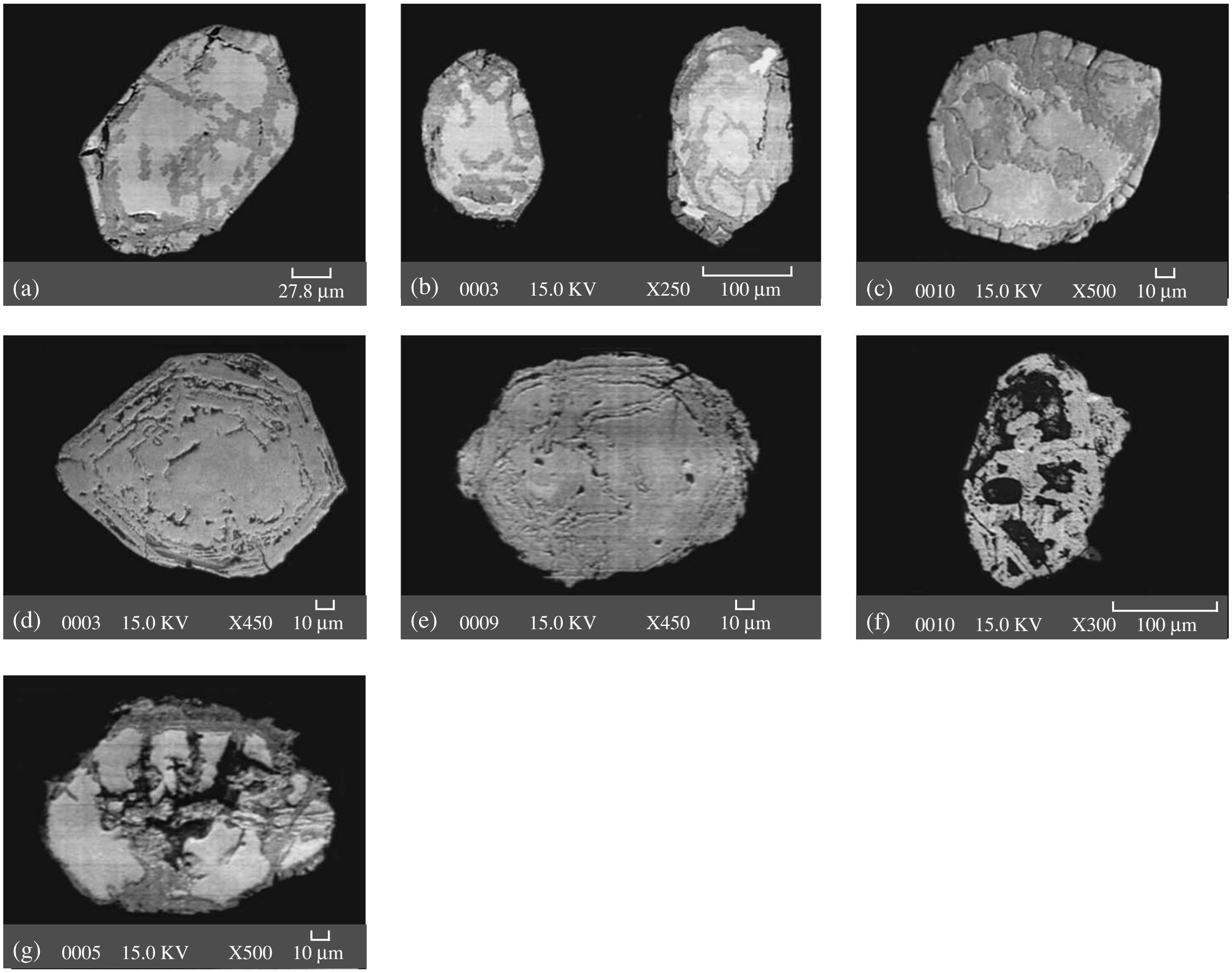

Fig. 1. BSE images of polished sections of grains of the original metamict zircon and this mineral after its interaction with fluids at a temperature of 400°C, pressure of 1 kbar, and an exposure of 7 days: (a) original zircon; (b) H_2O; (c) 1 m NaCl; (d) 1 m NaCl + 0.5 m HCl; (e) 0.1 m Na_2CO_3; (f) 1 m Na_2CO_3; (g) 1 m NaOH.

1 m **NaOH, 400°C, 1 kbar, 7 days.** Metamict zircon grains actively dissolve in alkaline solutions along metamict growth zones and zones altered by metasomatic processes in both the peripheries of the grain and its core (Fig. 1g).

Microprobe Analysis

Original zircon. The microprobe analyses of the original zircon shows that its zones altered by metasomatic processes are enriched in Ca, Fe, Mn, Na, Mg, and U relative to the primary matrix.

EMPA profiles led us to the conclusion that all of our zircon grains can be subdivided into three zones according to their compositional heterogeneity. The primary matrix of the original zircon is characterized by a more even distribution of Si, Zr, Hf, and U (zone I) compared to zones of metasomatically altered zircon, which display direct correlations between the distributions of Si, Zr, and Hf and negative correlations between these elements and U (zone II) (Fig. 2a). The marginal zones of the grain exhibit a decrease in the concentrations of Si, Zr, and U and a slight increase in the concentration of Hf (zone III).

H_2O, 400°C, 1 kbar, 7 days. According to the character of EMPA profiles, zone II and III can be distinguished in the examined part of the grain, whereas zone I corresponding to the primary matrix of the zircon is absent from the profiles (Fig. 2b). A conspicuous feature of zone II is a change in the relations in the distributions of Si, on the one hand, and Zr and Hf, on the other. The direct correlations between these three elements from the core to periphery of the grain gives way to negative correlations of Si with Zr and Hf. At the

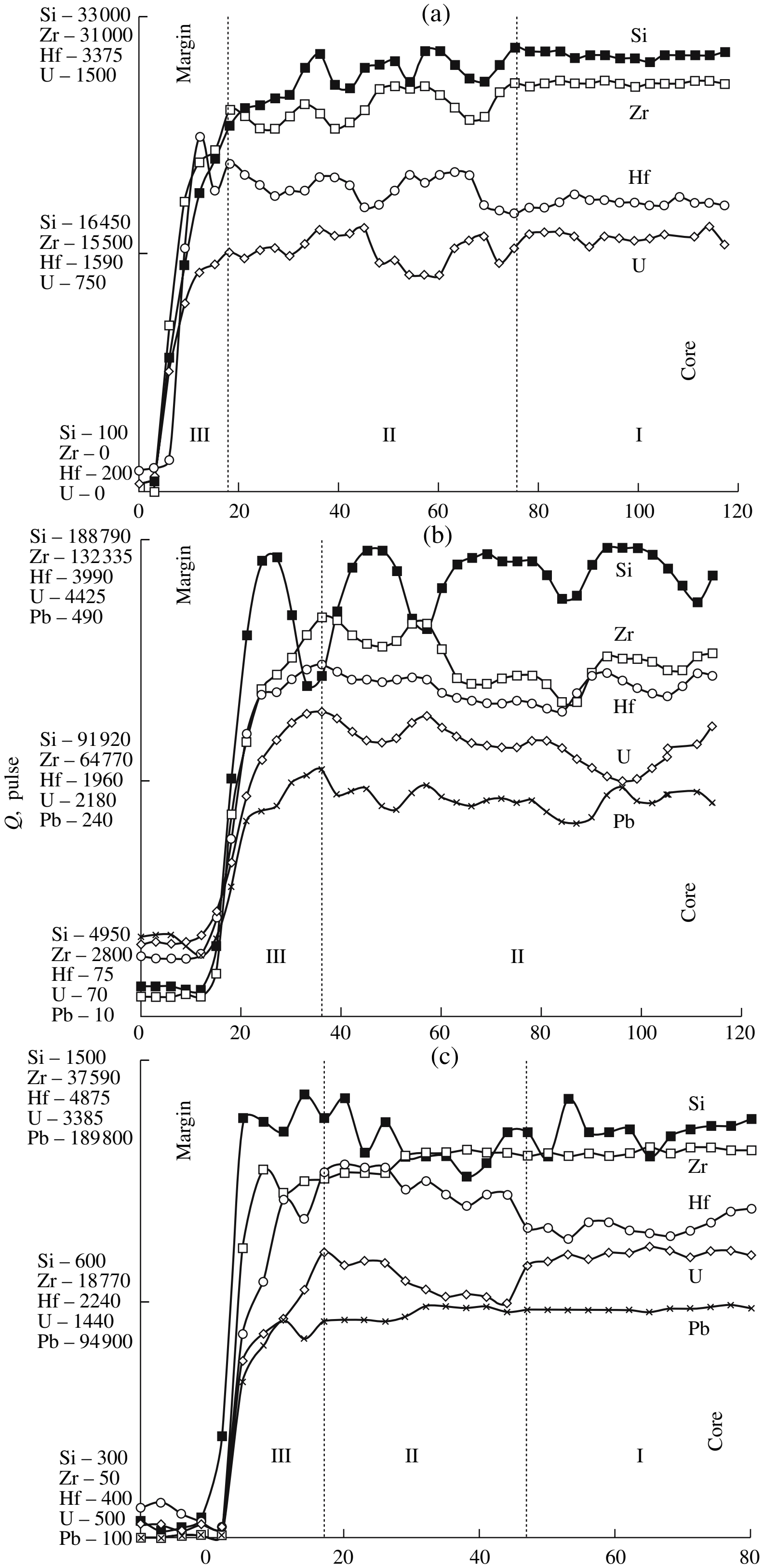

Fig. 2. Profiles (cores–rims) of Si, Zr, Hf, U, and Pb distributions in the original grain of metamict zircon and this mineral after its interaction with fluid at a temperature of 400°C, a pressure of 1 kbar, and an exposure of 7 days: (a) original zircon; (b) H_2O; (c) 1 m NaCl; (d) 1 m NaCl + 0.5 m HCl; (e) 1 m NaOH; I, II, and III are zones provisionally recognized according to fluctuations in the element distributions.

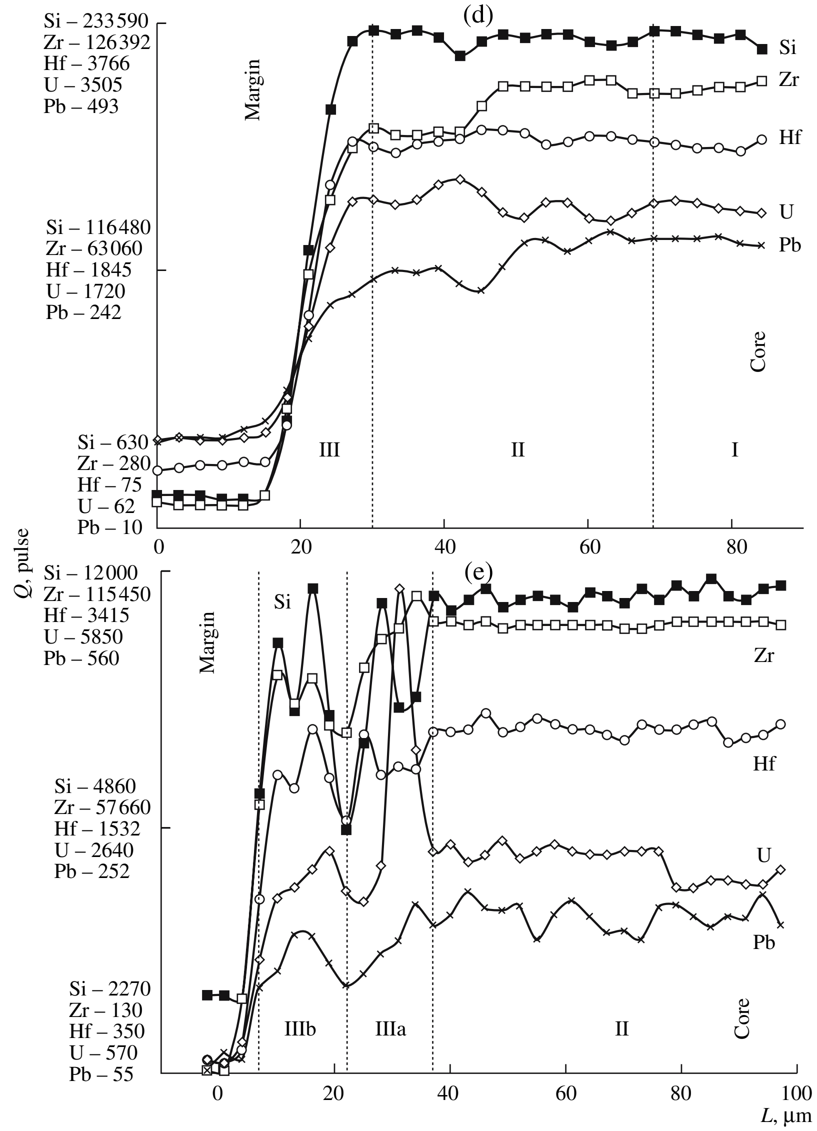

Fig. 2. Contd.

same time, U is not correlated with Si, Zr, and Hf in the core of the grain and is positively correlated with Zr and Hf in its outer zones. A negative correlation of Pb and U in the core of the grain gives way to their positive correlation in the peripheral part. Zone III corresponds to the altered marginal part of the grain with characteristic diffusion profiles of cations except Si.

1 m **NaCl, 400°C, 1 kbar, 7 days.** According to the EMPA profiles of Zr, Hf, U, and Pb concentrations, the examined part of the grain can be subdivided into three zones. In the first of them, Si, Zr, Hf, U, and Pb concentrations display insignificant concentration fluctuations. Zone II is characterized by a slight increase in the concentrations of Si, Hf, and U and a smooth decrease in the concentrations of Zr and Pb toward the boundary with zone III.

The boundary of the grain (zone III) shows evidence of diffusion-controlled losses of Hf, U, Zr, and Pb and a slight increase in the Si concentration (Fig. 2c).

1 m **NaCl + 0.5** m **HCl, 400°C, 1 kbar, 7 days.** According to the character of the EMPA profiles, the examined part of the grain can be provisionally subdivided into three zones. Zone I is characterized by a relatively homogeneous distribution of Si, Zr, Hf, U, and Pb concentrations. Zone II displays an increase in the variations of the concentrations of these elements toward the margin of the grain, with U negatively correlated with the other four elements. The outer part of this zone is marked by a decease in the concentrations of Zr and Pb and an increase in the U concentration. Zone III (in the grain margin) shows profiles of all five elements corresponding to their diffusion-controlled losses (Fig. 2d).

1 m NaOH, 400°C, 1 kbar, 7 days. Judging from the EMPA profiles, the examined part of the grain can be subdivided into two zones (II and III). Zone II is characterized by relatively small variations in the Si, Zr, Hf, U, and Pb concentrations. Zone III is separated into two parts (IIIa and IIIb) by an interval of dissolved zircon, as follows from the rapid decrease in the concentrations of all of the elements. Zone IIIa (away from the grain margin) shows a decrease in the Zr, Hf, and Pb concentrations and a drastic increase in the U concentration, which is negatively correlated with the Si concentration. In zone IIIb (in the grain margin), a general decrease in the concentrations shows coinciding maxima of Si, Zr, Hf, and Pb concentrations and their negative correlation with the U concentration (Fig. 2e).

Isotopic Research

Dependence on pH and fluid composition. The dependences of ^{206}Pb and ^{238}U dissolution on pH during the interaction of metamict zircon with solutions of various composition at 400°C, 1 kbar, and exposures of 3 and 7 days are summarized in the table.

Within the pH range of 2.0–9.8, the dissolution of ^{206}Pb shows two maxima and two minima (Fig. 3). The dissolution maxima of ^{206}Pb correspond to pH 2 (1 m NaCl + 0.5 m HCl) and pH 8.9–9.1 (1 m $NaHCO_3$, 0.1 m, 1 m, and 2 m $NaHCO_3$). In an 1 m NaCl + 0.5 m HCl solution, the concentration of ^{206}Pb in the zircon decreased to 1.77×10^{-7} mol/g (point 6) compared to the ^{206}Pb concentration in the original sample equal to 33.1×10^{-7} mol/g (point 1). A significant decrease in the ^{206}Pb concentration in zircon was observed during its interaction with 1 m $NaHCO_3$ (5.14×10^{-7} mol/g, point 17) and 0.1 m Na_2CO_3 (5.82×10^{-7} mol/g, point 18), (1 m Na_2CO_3 (2.79×10^{-7} mol/g, point 19).

The amount of ^{206}Pb remaining in the zircon after its interaction with 1 m $NaHCO_3$ and 0.1 m Na_2CO_3 solutions for 7 days and a pressure of 1 kbar was practically identical: 5.14×10^{-7} mol/g (point 17) and 5.82×10^{-7} mol/g (point 18). A change in the Na_2CO_3 concentration from 0.1 m to 1 m in the solutions notably increases the ^{206}Pb dissolution, and its concentration decreases from 5.82×10^{-7} (point 18) to 2.79×10^{-7} mol/g (point 19).

Pb dissolution depended even stronger on the duration of the experiments and the pressure. For example, the ^{206}Pb concentration in zircon after its interaction with 2 m Na_2CO_3 solution under a pressure of 1 kbar for 3 days was higher (11.4×10^{-7} mol/g, point 23) than that in the experiment with 1 m Na_2CO_3 and an exposure for 7 days (2.79×10^{-7} mol/g, point 19). The amount for ^{206}Pb remaining in the zircon after its interaction with 2 m Na_2CO_3 aqueous solution for 14 days decreased to 1.94×10^{-7} mol/g (point 22). When the pressure in the experiments was changed from 1 to 5 kbar, the ^{206}Pb dissolution notably increased, and its concentration in the zircon after the experiment was no higher than 0.18×10^{-7} mol/g (point 24).

The Pb dissolution was lower at pH from 5.4 to 6.0 (H_2O and 1 or 2 m NaCl solutions) and pH 9.8 (1 m NaOH). The ^{206}Pb concentrations in the zircon after its interaction with these solutions were 25.3×10^{-7} mol/g for H_2O (point 4), 18.6×10^{-7} mol/ g for 1 m NaCl (point 7), and 21.4×10^{-7} mol/g (average of three measurements) for 1 m NaOH (points 28–30).

In order to reveal similar Pb and U behavior during zircon interaction with fluids, we conducted three replicate experiments with 1 m NaOH solutions at a temperature of 400°C, a pressure of 1 kbar, and an exposure for 7 days. The variation coefficient of the ^{206}Pb measurements was 1.2% (2σ), and that for ^{238}U was 3.2% (2σ), which did not exceed the analytical errors in the concentrations of Pb and U isotopes (see above).

When metamict zircon interacted with aqueous solutions at 400°C, 1 kbar, and exposures for 3 and 7 days, with the pH of these solutions varied from 2.0 to 9.8, the ^{238}U concentration in the zircon practically did not change (table, Fig. 3), except only slight U dissolution in carbonate solution under a pressure of 1 kbar and an exposure for 3 days and an insignificant increase in the ^{238}U concentration in the zircon after its interaction with 1 m NaOH.

Temperature dependence. We examined the dependences of Pb and U dissolution on temperature during the interaction of metamict zircon with solutions of three compositions (H_2O, 2 m NaCl, and 2 m Na_2CO_3 under a pressure of 1 kbar and exposures for 3, 7, and 14 days (table). In addition, we conducted experiments in microautoclaves to examine the behavior of Pb and U of zircon in H_2O and 2 m NaCl solutions at a temperature of 200°C, a pressure of 0.01 kbar, and an exposure for 3 days.

When zircon interacted with H_2O for 3 days at 200° C, the ^{206}Pb and ^{238}U concentrations in this mineral notably decreased, to 1.95×10^{-7} mol/g (point 2) and 14.0×10^{-7} mol/g (point 2), respectively. However, at 400°C, the ^{206}Pb concentration changed insignificantly (28.8×10^{-7} mol/g, point 3), and was as low as 3.50×10^{-7} mol/g (point 5) at 600°C. An increase in the exposure from 3 days (point 3) to 7 days at a temperature of 400°C did not significantly affect the ^{206}Pb concentration (25.3×10^{-7} mol/g, point 4). The ^{238}U concentration in the zircon samples exposed under the same conditions at temperatures of 400°C (point 3) and 600°C (point 5) practically did not change compared to the concentration in the original sample (Fig. 4).

In order to examine the dependences of Pb and U dissolution on temperature during the interaction of metamict zircon with 2 m NaCl solution under a pressure of 1 kbar and an exposure for 3 days, we carried out two series of experiments (table). In the first of them, the ^{206}Pb (0.52×10^{-7} mol/g) and ^{238}U (16.4×10^{-7} mol/g) concentrations in the zircon (point 8) notably decreased after its interaction with 2 m NaCl solution at 200°C. However, no significant dissolution of ^{206}Pb and ^{238}U was detected within the temperature range of 300–500°C

Pb and U isotopes in zircon after its interaction with fluid

No.	Fluid composition	pH	T°C	P, kbar	t, days	$^{206}Pb/^{204}Pb$	$^{206}Pb \times 10^{-7}$, mol/kg	log ^{206}Pb	$^{208}Pb \times 10^{-7}$, mol/kg	log ^{208}Pb	$^{238}U \times 10^{-7}$, mol/kg	log ^{238}U	$^{207}Pb/^{235}U$	$^{206}Pb/^{238}U$
1	Original zircon					4100	33.1	–5.48	1.760	–6.75	101	–5.00	7.240	0.3237
2	H_2O	7	200	0.01	3	3963	1.95	–6.71	0.108	–7.97	14	–5.85	2.928	0.1394
3	H_2O	5.39	400	1	3	849	28.8	–5.54	1.450	–6.84	82.6	–5.08	7.989	0.3511
4	H_2O	5.39	400	1	7	3700	25.3	–5.60	1.330	–6.88	92.7	–5.03	6.131	0.2734
5	H_2O	5.39	600	1	3	31	3.50	–6.46	0.979	–7.01	89.7	–5.05	1.126	0.0474
6	1 m NaCl + + 0.5 m HCl	1.87	400	1	7	283	1.77	–6.75	0.142	–7.85	107.0	–4.97	0.354	0.0165
7	1 m NaCl	5.52	400	1	7	3360	18.6	–5.73	0.937	–7.03	93.5	–5.03	4.439	0.1986
8	2 m NaCl	6.0	200	0.01	3	2500	0.52	–7.28	0.020	–8.70	16.4	–5.79	0.630	0.0315
9	2 m NaCl	6.0	300	1	3	166	30.1	–5.52	2.030	–6.69	91.3	–5.04	7.793	0.3408
10	2 m NaCl	6.0	400	1	3	4540	25.0	–5.6	1.210	–6.92	97.1	–5.01	5.816	0.2593
11	2 m NaCl	6.0	500	1	3	2270	29.1	–5.54	1.245	–6.90	98.3	–5.01	6.847	0.2984
12	2 m NaCl	6.0	600	1	3	54	2.03	–6.69	0.196	–7.71	84.9	–5.07	0.613	0.0264
13	2 m NaCl*	6.0	300	1	3	551	4.41	–6.36	0.332	–7.48	37.4	–5.43	2.627	0.1192
14	2 m NaCl*	6.0	400	1	3	910	12.5	–5.90	0.727	–7.14	75.3	–5.12	3.859	0.1688
15	2 m NaCl*	6.0	500	1	3	733	5.96	–6.23	0.342	–7.47	79.0	–5.10	1.768	0.0769
16	2 m NaCl*	6.0	600	1	3	240	1.45	–6.84	0.278	–7.56	63.4	–5.20	0.565	0.0237
17	1 m $NaHCO_3$	8.59	400	1	7	2220	5.14	–6.29	0.274	–7.56	95.5	–5.02	1.200	0.0538
18	0.1 m Na_2CO_3	9.0	400	1	7	2556	5.82	–6.24	0.306	–7.51	96.8	–5.01	1.346	0.0601
19	1 m Na_2CO_3	9.07	400	1	7	1680	2.79	–6.55	0.149	–7.83	96.2	–5.02	0.642	0.0290
20	2 m Na_2CO3	9.07	200	1	14	5170	24.2	–5.62	1.340	–6.87	72.6	–5.14	7.220	0.3336
21	2 m Na_2CO_3	9.07	300	1	14	3660	14.3	–5.84	0.836	–7.08	35.7	–5.45	8.784	0.4013
22	2 m Na_2CO_3	9.07	400	1	14	740	1.94	–6.71	0.071	–8.15	95.4	–5.02	0.428	0.0203
23	2 m Na_2CO_3	9.07	400	1	3	4224	11.4	–5.95	0.580	–7.24	19.2	–5.72	2.094	0.0949
24	2 m Na_2CO_3	9.07	400	5	3	354	0.18	–7.80	0.011	–9.00	82.0	–5.09	0.049	0.0022
25	2 m Na_2CO_3	9.07	600	1	3	2690	1.54	–6.81	0.082	–8.00	77.9	–5.11	0.443	0.0198
26	2 m Na_2CO_3	9.07	800	1	3	210	0.68	–7.17	0.045	–8.35	126.0	–4.90	0.119	0.0054
27	2 m Na_2CO_3	9.07	800	5	3	1140	0.67	–7.20	0.036	–8.40	92.4	–5.03	0.161	0.0072
28	1 m NaOH	9.75	400	1	7	12000	19.3	–5.71	0.798	–7.10	115.0	–4.94	3.843	0.1674
29	1 m NaOH	9.75	400	1	7	19000	23.1	–5.64	1.030	–6.99	154.0	–4.81	3.763	0.1626
30	1 m NaOH	9.75	400	1	7	4000	21.9	–5.66	1.030	–6.99	112.0	–4.95	4.489	0.1954
31	3% HNO_3	0.3	200	0.01	1	6050	4.44	–6.35	0.200	–7.70	27.2	–5.565	3.752	0.1635

Note: * Zircon after its interaction with fluid was treated with 15% HNO_3.

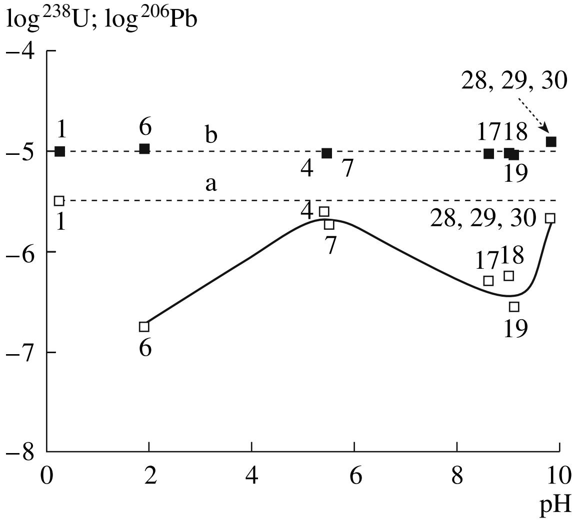

Fig. 3. Dependence of the ^{206}Pb (open circles) and ^{238}U (solid squares) concentrations in the original metamict zircon and those after its reaction with fluid (at 400°C, 1 kbar, and an exposure for 7 days) on the pH of the fluid. In this and following diagrams, the analytical errors of the ^{206}Pb and ^{238}U concentrations do not exceed the sizes of the data point symbols, and the numbers of these data points correspond to the ordinal numbers of zircon samples in the table. The dashed lines correspond to (a) the ^{206}Pb and (b) ^{238}U concentrations in the original zircon. The values of the dashed lines are the same in Figs. 4–6.

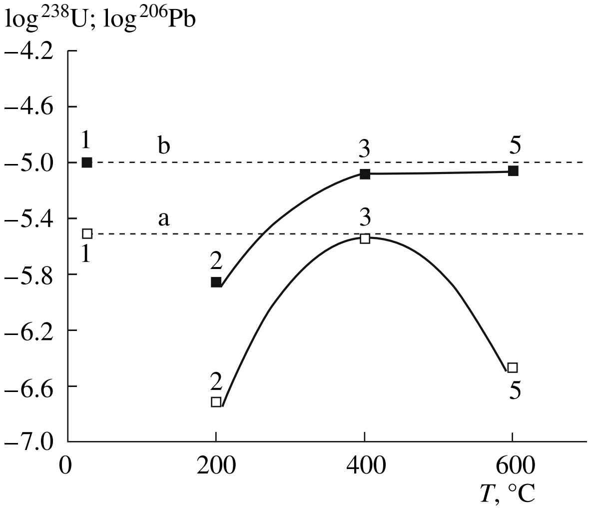

Fig. 4. Temperature dependences of the ^{206}Pb (open squares) and ^{238}U (solid squares) concentrations in the original metamict zircon and that after its reaction with H_2O.

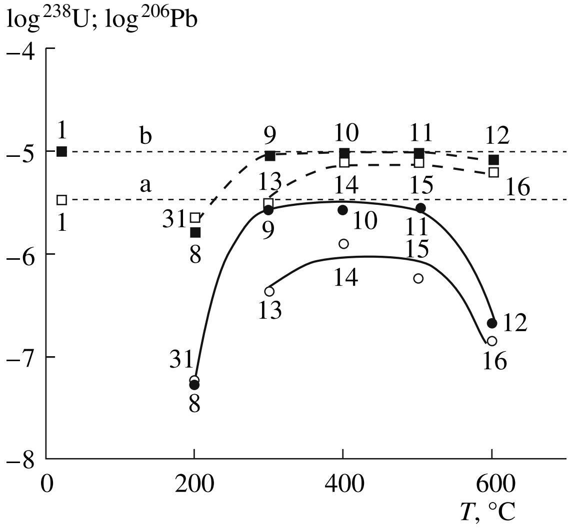

Fig. 5. Temperature dependences of the ^{206}Pb (circles) and ^{238}U (squares) concentrations in the original metamict zircon and that after its reaction with 2 m NaCl fluid. Open symbols denote ^{206}Pb and ^{238}U concentrations in exposed zircon samples treated with 15% HNO_3 solution.

(Fig. 5). At 600°C, the zircon lost significant amounts of both Pb and U, and the ^{206}Pb concentration in the zircon decreased more significantly (2.03×10^{-7} mol/g, point 12) than the ^{238}U concentration (84.9×10^{-7} mol/g, point 12) compared to the concentrations in the original sample (33.1×10^{-7} and 101×10^{-7} mol/g, respectively).

The second series of experiments differed from the first one in that the zircon after its interaction with 2 m NaCl solution was treated with 15% HNO_3 acid in a microautoclave at 200°C, ~0.01 kbar for one day with the aim of removing easily dissolvable Pb and U. The analysis of the ^{206}Pb and ^{238}U concentrations (points 13–16) in the zircon exposed at temperatures of 300–600°C demonstrates that some ^{238}U and much ^{206}Pb are readily dissolvable. The smallest ^{206}Pb and ^{238}U losses from zircon were detected at temperatures of 400–500°C (Fig. 5).

Our experiments on the interaction of metamict zircon with 2 m Na_2CO_3 solution were conducted within various temperature ranges, at two different exposures, and a pressure of 1 kbar: 200–400°C, exposure for 14 days; and 400–800°C, exposure for 3 days.

Judging from the discoloration of zircon, only part of its grains interacted with solution in the experiment at a temperature of 200°C in spite of the long exposure. Because of this, the concentrations of ^{206}Pb (24.2×10^{-7} mol/g, point 20) and ^{238}U (72.6×10^{-7} mol/g, point 20) only insignificantly changed from those in the original zircon (point 21).

Significant Pb dissolution took place at 300 and 400°C, because the ^{206}Pb concentration in the zircon was 14.3×10^{-7} mol/g (point 21) and 1.94×10^{-7} mol/g (point 22), respectively (Fig. 6). A change in the interaction time from 14 to 3 days at 400°C resulted in a decrease in the ^{206}Pb loss, whose concentration in the zircon decreased to 11.4×10^{-7} mol/g (point 23). An increase in the pressure from 1 to 5 kbar at the same exposure (3 days) brought about an even greater decrease in the ^{206}Pb concentration (0.18×10^{-7} mol/g, point 24).

In the temperature range of 400–800°C and an exposure for 3 days, the ^{206}Pb content in the sample decreased by more than one order of magnitude: from 11.4×10^{-7} at 400°C (point 23) to 1.54×10^{-7} mol/g at 600°C (point 25) and 0.68×10^{-7} mol/g at 800°C (point 26). A pressure increase from 1 to 5 kbar at 800°C did not change the Pb dissolution: the ^{206}Pb concentration in the zircon did not change and was 0.68×10^{-7} and 0.67×10^{-7} mol/g, respectively (points 26 and 27).

The behavior of U during the interaction of metamict zircon with 2 m Na_2CO_3 solution within the temperature range of 300–800°C differs from the behavior of Pb. Judging from our measurements, a temperature increase from 300 to 400°C leads to an increase in the ^{238}U concentration in the zircon samples exposed for 14 days from 35.7×10^{-7} mol/g (point 21) to 95.4×10^{-7} mol/g (point 22) (Fig. 6).

An increase in the ^{238}U concentration was also observed when the temperature was increased from 400 to 800°C at an exposure for 3 days: 19.2×10^{-7} mol/g at 400°C, 77.9×10^{-7} mol/g at 600°C, and 126×10^{-7} mol/g at 800°C (points 23, 25, and 26, respectively). The ^{238}U concentration in the sample exposed at a temperature of 800°C and a pressure of 5 kbar was 92.4×10^{-7} mol/g (point 27) and very little differed from the ^{238}U concentration of the original zircon (Fig. 6).

In order to determine whether uranogenic Pb can be preferably dissolved compared to thorogenic Pb in metamict zircon, the data points of all analyses were plotted in a log ^{208}Pb vs. log ^{206}Pb diagram (Fig. 7). Rejecting two points (5 and 16) that showed the greatest deviations from the regression line, we calculated the parameters of this linear dependence: $\log {}^{208}\text{Pb} = (0.966 \pm 0.058) \log {}^{206}\text{Pb} - (1.47 \pm 0.37)$, MSWD = 21. The errors of the regression parameters were reported for a 95% confidence level. With regard for the calculated errors of the regression parameters, the slope of the line indicates that the dissolution rates of ^{206}Pb and ^{208}Pb in metamict zircon are equal.

DISCUSSION

Our results demonstrate that the interaction of metamict zircon with aqueous solutions of various composition at elevated temperatures and pressures involves a number of concurrent processes, some of which result in Pb and U losses from the zircon. The main observed processes are the congruent and incongruent dissolution of metamict zircon and the concurrent processes of the sorption of elements, crystallization of newly formed phases, and the restoration of the zircon crystal lattice [9]. The intensities of these processes are controlled by the temperature, pressure, exposure, and the composition of the solution.

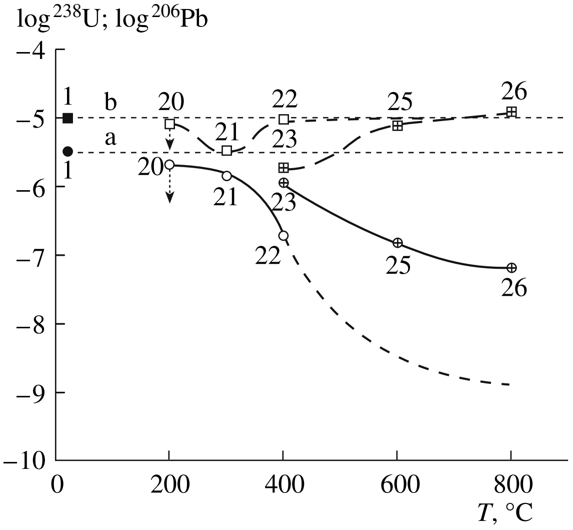

Fig. 6. Temperature dependences of the ^{206}Pb (circles) and ^{238}U (squares) concentrations in the original metamict zircon (solid symbols) and those after its reaction with 2 m Na_2CO_3 fluid (open symbols). Open symbols denote experimental exposures for 14 days, symbols with crosses correspond to experiments for 3 days. The heavy dashed line is an extrapolation. Arrows near points 20 indicates the probably lower position of these points.

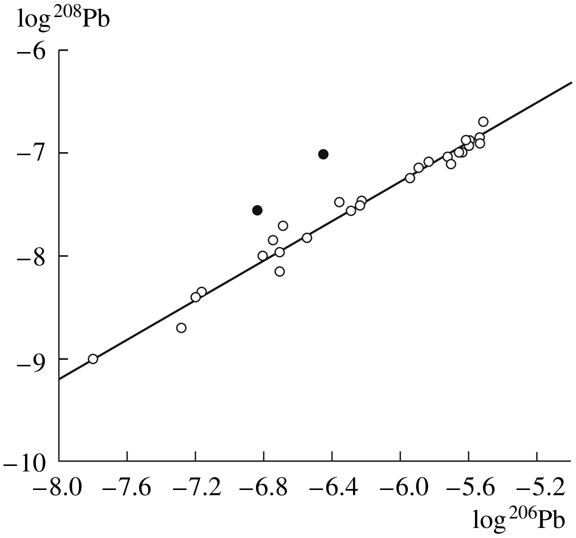

Fig. 7. Correlation between the concentrations of ^{208}Pb (thorogenic) and ^{208}Pb (uranogenic) in the original metamict zircon and those after its reaction with fluid of various composition at various temperatures. Solid symbols correspond to points 5 and 16 rejected from the regression calculations.

According to electron microscopic data, metamict zircon starts to dissolve in aqueous solutions of various composition along cracks, growth zones, and domains of metasomatically altered material and primary matrix already at a temperature of 400°C and pressure of 1 kbar (Fig. 1). The dissolution of metamict zircon is at a minimum in water and notably intensifies in carbonate and alkaline solutions, which is consistent with the results of thermodynamic simulations of zircon resistance to the effect of fluids [13]. The partial congruent dissolution of zircon is associated with the passage of Pb and U into solution. The experimental conditions did not allow us to quantify the amounts of Pb and U that passed into solution during the congruent dissolution of metamict zircon because its congruent dissolution is coupled with the much more intense incongruent removal of Pb and U from the whole volume of the metamict zircon sample.

According to EMPA data, the incongruent dissolution of zircon is likely predated by the redistribution of Zr, Hf, U, and Pb in domains of metasomatically altered zircon and the migration of these elements toward the boundaries. The margins of the zircon grain suffer diffusion-controlled losses of all these elements except Si, which enriches the margins in neutral and acidic solutions. When zircon occurs in contact with an aqueous alkaline solution, a reaction zone develops in the grain with a distribution of elements differing from that in the original zircon. It was demonstrated previously that, when metamict zircon is in contact with a carbonate solution at 400°C and higher, baddeleyite and Zr–Na silicate are formed in the peripheral parts of zircon grains [9].

In analyzing the character of Pb and U dissolution from metamict zircon depending on pH and temperature, it should be taken into account that the solutions are not saturated with these elements because the solid products of the reaction contain no newly formed individual Pb and U minerals. Because of this, our results provide a qualitative visualization of the aggressiveness of the action of fluids of various composition on Pb and U.

The analysis of the effect of pH on Pb dissolution indicates that the greatest amount of this element passes into acidic and carbonate solutions (table, Fig. 3). It follows from the comparison of the results of the hydrothermal treatment of metamict zircon with H_2O and 1 m NaCl + 0.5 m HCl that the occurrence of HCl in the solution hampers the hydrolysis of Pb ions and increases their release into the liquid phase as compared with pure H_2O because of the effect of pH. In HCl solutions, an increase in their salinity also leads to some increase in the Pb solubility due to the formation of low-soluble chloride aquacomplexes [14, 15]. Our results are consistent with the data [2] on the interaction of fluids with zircon, which also testify that HCl solutions are chemically aggressive with respect to Pb.

The Pb solubility in neutral and alkaline solutions is at a minimum. However, it increases in the presence of Na carbonate or hydrocarbonate. The amount of Pb passing into solution increases as the molality of Na carbonate was increased from 0.1 m to 1 m (Fig. 3, points 18, 19), the duration of the experiments was increased from 3 to 14 days (points 20, 23), and the pressure was increased from 1 to 5 kbar (points 23, 24).

The comparison of the results of the hydrothermal experiments in carbonate and alkaline solutions indicates that Pb more actively passes into the liquid phase in solutions of Na carbonate or bicarbonate. In carbonate solutions, the formation of Pb silicate during zircon decomposition is hampered by the carbonate ion, which replaces the silicate ion in its salts. Pb carbonate is readily soluble in acids and passes into solution when the sample is washed with 5% HCl solution after zircon extraction from the ampoule. When zircon interacts with carbonate solutions, the solid phase retains, according to our data, no more than 6–17% Pb.

In strongly alkaline solutions (1 M NaOH), more than 60% Pb remains in the solid phase. These differences in the Pb behavior in carbonate and alkaline solutions are explained by the presence of the silicate ion in alkaline solutions and the crystallization of low-soluble Pb silicate [14].

In the same experiments, the behavior of U differs from that of Pb throughout the whole pH range examined in the experiments (from 2 to 9.8). The exposed zircon samples retain more than 90% ^{238}U. However, as was demonstrated in [16], up to 16% ^{238}U is dissolved over a few initial hours of the interaction of metamict zircon with aqueous solutions of 2 m Na_2CO_3 and 1 m NaCl + 0.5 m HCl. After that, the ^{238}U concentration in the metamict zircon rapidly increases to the initial values, perhaps, because of sorption and the recrystallization of metamict zircon. Our experiments confirmed the sorption of up to 34% ^{235}U and up to 11% ^{208}Pb [19] or more [3] on zircon crystals in acidic solutions.

In alkaline and carbonate solutions, the constancy of ^{235}U concentration in zircon is likely explained by the partial congruent dissolution of metamict zircon and the incorporation of U from the solution into the newly crystallizing baddeleyite [5, 9, 17, 18]. It should be taken into account that both minerals synthesized in our experiments were analyzed simultaneously.

Temperature notably influences U and Pb dissolution, irrespective of the composition of the solution reacting with metamict zircon. The lines of ^{206}Pb and ^{238}U dissolution when metamict zircon is in contact with H_2O and 2 m NaCl have bell-shaped configurations. This reflects the significant dissolution of Pb and U at temperatures below 300°C and above 500°C (Figs. 4, 5). An analogous morphology of the ^{206}Pb lines are shown by samples of exposed zircon treated with 15% HNO_3. The ^{206}Pb and ^{238}U concentrations in the zircon sample exposed in an autoclave at 300°C and then treated with 15% HNO_3 are virtually identical to the concentrations of these elements in the original zircon sample treated with 3% HNO_3 solution. This fact testifies to the absence of significant metamict zircon recrystallization at a temperature of 300°C, a process that could be coupled with partial conservation of Pb atoms.

The comparison of the ^{206}Pb concentrations in samples 8–15 (table) provides a general idea about changes in the setting of Pb atoms in the zircon structure depending on the fluid temperature (Fig. 5). Significant Pb losses at temperatures below 300°C are explained by the fact that up to 90% Pb atoms are weakly bounded in the matrix of the original metamict zircon [9]. The activation energy of the transition of this Pb into solution does not exceed 4 kcal/mol [16]. Zircon recrystallization starts at temperatures above 300°C and is associated with the restoring of the crystal structure of the mineral, and because of this, Pb dissolution is hampered. The activation energy of this process increases to at least 17 kcal/mol [16]. However, at a temperature above 500°C, the active dissolution of zircon itself begins and starts with its phases enriched in Pb and U. This process defines the right-hand branch of the dissolution line in Figs. 4–6.

Analogously to Pb, before the onset of metamict zircon recrystallization at temperatures above 300°C, up to 60% ^{238}U can be dissolved when the mineral occurs in contact with 15% HNO_3. However, at temperatures of 400–600°C, U atoms are strongly enough bound with the zircon structure.

Analogous relations and tendencies in the dissolution of ^{206}Pb and ^{238}U are also observed when metamict zircon interacts with Na carbonate solution. Because not all grains have reacted with the solution in the experiment at 200°C, the ^{206}Pb and ^{238}U concentrations only insignificantly differed from the concentrations in the original zircon. Because of this, the position of points 20 in Fig. 6 should be obviously lower, and we were able to draw only the right-hand branches of the lines for the ^{206}Pb and ^{238}U losses.

The ^{206}Pb losses continuously increased when the temperature was increased from 300 to 800°C and the experiment duration was increased from 3 to 14 days (Fig. 7). The dissolution of ^{206}Pb increased particularly notably when the pressure was increased from 1 to 5 kbar at 400°C, which likely facilitated the deeper and more intense penetration of fluid in the central parts of the matrix of the still incompletely recrystallized metamict zircon.

A more complicated dissolution dependence within the same temperature range was established for ^{238}U in metamict zircon (Fig. 7). Losses of ^{238}U were determined at two temperatures: 300°C at an exposure for 14 days and 400°C at an exposure for 3 days. A drastic decrease in the ^{238}U loss from zircon was observed when the pressure was increased from 1 to 5 kbar at 400°C and an exposure for 3 days.

In both cases, a further temperature increase resulted in an increase in the ^{238}U concentration to the values of the original zircon. This is explained by, first, the fact that the crystal structure of zircon is gradually restored at these temperatures, and U, an isostructural cation, is incorporated in the structure via replacing Zr. Second, this temperature range is characterized by baddeleyite crystallization, with this mineral also capturing U. Along with baddeleyite, Zr–Na silicate is formed in carbonate solutions starting at 400°C, but no Pb and U accommodation in this mineral was detected [9].

Significant Pb and U losses were observed when radioactively distorted zircon interacted with 2 M $AlCl_3$ and 1 M HCl–$CaCl_2$ for 56 days at a temperature of 175°C [7]. Intense zircon recrystallization with the development of rims of newly formed minerals was identified when zircon interacted with 2 M $CaCl_2$ solution for 31 days at 450°C and a pressure of 1.3 kbar [6].

Irrespective of the experimental conditions under which the behavior of zircon in contact with fluids of various composition was examined at elevated temperatures and pressures, it was determined that the dissolution of the ^{206}Pb and ^{208}Pb is not accompanied by their fractionation (Fig. 7).

Based on the experimental data, we calculated the ^{206}Pb/^{238}U and ^{207}Pb/^{235}U isotopic ratios, which are sensitive indicators of relative Pb and U mobility. The arrangement of all data points in a ^{206}Pb/^{238}U–^{207}Pb/^{235}U diagram provides a general idea about Pb and U losses from metamict zircon during its interaction with fluid (Fig. 8). The position of the data that points to the right of the original zircon point suggests the preferable loss of U with respect to Pb, regardless of

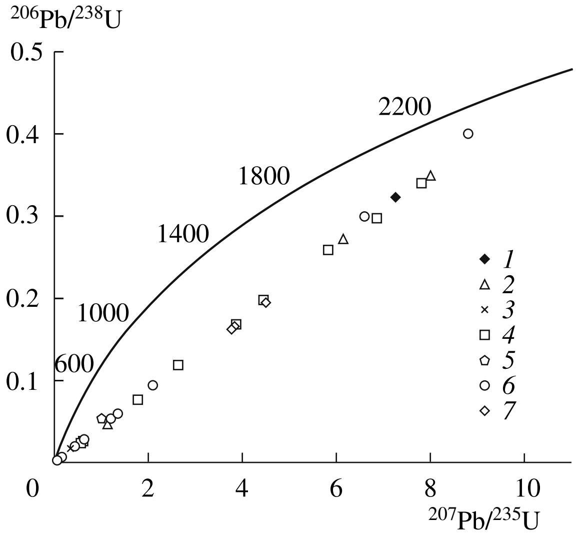

Fig. 8. Concordia plot for the original metamict zircon and that after its reaction with fluid of various composition at various temperatures. (*1*) Original zircon 1 and (*2*) zircon after its reaction with fluids of various composition: (*2*) H_2O (3–5), (*3*) 1 m NaCl + 0.5 m HCl, (*4*) 1 m and 2 m NaCl (7–16), (*5*) 1 m $NaHCO_3$ (17), (*6*) 0.1 m, 1 m, and 2 m Na_2CO_3 (18–27), and (*7*) 1 m NaOH (28–30).

the fluid composition, at temperatures no higher than 300–400°C. Conversely, the Pb losses from metamict zircon at higher temperatures are greater than the U losses. The most aggressive solution, which distorts the closed character of the U–Pb system of zircon at these temperatures, is a carbonate fluid. When metamict zircon occurs in contact with a fluid of given composition, the change in the Pb/U ratio is proportional to the temperature increase.

Our experiments were conducted with H_2O and aqueous chloride and carbonate solutions, which are the main components of postmagmatic, metamorphic, and metasomatic fluids that repeatedly affect zircon in nature. The results of our research testify to profound compositional and structural transformations of the original metamict zircon, up to the restoration of its crystal structure and the development of newly formed zones of different composition. Because of this, the TIMS dating of this zircon with the aim of determining its crystallization age and the timing of the overprinted metamorphic or metasomatic processes faces significant difficulties. To accomplish this task, it seems to be more promising to date the mineral by methods of high spatial resolution, such as SHRIMP, LA-MC-ICP-MS, and CHIME [20].

The relations and tendencies revealed in the course of our study enable the researcher to adequately assay the behavior of Pb and U isotopes in zircon when it interacts with fluids of various composition during metamorphic and metasomatic processes and to more accurately interpret the measured age values.

CONCLUSIONS

1. The interaction of zircon with fluids of various composition, whose pH can vary from 1.9 to 9.7, at a temperature of 400°C and a pressure of 1 kbar, in experiments lasting 7 days does not result in U losses, and Pb is most strongly dissolved in acidic and carbonate solutions.

2. The dissolution of Pb and U in H_2O and aqueous chloride and carbonate solutions can be subdivided into two temperature regions: low- (<300°C) and high-temperature (>500°C). The low-temperature region is characterized by the preferential dissolution of U, whereas the high-temperature region is, conversely, marked by the more rapid dissolution of Pb.

3. Regardless of the experimental conditions during the dissolution of metamict zircon, we did not identify any fractionation of the ^{206}Pb and ^{208}Pb isotopes.

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