

EXPERIMENTAL STUDY OF ZIRCONIUM SPECIATION IN HYDROTHERMAL SOLUTIONS

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Zirconium stability constant supercritical values are needed for estimation of zircon migration in hydrothermal fluids. N.V.Vladikin's Covdor Baddeleite sample was used. The following impurities are determined (weight %): Hf - 0.7, Nb - 0.3, Y < 0.3, Fe < 0.02 and Na₂O, MgO, SiO₂, K₂O, CaO, Ni 0.01 – 0.05 by Roschina I.A. using microsond technique. Baddeleite is selected for experiment study due to its simple composition in compare with other zirconium minerals. Though zirconium and baddeleite are magmatic minerals but zirconium remobilization, precipitation and formation of zirconium enriched rock are possible by metamorphogenic (and fluorine rich) fluids related to rested magmatic melts [1, 2, 3].

The baddeleite (ZrO₂) solubility measurements at 500°C, 1000 bars in HCl, HF aqueous solutions of the concentrations as in nature is done using capsula technique and ICAP 9000 (sensitivity is 0.05 microg/ml) solution analysis.

ZrO₂ – H₂O – HCl system. Baddeleite solubility in HCl aqueous solutions is performed in the whole concentration range (0.01–1 m HCl). It is showed the solubility of baddeleite is so low as the sensitivity of analytical procedure. Zirconium concentration determined is not enough for complex formation. Zirconium concentration estimated values show zirconium-chlorine complex formation is not occurred in supercritical fluids. It looks the same as at standard temperature and pressure.

ZrO₂ – H₂O – HF system. High concentration of baddeleite is determined in fluorine aqueous solutions of from 0,0027 to 2,74 m. Baddeleite solubility is equal from $5 \cdot 10^{-6}$ to $6,8 \cdot 10^{-2}$ m (tabl.1, fig.1). Equilibrium constant values of $\text{ZrO}_2(\text{cr}) + (2-n)\text{H}_2\text{O} + n\text{HF}^0 = \text{Zr}(\text{OH})_{4-n}\text{F}_n^0$ reactions are calculated for the experimental interval of HF aqueous solution concentrations by determination of constancy of equilibrium constant values (tabl.2). X-Ray analysis shows the baddeleite is dominant phase in all experiments. Its properties change a little (in the technique sensitivity limit).

Table1. Baddeleite solubility in HF aqueous solutions at 500°C, 1000 bars

Initial HCl molality	Zr(aq), $\text{m} \cdot 10^{-4}$
0.0027	0.0801
	0.0536
	0.088
0.01	0.057
	0.0426
0.027	0.113
	0.114
0.05	0.315
	0.0757
0.137	0.822
	2.74
	1.41
0.274	9.76
	7.45
	5.26
1.37	301
2.74	682

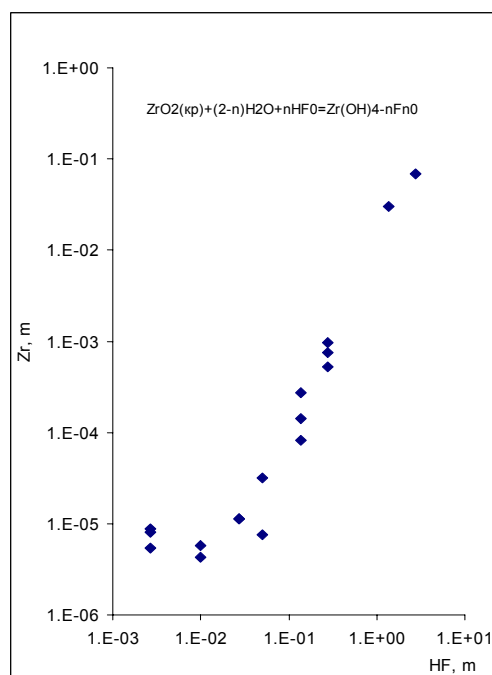


Fig.1. Baddeleite solubility in HF aqueous solutions at 500°C, 1000 bars

Table2. Calculation of equilibrium constant of $\text{ZrO}_2(\text{kp}) + (2-n)\text{H}_2\text{O} + n\text{HF}^0 = \text{Zr}(\text{OH})_{4-n}\text{F}_n^0$ at 500°C, 1000 bars

Initial HF molality	Equilibrium molality of HF^0	Zr(aq) (experiment), $\text{m} \cdot 10^{-4}$	$K = \text{Zr(aq)} / a\text{HF}^0 \cdot 10^{-5}$	$K = \text{Zr(aq)} / a^2\text{HF}^0 \cdot 10^{-5}$	$K = \text{Zr(aq)} / a^3\text{HF}^0 \cdot 10^{-5}$
0.0027	0.0027	0.074	-	-	-
0.01	0.01	0.050	-	-	-
0.027	0.027	0.114	42.2	1564	57920
0.05	0.05	0.20	40.0	800	16000
0.137	0.137	1.66	121	884	6456
0.274	0.272	7.49	274	1006	3697
1.37	1.03	301	2922	2837	2755
2.27	1.44	682	4736	3289	2284

For reaction of $\text{ZrO}_2(\text{kp}) + (2-n)\text{H}_2\text{O} + n\text{HF}^0 = \text{Zr}(\text{OH})_{4-n}\text{F}_n^0$ the bold values are selected at $n=0$ $K=5 \cdot 10^{-6}$, $\text{pK}=5.30$, at $n=1$ ($\text{Zr}(\text{OH})_3\text{F}^0$) $K=4.11\text{E}-04$, $\text{pK}=3.39$, at $n=2$ ($\text{Zr}(\text{OH})_2\text{F}_2^0$) $K=8.42\text{E}-03$, $\text{pK}=2.075$, at $n=3$ (ZrOHF_3^0) $K=2.912\text{E}-02$, $\text{pK}=1.535$

So in supercritical fluids and at standard conditions zirconium-chlorine complex are not formed. At 500°C and 1 kbar zirconium-fluorine complexes ($\text{Zr}(\text{OH})_2\text{F}_2^0$ и $\text{Zr}(\text{OH})_3\text{F}^0$) are formed in acidic fluoride solutions. It is the same as for Ti-F complex formation estimated in supercritical solutions by rutile solubility measurements [4].

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