

An experimental study of the decomposition of steenstrupine in Na_2CO_3 solution

Jens Konnerup-Madsen, Paul Martin Holm and John Rose-Hansen

This study is part of a more detailed investigation of the stability and the natural decomposition process of steenstrupine, initiated to help delineate the conditions during the later stages of solidification of the Ilímaussaq rocks. Interest in steenstrupine also arises from the potential importance regarding Kvanefjeld as a uranium ore reserve, steenstrupine being the most important uranium-bearing mineral in the Kvanefjeld area (Sørensen *et al.*, 1974; Makovicky, 1981). Major emphasis has been placed on the decomposition of steenstrupine in Na_2CO_3 solution in the 200° to 600°C range at pressures up to 1000 bars.

Experimental methods and materials

The hydrothermal runs are made in 12-inch 'cold-seal' bombs (Tuttle, 1949) heated externally in vertical resistance furnaces. Quenching is carried out by applying compressed air followed by immersion in water, resulting in a quenching time to room temperature of less than 3 minutes. Temperatures are measured with calibrated internal thermocouples and are considered accurate to within $\pm 2^\circ\text{C}$ of the recorded value. Measurements indicate that the thermal gradient in the sample region does not exceed 10°C over the temperature and pressure range of this study. Pressure is measured with a transducer and is considered accurate to ± 10 bars.

Charges consist of coarsely ground (0.25–0.5 mm) steenstrupine and added solution of Na_2CO_3 , and also NaHCO_3 , NaCl , and mixtures of these. The charges are sealed in gold capsules and consist of about 30 mg steenstrupine and 30–100 mg solution. A few runs were made with controlled oxygen fugacity using the conventional double capsule technique (Huebner, 1971) and hematite + magnetite as buffer. After quenching the capsules are cut open and the content washed out and filtered. The nature of the solid products is ascertained by standard methods of optical, X-ray and microprobe analysis. The solutions are analysed for uranium with delayed neutron activation analysis.

The steenstrupine concentrate used comes from a steenstrupine-rich analcime-albite-aegirine pegmatite (GGU 199104) collected by S. Karup-Møller (DTH). The chemical composition of the steenstrupine as determined by microprobe analysis is given in Table 1.

The choice of solutions used in the experiments was based on the presence of trona and thermonatrite, occasionally associated with villiaumite, in cavities in drill cores from the Kvanefjeld area (Sørensen *et al.*, 1970), and from the presence of saturated NaCl solutions in fluid inclusions in minerals (Konnerup-Madsen *et al.*, 1979).

Experimental results

The results of the experiments have up till now been evaluated primarily in terms of the concentration of uranium in solution after runs as this value *a priori* was considered to

Table 1. Concentration of uranium in solutions coexisting with steenstrupine and experimental conditions of runs

RUN	TEMPERATURE °C	PRESSURE BARS	TIME HOURS	BUFFER *	SOLUTION	U CONCENTRATION µG/ML **
43	200	1000	144	-	1M Na ₂ CO ₃	251.9
32	207	1000	144	-	-	770.1
42	250	500	144	-	-	197.6
16	292	500	144	-	-	479.5
44	300	1000	24	-	-	1063.8
45	304	1000	46	-	-	256.4
46	300	1000	96	-	-	269.9
17	300	1000	144	-	-	478.7
47	300	1000	144	+	-	584.6
33	360	1000	144	-	-	405.1
01	403	500	145	+	-	90.0
02	417	500	145	-	-	65.5
12	402	500	144	+	-	17.6
22	391	1000	144	+	-	15.0
15	404	1000	144	-	-	68.4
08	480	500	143	-	-	111.5
30	493	250	140	-	-	71.7
31	498	750	140	-	-	47.5
19	502	1000	47	-	-	29.3
20	490	1000	72	-	-	15.9
29	492	1000	141	-	-	9.3
25	496	1000	144	-	-	10.2
21	495	1000	238	-	-	7.6
14	607	500	144	-	-	11.3
23	590	1000	142	-	-	8.8
34	278	1000	141	-	1M NaHCO ₃	797.1
49	300	1000	144	-	1000 PPM NAF	395.8
40	314	1000	168	-	1M Na ₂ CO ₃ + 10 PPM NAF	222.2
39	309	1000	167	-	1M Na ₂ CO ₃ + 100 PPM NAF	31.5
38	302	1000	166	-	1M Na ₂ CO ₃ + 1000 PPM NAF	145.8
26	484	1000	144	-	H ₂ O	9.2
36	493	1000	143	-	0.01M Na ₂ CO ₃	32.5
28	495	1000	141	-	0.1M Na ₂ CO ₃	15.8
37	506	1000	143	-	1M NaCl	22.3

* APPLICATION/NON-APPLICATION OF HEMATITE + MAGNETITE BUFFER INDICATED BY +/-

** URANIUM CONCENTRATIONS CALCULATED ON THE BASIS OF THE CONCENTRATION IN THE FIRST LEACHATE. EXPERIMENTS SHOWED THIS TO ACCOUNT FOR MORE THAN 97 % OF THE TOTAL AMOUNT OF URANIUM OBTAINED BY SUCCESSIVE LEACHINGS OF RUN MATERIAL, LEACHING PERFORMED WITH DOUBLE-DISTILLED, DEIONIZED WATER.

respond approximately to the degree of decomposition of steenstrupine. The results are listed in Table 2 together with the experimental conditions and are presented graphically in fig. 1.

The solid run products have at present only been cursorily examined. *Steenstrupine* is present in all runs and even at the highest temperatures only a roughly 10 µm wide reaction rim constitutes the main optical difference from the starting material. *Monazite* was indicated by X-ray diffraction in all runs above approximately 300°C. *Thermonatrite* was identified in all runs with Na₂CO₃ solutions and is typically present in the form of about 20 µm long quench rosettes or thin plates and needles. In addition to these phases colourless, apparently

Table 2. Microprobe analyses of steenstrupine in experimental studies

	STARTING MATERIAL	200 °C		400 °C		500 °C		
		CENTRE	RUN 32 RIM	CENTRE	RUN 22 RIM	CENTRE	RUN 25 RIM	MINERAL X
NA	2.2	3.0	8.0	9.4	9.0	12.5	13.0	1.4
AL	0.4	ND	ND	0.3	0.3	0.3	0.4	0.1
SI	13.3	14.4	12.0	11.1	11.7	10.0	12.0	22.7
P	5.0	5.5	5.3	5.8	5.4	5.0	4.4	0.0
CA	1.5	1.7	1.8	2.0	2.0	1.7	1.9	0.1
TI	0.2	0.2	0.2	0.2	0.1	0.2	0.1	< 0.07
MN	3.4	5.0	3.0	3.0	5.3	3.5	3.0	< 0.08
FE	3.3	3.7	3.0	6.5	2.0	2.5	5.0	< 0.07
Y	0.3	0.4	0.3	0.1	0.3	0.1	0.2	0.9
ZR	1.3	3.9	1.0	3.0	4.2	3.1	1.9	< 0.27
LA	9.3	ND	ND	10.9	9.0	10.2	8.2	2.6
CE	13.6	14.2	11.0	14.0	15.9	15.8	14.0	7.4
PR	1.9	1.7	1.8	2.6	1.8	1.9	1.9	0.9
ND	9.3	9.2	8.0	9.9	11.0	9.6	10.0	4.5
TH	4.0	4.1	4.7	3.2	4.1	4.5	3.7	2.2

NOTES: ND NOT DETERMINED

< BELOW DETECTION LIMIT AS STATED

NB DETERMINED BUT IN ALL CASES BELOW DETECTION LIMIT (0.23 WEIGHT PCT.)

orthorhombic crystals showing moderate birefringence were observed to have grown on the rims of steenstrupine grains in all runs with Na_2CO_3 solution at temperatures above approximately 300°C. These crystals are up to 10 μm long and show slight effervescence in dilute HCl. They occur in increasing amounts with increase in run temperature. An average microprobe analysis of this mineral X is given in Table 2 together with microprobe analyses of steenstrupine grains obtained at 200°, 400° and 500°C and the starting steenstrupine material.

Discussion of results

The most significant result of the present preliminary experiments is the marked decrease in uranium concentration in 1M Na_2CO_3 solutions in contact with steenstrupine with increase in temperature (fig. 1 A). Similar results are obtained with other solution types and with 1M Na_2CO_3 solutions buffered to hematite-magnetite oxygen fugacities (fig. 1 B). The lack of influence from hematite-magnetite buffering of the oxygen fugacity may, however, be due to a combination of low temperatures and short durations of experiments (Ulmer, 1971, pp. 140–141). Variations in pressures do not appear to influence the results in any systematic way (fig. 1 A).

In a strict sense the relations expressed in fig. 1 only apply to an experimental duration of about 6 days. Runs at 300° and 500°C at 1000 bars with the duration of runs from 1 to 10 days

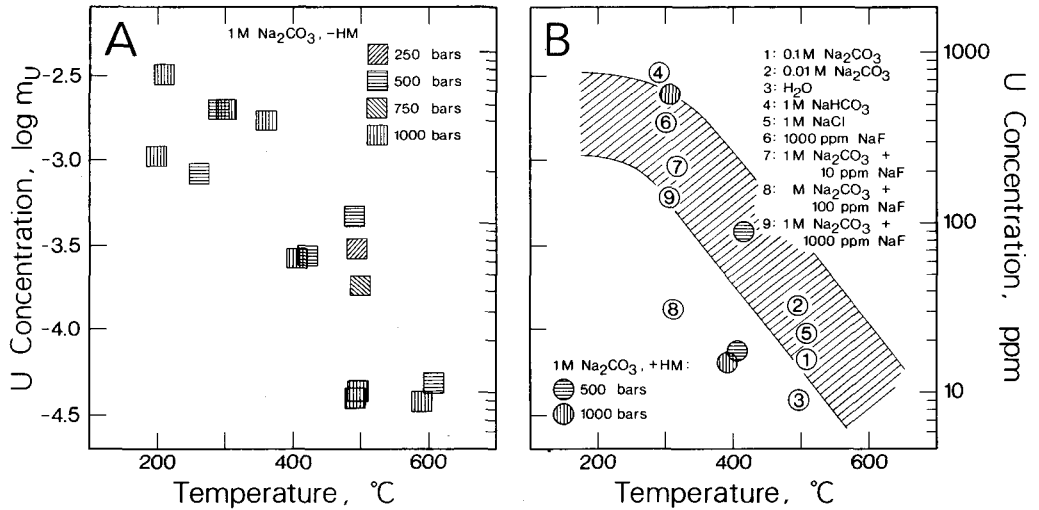


Fig. 1. Concentration of uranium (shown both on a log(mole U) and a ppm scale) in solutions coexisting with steenstrupine versus temperature. (A) Results for 1M Na₂CO₃ solutions at various pressures as shown in figure, with an experimental duration of 6 days and no buffering of oxygen fugacity (-HM). (B) Results for various solutions with an experimental duration of 6–8 days at a pressure of 1000 bars, and for 1M Na₂CO₃ solutions buffered with hematite-magnetite (+HM) at the pressures shown.

show variations in the concentration of uranium in solution (Table 1). Whereas the results at 300°C (runs 44, 45, 46, and 47) are ambiguous, the results at 500°C (runs 19, 20, 29, 25, and 21) show a marked decrease in concentration with the length of the experiment but with a levelling out for run durations around 6 days (Table 1). These experiments indicate disequilibrium and hence the results do not depict maximum uranium concentrations but the values corresponding to the stated experimental duration. The observed decrease in concentration of uranium in solution with increasing temperature and with increase in time at 500°C may be tentatively linked with the (kinetics of) formation of the unidentified phase (mineral X, Table 1) on the rims of steenstrupine grains. As this phase is richer in uranium than the coexisting steenstrupine (Table 1, last columns) its formation would tend to lower the amount of uranium in solution at higher temperatures.

The main changes in composition of steenstrupine with temperature are the large increase in Na and the slight decrease in Si. The decrease in the uranium content of steenstrupine is already observed at 200°C and hence supports the proposal that the decrease in uranium in solution at higher temperatures is in part due to incorporation of uranium in other phases such as monazite and/or mineral X (Table 1).

Microprobe analyses of mineral X (average analysis given in Table 1) show it to be very inhomogeneous in composition, especially regarding U and the relative amounts of the REE, whereas Si appears to be very constant. Inspection of the chemical analyses suggests this mineral to be a tectosilicate. Based on the chemical compositions, and taking the nature of the coexisting solutions into consideration, calculations indicate that this phase may tentatively be described as a Na(REE, Th, U)₂(SiO₂)₁₃-carbonate/bicarbonate. The incor-

poration of carbonate ions possibly takes place only at the considerable pressures of carbon dioxide obtained in the higher temperature runs. However, further data on this phase are needed in order to characterize it more thoroughly.

Concluding remarks

The study indicates that treatment of steenstrupine with Na_2CO_3 solutions does not involve a destruction of steenstrupine but that it can respond by changes in composition without significant structural changes. The concentration of uranium in solution in contact with steenstrupine furthermore does not merely reflect equilibrium with steenstrupine but is affected by formation of other phases such as monazite and/or a possibly new phase (mineral X).

In the Ilímaussaq intrusion rim zones of zoned crystals of steenstrupine are often deficient in uranium compared to the central parts, suggesting that oxidation of rims formed UO_2^{2+} and that some of the uranium was then removed by leaching (Sørensen, 1962). Studies by Buchwald & Sørensen (1961) and by Makovicky *et al.* (1979) show that the higher uranium contents are observed in the most altered parts of the steenstrupine grains. The present study shows a leaching process to be most effective at comparatively low temperatures. Similar relations between uranium in solution and temperature as depicted in fig. 1 were observed by Lemoine (1975) and Naumov (1961) for UO_2 and UO_3 in NaHCO_3 solutions and were explained in terms of equilibria involving carbonate ion complexing. In the present experiments similar relations are considered likely but have in part been blurred by formation of (and equilibrium with) other uranium-bearing phases.

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Institut for Petrologi,
University of Copenhagen,
Øster Voldgade 10,
DK-1350 Copenhagen K.