

# Experimental study of the equilibrium between pollucite, albite and hydrothermal fluid in pegmatitic systems

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## Abstract

Pollucite is a silicate mineral of the rare element caesium, occurring in granitic pegmatites. Experiments have been carried out at 450, 600, and 750 °C, 1.5 kbar, to study the equilibrium between pollucite, albite and the co-existing hydrothermal solution. When pollucite co-exists with albite, the alkaline composition of the solution is buffered. The Cs/Na ratio of the solution has been determined to be 0.11 at 450 °C, 0.22 at 600 °C and 0.23 at 750 °C. Pollucite contains about 15 mol.% of sodium, whereas albite is almost purely sodic. In nature, pollucite with more than 82 mol.% caesium has never been found. This can be explained by the absence of solutions in granitic pegmatites having a higher Cs/Na ratio than those determined by us.

**KEYWORDS:** pollucite, albite, hydrothermal fluid, pegmatite, caesium.

## Introduction

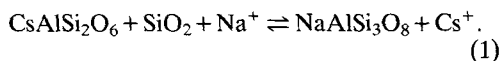
THE distribution of chemical elements between co-existing minerals and fluid during the crystallization or the alteration of rocks is an important basic aspect of geochemistry. It is closely related to the general laws of chemical bonding and crystal chemistry. The interactions between fluids and minerals during hydrothermal processes is dependent on the nature of the minerals, temperature conditions, pressure and composition of the fluid. Numerous experimental studies, focussed on these reactions, have given a clear insight into the partitioning of major as well as trace elements in various systems, such as the alkali-feldspars, plagioclases, feldspathoids and micas. They can be applied to the minerals of pegmatites, which are considered to crystallize from water-rich residual felsic magmas. Equilibria between the minerals and hydrothermal fluids are thus fundamental to an understanding of the processes of pegmatite formation.

Pollucite is the only important silicate mineral of caesium, occurring frequently in lithium-rich pegmatites which reached the ultimate degree of rare-alkali fractionation. Albite is generally present in the system as an associated mineral. Due to the very low Clarke value of caesium, 1.7 ppm (Taylor and McLennan, 1981) and special crystal-

lochemical properties (the prohibitive ionic size of 1.67 Å<sup>o</sup>), it does not participate in the first structural grouping derived from the melts and gradually accumulates in the lowest melting mobile derivatives of such melts (Černý *et al.*, 1981; Goad and Černý, 1981). This is because of the strong partitioning of caesium into the melt and vapour phases as shown experimentally by Carron and Lagache (1980) for chloride-based systems. Pollucite is the ultimate expression of caesium accumulation in the very last residua of granitic fractionation. According to Solodov (1966), a concentration of 1.0 wt.% caesium is required in the pegmatite melt to trigger the crystallization of pollucite.

## Principle of the study

The equilibrium studied here is



When pollucite is in contact with a hydrothermal solution containing a sodium salt, a part of Cs goes into the solution and the same amount of Na from the solution enter the pollucite. If  $a_{\text{Na}^+}$  and  $a_{\text{Cs}^+}$  are the activities of the cations Na and Cs in solution and  $a_{\text{Po}}$ ,  $a_{\text{Ab}}$  and  $a_{\text{Q}}$  are those of the pollucite, albite and quartz, applying the laws

of mass action at a given temperature and pressure, the equilibrium constant expression can be written as

$$a_{\text{Ab}}a_{\text{Cs}^+}/a_{\text{Po}}a_{\text{Q}}a_{\text{Na}}=K(P, T). \quad (2)$$

When quartz is present as a phase, its activity is unity and may be dropped from the equilibrium expression.  $a_{\text{Ab}}/a_{\text{Po}}$  is a function of pressure, temperature, and composition of the solid which can be defined by the ratio,  $n = \text{Cs}/\text{Na}$ . The above equation becomes

$$a_{\text{Cs}^+}/a_{\text{Na}^+} = F(P, T, n). \quad (3)$$

This relation shows that at equilibrium, the ratio of activities of  $\text{Na}^+$  and  $\text{Cs}^+$  in solution is a function of the temperature, pressure, and composition of the solid phase.

### Experimental procedure

Burnham and Nekvasil (1986) have shown that the lowest temperature of the liquidus of the water-saturated quartz-orthoclase melt is at about 660°C and 2 kbar. This system is close to that of granitic pegmatites. Pollucite-bearing pegmatites are formed at relatively high temperature and low pressure, as evident from their structural geological location and from the accompanying phase assemblage (Černý and Ferguson, 1972; Černý and Simpson, 1978). Based on the above studies and information from the literature (Cerny, 1979; Neuvonen and Vesasalo, 1960), we have chosen three temperatures, 450, 600, and 750°C for the present study, in order to check the influence of temperature on the equilibrium. All the experiments were done at a confining pressure of 1.5 kbar and in all of them aqueous alkali chloride solutions of 1M and 4M were used. Analytical studies on fluid inclusions (Weisbrod and Poty, 1975, 1976; Poty *et al.*, 1977) show that such a choice covers the composition of natural fluids except for very dilute ones. There is no data on the phase domains in the system  $\text{CsCl}-\text{NaCl}-\text{H}_2\text{O}$ , but under the given experimental conditions, the system  $\text{NaCl}-\text{H}_2\text{O}$  is beyond the domain of unmixing (Sourirajan and Kennedy, 1962).

The starting materials for mineral synthesis were oxide mixtures of appropriate composition (referred to as gel), prepared by the classical gelling method (Hamilton and Henderson, 1968) of mixtures of colloidal silica suspension (Ludox), previously purified with ion-exchange resins, and the nitrate solutions of Al, Cs and Na. The gel was allowed to stand overnight at room temperature to ensure complete precipitation and then slowly evaporated to dryness. The completely dried gel was ground in an agate mortar and then transferred to a platinum crucible. The nitrates were decomposed slowly over a bunsen flame, and the gel was fired in a furnace at about 800°C. The chemical composition was verified by chemical analysis. Varying amounts (50 to 250 mg) of a mechanical mixture of pollucite gel and natural quartz in stoichiometric proportions, or albite gel were weighed in gold tubes of 2.5 to 4 cm length and 4.4 mm diameter, to which varying volumes (25 to 200  $\mu\text{l}$ ) of alkali chloride solutions were added. Some

experiments were performed with a mixture of 1 mole of pollucite, 1 mole of quartz and 1 mole of albite. For the experiments near albite composition, an excess of NaCl was added along with CsCl. The addition of NaCl to the system permits the control of the amount of Cs to be fixed in albite, thereby retaining a measurable amount of Cs in the solution after the run. The tubes were welded at both ends and were subjected to the required temperature and pressure in Bridgman type autoclaves. The temperature was controlled at  $\pm 2^\circ\text{C}$  by chromel-alumel thermocouples. The pressure could not be externally controlled and so it was calculated using PVT data from Kennedy (1950) and Burnham *et al.* (1969). Several of the experiments were done in duplicate to make sure of the reproducibility of the results. The duration of the experiments was 18 days at 750°C and varied from 18 to 30 days at 600°C, and 60 to 82 days at 450°C. The two sets of experiments performed at 600°C and 450°C led to similar results, indicating that steady state had been attained in all the experiments.

At the end of the run, the autoclave was cooled in a compressed air blast. The temperature fell from 600 to 100°C in about 10 minutes and to room temperature in about 20 minutes. The tubes were cut opened and the solid and aqueous phases were transferred to a clean agate mortar by a fine jet of water. The mixture was transferred to a plastic vial and centrifuged to separate solid and liquid phases. The crystalline grains were washed several times. Previous studies have shown the presence of adsorbed Cs on albite (Roux, 1971; Iiyama, 1974; Volfinger and Robert, 1980). So, for the experiments with albite and CsCl, the solids were washed with 0.5N KCl solution, which was found to be effective in removing the adsorbed Cs. The solid phase was dried and the solution was made up to a fixed volume. The alkali composition of both were determined by flame emission spectro-photometry. The precision obtained for Na and Cs was better than 3%. For the solution, the chloride composition was checked, permitting verification that most of the solution had been recovered. As the starting compositions of the solid and solution were known and their final composition could be determined, complete information was obtained for the partitioning of alkalis between solid and solution for each run. The crystalline solid phases were identified by X-ray diffraction and observed by scanning electron microscopic techniques.

### Results and discussion

The results are presented in Tables 1, 2 and 3, and graphical representation is shown by the classical isotherm-isobar distribution diagrams (Fig. 1 *a*, *b* and *c*) in which the composition of the solid is plotted against that of the solution expressed by  $\text{Na}/(\text{Na}+\text{Cs})$  ratios which vary from 0 to 1. Calculations are made for solids in micromoles ( $\mu\text{M}$ ) for 100 milligrams (mg) and for solutions in micromoles for 100 microlitres ( $\mu\text{l}$ ). In Fig. 2 the partition coefficients  $P$ , of Na

Table 1. Results of the experiments at 450°C, 1.5kbar.

(Explanations in the text)

D	Reactants			Bulk solid Comp.			Soln. Comp.			P			
	mg	M	μl	μM/100mg	Na	Cs	X	Na	Cs		Y	K/Y	
60	Po+Q	250	NaCl	1	25	Po+Q	11	225	0.05	40	61	0.40	0.13
60	Po+Q	150	NaCl	1	25	Po+Q	14	221	0.06	46	56	0.45	0.13
60	Po+Q	100	NaCl	1	25	Po+Q	17	221	0.07	53	47	0.53	0.13
82	Po+Q	100	NaCl	1	25	Po+Q	17	226	0.07	52	48	0.52	0.14
60	Po+Q	100	NaCl	1	50	Po+Q	23	227	0.09	60	40	0.60	0.15
82	Po+Q	100	NaCl	1	50	Po+Q	22	230	0.09	67	33	0.67	0.13
60	Po+Q	100	NaCl	1	100	Po+Q	28	234	0.11	73	23	0.76	0.15
82	Po+Q	100	NaCl	1	150	Po+Q	30	233	0.11	82	13	0.86	0.13
60	Po+Q	50	NaCl	1	100	Po+Q+Ab	53	205	0.21	79	12	0.87	0.24
60	Po+Q	50	NaCl	1	150	Po+Q+Ab	61	203	0.23	80	11	0.88	0.26
60	Po+Q	50	NaCl	4	50	Po+Q+Ab	70	190	0.27	330	35	0.90	0.30
82	Ab	50	CsCl	1	150	Po+Q+Ab	90	220	0.29	82	10	0.89	0.32
60	Po+Q	50	NaCl	4	75	Po+Q+Ab	94	179	0.34	365	36	0.91	0.37
60	Po+Q	50	NaCl	4	100	Po+Q+Ab	124	161	0.44	309	36	0.90	0.49
82	Ab	50	CsCl	1	100	Po+Q+Ab	160	156	0.51	87	10	0.90	0.57
82	Po+Q+Ab	100	NaCl	1	50	Po+Q+Ab	151	132	0.53	89	9	0.91	0.58
82	Po+Q+Ab	50	NaCl	1	100	Po+Q+Ab	184	118	0.61	86	10	0.90	0.68
60	Po+Q	50	NaCl	4	150	Po+Q+Ab	180	116	0.61	330	36	0.90	0.68
82	Po+Q+Ab	50	NaCl	1	150	Po+Q+Ab	192	101	0.66	84	8	0.91	0.73
82	Po+Q+Ab	50	NaCl	1	200	Po+Q+Ab	210	90	0.70	87	10	0.90	0.78
82	Ab	50	{CsCl 1 20 + NaCl 1 80 CsCl 1 20			Po+Q+Ab	355	22	0.94	89	9	0.91	1.03
82	Ab	100	{CsCl 1 20 + NaCl 1 80 CsCl 1 10			Po+Q+Ab	362	12	0.97	89	8	0.92	1.05
82	Ab	100	{CsCl 1 10 + NaCl 1 40			Po+Q+Ab	365	6	0.98	92	7	0.93	1.05

D days

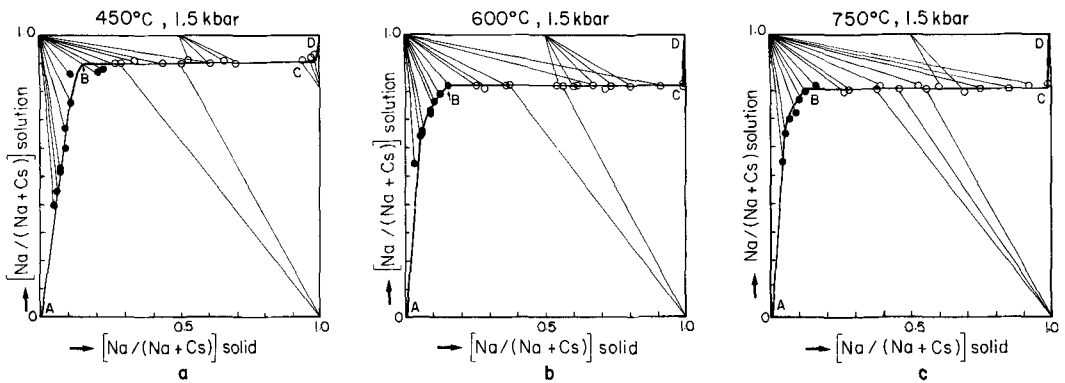


Fig. 1. (a, b, and c), Isotherm-isobar of distribution curves at 450°C (a), 600°C (b), and 750°C (c). Slanting lines connect the starting assemblage and the final assemblage (circles) for individual experiment. The solid circles represent (Po + Q + Unknown phase Z) and open circles represent (Po + Q + Ab).

between solids and solutions are plotted against the solid composition. P is expressed by

$$P = \frac{Na}{(Na + Cs)_{solid}} / \frac{Na}{(Na + Cs)_{solution}} \quad (4)$$

The variations in chemical composition

between the reactants and products are in agreement with the variations in mineralogical composition, i.e. the crystallization of albite from (Po+Q) is followed by an enrichment of Na in the solid whereas the solution becomes enriched in Cs and vice versa. In the experiments, ion-exchange and mineral growth occur at the same

Table 2: Results of the experiments at 600°C, 1.5kbar.

(Explanations in the text)

D	Reactants			Bulk solid Comp. μM/100mg			Soln. Comp. P μM/100μl					
	mg	M	μl	Na	Cs	X	Na	Cs	Y	X/Y		
18	Po+Q	250	NaCl 1	25	Po+Q	8	237	0.03	50	43	0.54	0.06
18	Po+Q	150	NaCl 1	25	Po+Q	12	223	0.05	56	32	0.64	0.08
18	Po+Q	100	NaCl 1	25	Po+Q	15	237	0.06	57	31	0.65	0.09
30	Po+Q	100	NaCl 1	25	Po+Q	13	217	0.06	61	31	0.66	0.09
18	Po+Q	100	NaCl 1	50	Po+Q	22	226	0.09	67	26	0.73	0.12
30	Po+Q	100	NaCl 1	50	Po+Q	22	211	0.09	65	26	0.72	0.13
20	Po+Q	100	NaCl 1	75	Po+Q	26	228	0.10	73	23	0.76	0.13
20	Po+Q	100	NaCl 1	100	Po+Q	30	216	0.12	76	21	0.79	0.15
30	Po+Q	100	NaCl 1	150	Po+Q	43	237	0.15	77	17	0.82	0.18
18	Po+Q	50	NaCl 1	100	Po+Q+Ab	68	200	0.25	72	16	0.82	0.31
18	Po+Q	50	NaCl 1	150	Po+Q+Ab	80	203	0.28	75	17	0.81	0.35
18	Po+Q	50	NaCl 4	50	Po+Q+Ab	100	179	0.36	317	68	0.82	0.44
30	Ab	50	CsCl 1	150	Po+Q+Ab	108	187	0.37	74	16	0.82	0.45
30	Po+Q+Ab	100	NaCl 1	50	Po+Q+Ab	146	123	0.54	80	18	0.82	0.66
30	Ab	50	CsCl 1	100	Po+Q+Ab	181	141	0.56	77	18	0.81	0.69
30	Po+Q+Ab*	100	NaCl 1	100	Po+Q+Ab	184	124	0.60	78	18	0.82	0.73
30	Po+Q+Ab	100	NaCl 1	100	Po+Q+Ab	187	121	0.61	77	17	0.82	0.74
30	Po+Q+Ab	50	NaCl 1	100	Po+Q+Ab	223	111	0.67	77	17	0.82	0.82
18	Po+Q	50	NaCl 4	100	Po+Q+Ab	242	98	0.71	296	68	0.81	0.88
30	Po+Q+Ab	50	NaCl 1	150	Po+Q+Ab	255	93	0.73	75	17	0.82	0.89
30	Po+Q+Ab	50	NaCl 1	200	Po+Q+Ab	283	69	0.80	79	18	0.82	0.98
18	Po+Q	50	NaCl 4	150	Po+Q+Ab	342	33	0.91	302	66	0.82	1.11
			CsCl 1	20								
30	Ab	50	+ NaCl 1	80	Po+Q+Ab	369	5	0.99	82	18	0.82	1.21
			+ CsCl 1	20								
30	Ab	100	+ NaCl 1	80	Po+Q+Ab	366	3	0.99	83	17	0.82	1.19
			+ CsCl 1	10								
30	Ab	100	+ NaCl 1	40	Po+Q+Ab	369	2	0.99	84	17	0.83	1.19
			+ CsCl 1	10								
30	Ab*	50	+ NaCl 1	40	Po+Q+Ab	258	3	0.99	41	9	0.82	1.20
			+ CsCl 1	10								

D days, Ab\* Natural Albite

time and the resulting aluminosilicates were re-equilibrated as shown earlier by Lagache and Weisbrod (1977).

Application of phase rule to the equilibrium indicates that five independent components are necessary to describe all the phases; Na and Cs for the solutions, Po, Ab and Q for the solids. If the four phases, pollucite, albite, quartz and vapour co-exist, the degree of freedom at a given pressure and temperature can be written as  $V = (5 - 4) = 1$  and therefore the system is univariant. In Fig. 1 (a, b and c) such a system is represented by the horizontal section of the isotherm, BC, along which the overall composition of the solid (X) varies. In the presence of the tri-mineral assemblage, the composition of the solution (Y) remains constant. In this case, the solutions are buffered by the mineral assemblage. This situation is the same for the experiments at the three temperatures, 450, 600, and 750°C, and the Y values are 0.90, 0.82, and 0.81 respectively.

In the solid-solution domains, AB and CD, the system is bivariant. The composition of the final solutions varies rapidly for very small variations

in the solid composition. There is a large domain of solid solution formation along AB. The maximum solubility of Na in pollucite is about 15 mol.% beyond which albite starts crystallizing. On the other hand, the solid-solution formation is practically negligible along CD. The trace-element fixation studies in albite (Roux, 1971; Volfinger and Robert, 1980) give the value of  $P_{Cs} = \text{crystal/vapour} = 0.0029$ . The maximum solubility of Cs in albite is 253 ppm, beyond which pollucite appears as a separate phase (Iiyama, 1974). The value of the ratio,  $Cs/(Cs+Na)$  in albite given by these authors explains the constant presence of pollucite and albite in our experiments. This is due to the fact that the tetrahedra of  $SiO_4$  and  $AlO_4$  are more compact in albite than in pollucite, and albite cannot offer voluminous sites for Cs. This shows that purely Cs feldspar is not stable in the selected experimental conditions.

The general trend observed in such experiments is that the rate of the reaction in the silica producing direction ( $Ab \rightarrow Po + Q$ ) is greater than that in the silica consuming direction, as observed by

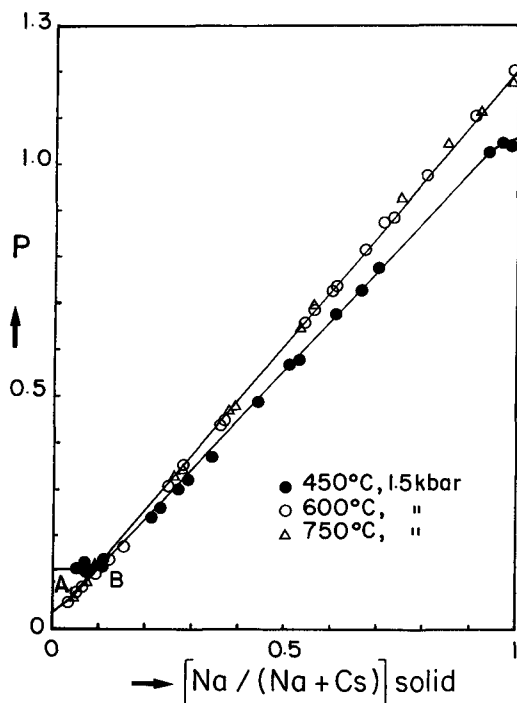


FIG. 2. Partition coefficient,  $P$  vs. solid composition.

Orville (1972) in the case of plagioclases. In the present experiments, since Na and Cs are both alkali elements, the duration of time is sufficient for equilibrium to be attained in the forward and reverse directions as shown by the connecting lines in Fig. 1 (*a*, *b* and *c*) between the starting non-equilibrium assemblage and the final equilibrium assemblage.

The results of the experiments at 750°C do not differ appreciably from the equilibrium at 600°C, but there are marked differences between the experimental results at 600 and 450°C. At 450°C, the equilibrium is shifted upwards and the trimineral assemblage co-exists in equilibrium with alkali chloride solutions richer in Na. As observed from Fig. 1 (*a*, *b* and *c*) along AB, for a given solution composition, pollucite is richer in Na at 450°C than at 600 and 750°C. This is also evident from the curve (Fig. 2), which shows that the partitioning of Na favours pollucite more at 450°C than at higher temperatures. At 450°C, along the pollucite solid-solution region AB, the partition coefficient remains constant. In the case of experiments at 600 and 750°C the partition coefficient of pollucite increases linearly along AB. This could imply that the solid solution becomes more

ideal as the temperature decreases. This surprising result has to be carefully considered. At low temperatures the stable structural sodium analogue of pollucite is analcime and the study of natural samples shows relatively extended solid-solution formation. Therefore one can expect an increase in the solubility of Na in pollucite as temperature decreases. This explains the preceding remarks. Černý (1974) has shown that the domain of sodian pollucite can extend up to 50% pollucite and our results also favour a large domain of solid solution at low temperature.

*Effect of solution concentration on equilibrium.* Several experiments were done with 4M alkali chloride solutions to check the influence of total concentration on the equilibrium. From the results, we can conclude that, under hydrothermal conditions, the ratio  $\text{Na}/(\text{Na}+\text{Cs})$  does not depend upon the total concentration of NaCl and CsCl, but only on their relative proportions, expressed by the parameter  $Y$  as shown earlier by Wyart and Sabatier (1962), Orville (1963), Iiyama (1964) and Debron (1965).

*Nature of the phases obtained.* The SEM studies (Fig. 3) show that pollucite crystallizes as small globular grains (0.5 to 2 $\mu\text{m}$ ). But the co-existing tabular albite is idiomorphic (10 $\mu\text{m}$ ) with well developed faces and characteristic twinning. Even though the experimental results are similar at 600 and 750°C, XRD study of the pollucite solid solution (AB) formed at 750°C showed an additional phase (Z) along with quartz. The intensities of the diffraction peaks remain the same in all the experiments indicating that there is only one extra phase present. The intensity of the peaks corresponding to quartz is much reduced when this new phase is present. The new peaks correspond to  $d$  values 3.58 (100% intensity), 3.60 (80% intensity) and 4.11Å (35% intensity). This new phase could not be identified with any of the aluminosilicates. It does not apparently affect the solid and solution concentrations which are almost the same as those at 600°C. The intensity of the peaks decreases as B is approached, and once albite starts crystallizing, it totally disappears. In the reverse reactions, this new phase is absent.

Two experiments were done with natural low albite instead of albite gel and the results show that it does not affect the solid and solution compositions. In all the experiments starting with gel, the albite formed is always of the high temperature form. In the experiments with natural albite, it remains in the low temperature form even at 750°C. A similar observation was reported by Wyart and Sabatier (1956).

The  $a$  cell parameter was calculated from the XRD data using the least squares unit cell refine-

Table 3: Results of the experiments at 750°C, 1.5kbar.

(Explanations in the text)

D	Reactants		Bulk Solid Comp.			Soln. Comp.				
	mg	M	$\mu\text{M}/100\text{mg}$	Na	Cs	X	Na	Cs	Y	P
18	Po+Q	250 NaCl	1 25	Po+Q+Z	10 242	0.04	38 32	0.55	0.07	
18	Po+Q	150 NaCl	1 25	Po+Q+Z	14 248	0.05	46 25	0.65	0.08	
18	Po+Q	100 NaCl	1 25	Po+Q+Z	19 248	0.07	53 23	0.70	0.10	
18	Po+Q	100 NaCl	1 50	Po+Q+Z	23 230	0.09	65 25	0.72	0.13	
18	Po+Q	100 NaCl	1 75	Po+Q+Z	25 226	0.10	75 23	0.77	0.13	
18	Po+Q	100 NaCl	1 100	Po+Q+Z	30 219	0.12	74 19	0.80	0.15	
18	Po+Q	100 NaCl	1 150	Po+Q+Z	42 222	0.16	72 15	0.82	0.20	
18	Po+Q	50 NaCl	1 100	Po+Q+Ab	66 190	0.26	72 18	0.80	0.33	
18	Po+Q	50 NaCl	1 150	Po+Q+Ab	81 205	0.28	76 18	0.81	0.35	
18	Ab	50 CsCl	1 150	Po+Ab	118 191	0.38	78 18	0.81	0.47	
18	Po+Q	50 NaCl	4 50	Po+Q+Ab	110 172	0.39	313 68	0.82	0.48	
18	Ab	50 CsCl	1 125	Po+Ab	130 154	0.46	72 17	0.81	0.57	
18	Po+Q	50 NaCl	1 75	Po+Q+Ab	154 137	0.53	319 71	0.82	0.65	
18	Ab	50 CsCl	1 100	Po+Ab	179 143	0.56	81 19	0.81	0.69	
18	Po+Q+Ab	100 NaCl	1 100	Po+Q+Ab	195 130	0.60	68 15	0.82	0.73	
18	Po+Q+Ab	50 NaCl	1 100	Po+Q+Ab	236 108	0.69	68 17	0.80	0.86	
18	Po+Q	50 NaCl	4 100	Po+Q+Ab	261 85	0.75	287 66	0.81	0.93	
18	Po+Q	50 NaCl	4 125	Po+Q+Ab	220 39	0.85	313 75	0.81	1.05	
18	Po+Q	50 NaCl	4 150	Po+Q+Ab	327 27	0.92	307 68	0.82	1.12	
18	Ab	100	CsCl 1 20 + NaCl 1 80	Po+Ab	367	3	0.99	82 18	0.83	1.19
18	Ab*	100	+ CsCl 1 20 + NaCl 1 80	Po+Ab	361	3	0.99	71 14	0.83	1.19
18	Ab	100	+ CsCl 1 10 + NaCl 1 40	Po+Ab	371	2	0.99	84 17	0.83	1.19

D days, Ab\* Natural Albite

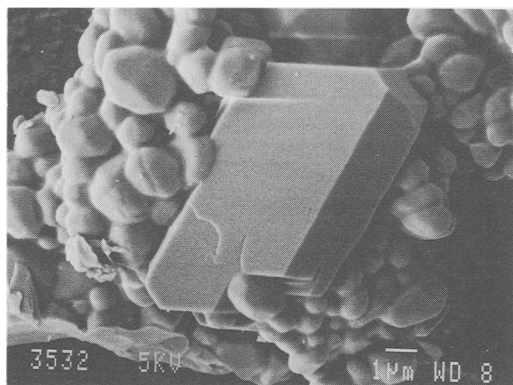


Fig. 3. Pollucite co-existing with albite (experiment at 600°C, 1.5 kbar).

ment program (Appleman and Evans, 1973). The standard error of calculation on the  $a$  value is in the range of 0.001 to 0.002. The results are presented in Table 4, along with those of other authors. When the Na ion which is smaller in size substitutes for the Cs ion, there is a slight decrease in the  $a$  value. These results can be compared with those of Martin and Lagache (1975), who had studied the series pollucite-leucite and pollu-

Table 4: Unit cell parameter of Synthetic Pollucite

	Temp.	$P_{\text{H}_2\text{O}}$	Mol. % Na	$a(\text{Å})$
Barrer and McCallum(1953)	160°C-450°C	Low Water.P	0.0	13.600
Kume and Koizumi(1965)	450°C	1kbar	0.0	13.653
Henderson and Taylor(1969)	1100°C	1bar	0.0	13.685
Suito et al. (1974)	600°C	1kbar	0.0	13.685
Martin and Lagache(1975)	600°C	1kbar	0.0	13.677
Present Work	450°C	1.5kbar	5.0	13.695
"	"	"	11.0	13.690
"	600°C	"	0.0	13.686
"	"	"	3.0	13.685
"	"	"	15.0	13.676
"	750°C	"	4.0	13.689
"	"	"	16.0	13.675

cite-Rb-leucite. The differences in the  $a$  values observed for the experiments at 450, 600, and 750°C do not seem to be significant.

#### Applications and conclusions

It has been reported (Černý, 1982) that the composition of natural pollucite does not exceed 82 mol. % pollucite in the pollucite-analcite ser-

ies. The present study shows that between 450 and 750°C, whenever the sodium content of the bulk solid (Po+Ab) is more than 15 mol.%, a Cs phase having almost the Cerny's composition of natural pollucite and a Na phase (albite) co-exist. The natural minerals can in fact contain more Na in solid solution than in the synthetic minerals. Two explanations can be given for this: (a) the natural minerals might have been formed at a lower temperature; or (b) the Si/Al ratio, which is always more than 2 in the case of natural minerals, is stoichiometric in synthetic pollucites. This might have facilitated a better incorporation of Na in the structure. The present study does not give any evidence for the second hypothesis.

As far as the first point is concerned, it is difficult to imagine that primary pollucite, which is one of the last phases to crystallize, can be formed at still lower temperatures. At low temperatures pollucite can equally be considered as a product of later metasomatism and hydrothermal alteration phenomena. In the low temperature conditions, pollucites which are richer in Na and belonging to the continuous pollucite-analcime series can occur and replace the pollucite-albite assemblage.

Our studies show that the pollucites rich in Cs may be the primary products of higher temperatures and those containing more than 15 mol.% analcime may be the pollucites of second generation.

The solutions co-existing with the primary pollucites have a Cs/Na ratio, which never exceeds 0.23 at 750°C, 0.22 at 600°C and 0.11 at 450°C. As no natural pollucite with more than 82 mol.% pollucite has ever been found, we can say that no solution having a Cs/Na ratio higher than the preceding values has existed in granitic pegmatites. The association of pollucite with albite therefore always buffers the solution composition having a definite ratio, which is dependent upon the temperature. A solution containing only 1/5 of Cs with respect to Na can permit the crystallization of a Cs mineral at 600°C and this proportion can be lowered to 1/10 at lower temperatures. We understand that in spite of the low Clarke value of Cs in nature, its enrichment in the solutions associated with rare-element pegmatites can result in the formation of a Cs mineral.

Finally, this study has permitted us to determine precisely the alkaline composition of Na and Cs in the rare-element pegmatite medium.

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#### References

- Appleman, D. E. and Evans, H. T. Jr. (1973) Least square unit-cell refinement with indexing. *U.S.G.S.-GD-73-003*, no. 20.
- Barrer, R. M. and McCallum, N. (1953) Hydrothermal chemistry of silicates. Part IV. Rubidium and Caesium Aluminosilicates. *J. Chem. Soc. London*, 4029-35.
- Burnham, C. W. and Nekvasil, H. (1986) Equilibrium properties of granitic magmas. *Am. Mineral.* **71**, 239-63.
- Holloway, J. R. and Davis, N. F. (1969) The specific volume of water in the range 1000 to 8900 bars, 20°C to 900°C. *Am. J. Sci.* **267A**, 80-90.
- Carron, J. P. and Lagache, M. (1980) Etude expérimentale du fractionnement des éléments Rb, Cs, Sr et Ba entre feldspaths alcalins, solutions hydrothermales et liquides silicatés dans le système Q-Ab-Or-H<sub>2</sub>O à 2 kb entre 700°C et 800°C. *Bull. Minéral.* **103**, 571-8.
- Černý, P. (1974) The present status of the analcime-pollucite series. *Can. Mineral.* **12**, 334-41.
- (1979) Pollucite and its alteration in geological occurrences and in deep burial radioactive waste disposal. In *Scientific Basis for Nuclear Waste Management I* (McCarthy, G. J., ed.) Plenum Publ. Corp., New York, 231-6.
- (1982) Mineralogy of rubidium and cesium. In *Granitic Pegmatites in Science and Industry* (Cerny, P., ed.) Mineral. Assoc. of Canada Short Course Handbook, **8**, 149-61.
- and Ferguson, R. B. (1972) The Tanco pegmatite at Bernic Lake Manitoba. IV. Petalite and Spodumene relations. *Can. Mineral.* **11**, 660-78.
- and Simpson, F. M. (1978) The Tanco Pegmatite at Bernic Lake, Manitoba. X. Pollucite. *Ibid.* **16**, 325-33.
- Trueman, D. L., Ziehlke, D. V., Goad, B. E. and Paul, B. J. (1981) The Cat Lake-Winnipeg River and the Wekusko Lake pegmatite fields, Manitoba. *Man. Mineral. Res. Div., Econ. Geol. Rep.* ER80-1.
- Debron, G. (1965) Contribution à l'étude des réactions d'échange d'ions alcalins et alcalinoterreux dans les feldspathoïdes. *Bull. Soc. fr. Minéral. Cristallogr.* **88**, 69-96.
- Goad, B. E. and Černý, P. (1981) Peraluminous pegmatitic granites and their pegmatite aureoles in the Winnipeg River district, Southeastern Manitoba. *Can. Mineral.* **19**, 177-94.
- Hamilton, D. L. and Henderson, C. M. B. (1968) The preparation of silicate compositions by a gelling method. *Mineral. Mag.* **36**, 832-8.
- Henderson, C. M. B. and Taylor, D. (1969) An experimental study of the leucite and analcime mineral groups. *First Rept. Progress in Experimental Petrology, Natural Environment Res. Council*, 45-50.
- Iiyama, J. T. (1964) Etude des réactions d'échange d'ions Na-K dans la série muscovite-paragonite. *Bull. Soc. fr. Minéral. Cristallogr.* **87**, 532-41.

- (1974) Behaviour of trace elements in feldspar under hydrothermal conditions. In *The Feldspars* (McKenzie, W. S. and Zussman, J., eds.) Manchester Univ. Press, New York, 553–73.
- Kennedy, G. C. (1950) Pressure–volume–temperature relations in water. *Am. J. Sci.* **248**, 540–64.
- Kume, S. and Koizumi, M. (1965) Synthetic pollucites in the system  $\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ – $\text{Cs}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2$ – $\text{H}_2\text{O}$ —their phase relationship and physical properties. *Am. Mineral.* **50**, 587–92.
- Lagache, M. and Weisbrod, A. (1977) The system: Two alkali feldspars–KCl–NaCl– $\text{H}_2\text{O}$  at moderate to high temperatures and low pressures. *Contrib. Mineral. Petrol.* **62**, 77–101.
- Martin, R. F. and Lagache, M. (1975) Cell edges and infra-red spectra of synthetic leucites and pollucites in the system  $\text{KAlSi}_2\text{O}_6$ – $\text{RbAlSi}_2\text{O}_6$ – $\text{CsAlSi}_2\text{O}_6$ . *Can. Mineral.* **13**, 275–81.
- Neuvonen, K. J. and Vesasalo, A. (1960) Pollucite from Luolamaki, Somero, Finland. *Bull. Comm. Geol. Finlande*, **188**, 133–48.
- Orville, P. M. (1963) Alkali ion exchange between vapor and feldspar phases. *Am. J. Sci.* **261**, 201–37.
- (1972) Plagioclase cation-exchange equilibria with aqueous chloride solutions: results at 700°C and 800°C and 2000 bars in the presence of quartz. *Ibid.* **272**, 234–272.
- Poty, B., Stalder, H. A. and Weisbrod, A. (1977) Fluid inclusion studies in quartz from fissures of Western and Central Alps. *Schweiz. Mineral. Petrol. Mitt.* **54**, 717–52.
- Roux, J. (1971) Fixation du Rubidium et du Césium dans la nepheline et dans l'albite à 600°C dans des conditions hydrothermales. *C.R. Acad. Sci. Paris. Sér. D*, **278**, 2397–400.
- Solodov, N. A. (1966) Relationship between ionization potentials of elements and the concentration necessary for the formation of their own minerals. *Dokl. Acad. Sci. U.S.S.R., Earth Sci. Sect.* **165**, 177–80.
- Sourirajan, S. and Kennedy, G. C. (1962) The system  $\text{H}_2\text{O}$ –NaCl at elevated temperatures and pressures. *Am. J. Sci.* **210**, 115–41.
- Suito, K., Lacam, A. and Iiyama, J. T. (1974) Stabilité des solution solides de la série pollucite-leucite sous une pression d'eau de 30 kbars. *C.R. Acad. Sci. Paris. Sér. D*, **278**, 2397–400.
- Taylor, S. R. and McLennan, S. M. (1981) The composition and evolution of the continental crust: rare earth element evidence from sedimentary rocks. *Phil. Trans. Roy. Soc. London A*, **301**, 381–99.
- Volfinger, M. and Robert, J. L. (1980) Structural control of the distribution of trace elements between silicates and hydrothermal solutions. *Geochim. Cosmochim. Acta*, **44**, 1455–61.
- Weisbrod, A. and Poty, B. (1975) Thermodynamics and geochemistry of the hydrothermal evolution of the Mayres pegmatite, South Eastern Massif Central (France). *Pétrologie* **1**, 1–16 and 89–102.
- (1976) Les inclusions fluides en pétrologie—géochimie; tendances actuelles. *Bull. Soc. fr. Mineral. Cristallogr.* **99**, 140–52.
- Wyart, J. and Sabatier, G. (1956) Transformations mutuelles des feldspaths alcalins. Reproduction du microcline et de l'albite. *Ibid.* **79**, 574–81.
- (1962) L'équilibre des feldspaths et des feldspathoïdes en présence de solution sodi-potassiques. *Norsk. geol. Tidsskr.* **42**, 317–29.

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