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# STABILITY AND SOLUBILITY OF POLLUCITE IN THE GRANITE SYSTEM AT 200 MPa $H_2O$

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## ABSTRACT

The chemistry and stability of pollucite (Pol, $CsAlSi_2O_6$) – leucite (Lct, $KAlSi_2O_6$) – analcime (Anl, $NaAlSi_2O_6•H_2O$) solid-solutions and the effects of added pollucite on phase relations in the haplogranite system were studied experimentally between 450° and 850°C at 200 MPa $H_2O$. Addition of Cs *via* dissolution of pollucite lowers the haplogranite solidus by ~40°C (to ~640°C) and displaces the minimum melt composition slightly toward the Qtz apex. The Cs content of melt saturated in pollucite solid-solution near the minimum is ~5 wt.% $Cs_2O$. There is substantial miscibility among Pol and Lct components at magmatic temperatures, but the Lct content of pollucite decreases linearly with decreasing temperature to zero Lct component at ~385°C. The Lct and Anl components vary inversely in pollucite solid-solutions as a function of temperature, such that the Anl and maximum Pol components of the pollucite solid-solution increase with decreasing temperature. Natural and synthetic pollucite equilibrates readily with melt or with hydrothermal solutions (and coexisting alkali feldspars) down to temperatures below ~400°C. The experiments do not unequivocally resolve a standing question of a miscibility gap in the Pol–Anl system at low temperature. The compositions of synthetic pollucite diverge by >15 mol.% in terms of Pol and Anl components at 450°C, but as in nature, the bulk of the synthetic pollucite is intermediate in composition between the extremes.

*Keywords*: cesium, pollucite, leucite, analcime, granite, pegmatite, radioactive waste disposal, experimental petrology.

## SOMMAIRE

La composition et le champ de stabilité des solutions solides pollucite (Pol, $CsAlSi_2O_6$), leucite (Lct, $KAlSi_2O_6$), et analcime (Anl, $NaAlSi_2O_6•H_2O$), ainsi que les effets d'un supplément de pollucite sur les relations parmi les phases dans le système haplogranitique, ont fait l'objet d'études entre 450° et 850°C à 200 MPa $H_2O$. L'addition de Cs par dissolution de la pollucite abaisse le solidus d'environ 40°C (jusqu'à environ 640°C) et déplace la composition du minimum dans ce système vers le pôle Qtz. La teneur en Cs du liquide silicaté saturé en pollucite près du minimum est d'environ 5% $Cs_2O$ en poids. L'étendue de la zone de miscibilité entre Pol et Lct aux températures magmatiques est appréciable, mais la teneur en Lct de la pollucite diminue de façon linéaire à mesure que diminue la température, et elle tombe à zéro à environ 385°C. La proportion des composants Lct et Anl dans la pollucite varie inversement en fonction de la température, de sorte que Anl et la teneur maximum de Pol augmentent à mesure que diminue la température. La pollucite naturelle et l'analogue synthétique atteignent l'équilibre facilement avec le bain fondu ou avec la solution hydrothermale (et avec les feldspaths coexistants), même en dessous de 400°C. Les expériences ne résolvent pas la question de l'existence d'une lacune de miscibilité dans le système Pol–Anl à ces faibles températures. Les compositions de pollucite synthétique s'écartent de plus de 15% en termes molaires des composants Pol et Anl à 450°C, mais de même que dans la nature, dans la plupart des cas, la pollucite synthétique est intermédiaire entre les compositions extrêmes.

(Traduit par la Rédaction)

*Mots-clés*: césium, pollucite, leucite, analcime, granite, pegmatite, enfouissement des déchets radioactifs, pétrologie expérimentale.

## INTRODUCTION

A general feature of evolved granites and pegmatites derived from mostly metasedimentary sources is their elevated contents of cesium (*e.g.*, the LCT class of granite-associated mineral deposits: Černý 1991) relative to other types of granite. Though Li-rich trioctahedral micas can accommodate large mole fractions of Cs in the interlayer site (Černý & Burt 1984), cesium is incompatible in feldspars and most micas (*e.g.*, Icenhower & London 1995, 1996a), and hence Cs is concentrated in residual melts that may

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form pegmatites. Some very highly fractionated pegmatites contain the primary mineral phase pollucite, and thus are interpreted to have reached melt saturation in a Cs-phase (albeit late in their evolution).

Pollucite (refers to the phase), nominally $CsAlSi_2O_6$ (refers to the component, Pol), forms solid solutions with analcime (Anl) and more limited solutions (at least in naturally occurring compositions) with the components of leucite (Lct) and its Rb-analogue. The cations Cs, Rb, and K mix on one site in the pollucite structure (grouped as the CRK component: Beger 1969, Černý 1974), which also contains molecular $H_2O$. Solid solution toward pollucite generally entails substitution of $H_2O$ in analcime for a CRK cation, accompanied by the introduction of charge-balancing Na on a second site (*e.g.*, Černý 1974, Teertstra *et al.* 1992). The general formula for pollucite – analcime solid solutions, $(Cs_xNa_y)(Al_{x+y}Si_{3-x-y}O_6{\bullet}(1-x)H_2O$ (P. Černý, pers. commun., 1997; *cf.* Beger 1969, Černý 1974) where $2y \geq 1-x \geq y$ and $x+y \simeq 0.90$ indicates variable Si/Al > 2 across the series. Teertstra *et al.* (1992) identified domains of sharply contrasting proportions of pollucite and analcime in natural pollucite, and on this basis proposed a miscibility gap at low (subsolidus) temperature (also see Drysdale 1992). Lagache (1995) found no evidence for immiscibility at low temperature.

Other than limited experimentation in ceramic systems (*e.g.*, Beall & Rittler 1982, and citations therein), the only previous experimental study of Cs in granitic melt of geological relevance was conducted by Henderson & Manning (1984). Their preliminary experiments did not achieve pollucite saturation or stability in $H_2O$-saturated haplogranite melt with 10 wt.% added $CsAlSi_2O_6$ glass, roughly equivalent to 3.5 wt.% added $Cs_2O$ in melt. They did, however, report a displacement of the haplogranite minimum toward Qtz at 100 MPa $H_2O$ with the addition of Cs *via* the pollucite component.

With these observations in mind, the experimental study reported here had two primary objectives: (1) document the effects of Cs (added *via* pollucite dissolution) in terms of freezing-point depression and minimum composition of melt in the hydrous haplogranite system, and (2) establish the Cs content of $H_2O$-saturated granitic melt near the thermal minimum at pollucite saturation, both as parts of ongoing work in this laboratory to examine the effects of added components in the haplogranite system and to predict melt compositions from mineral–melt equilibria. The results also bear on a third topic, evidence for or against a miscibility gap in the pollucite–analcime solid solution, though the experiments were not specifically designed (*i.e.*, optimized) to address this question.

## EXPERIMENTAL METHODS

Starting materials consisted of natural albite (Copelinha, Minas Gerais, Brazil), adularia (St. Gottard, Switzerland), and quartz (processed electronic grade, Spruce Pine, North Carolina) mixed in the wt.% proportion of $Ab_{38}Or_{29}Qtz_{33}$ (mix HGS4, Table 1), the composition of the haplogranite minimum at 200 MPa $H_2O$ (Tuttle & Bowen 1958). To this mixture were added 5, 10, 15, or 25 wt.% of natural pollucite (Table 2, TNO Pol) from the Tanco mine, Manitoba. The sample is from one of the large discoid masses of monomineralic pollucite near the top of the pegmatite body (Černý 1982, Černý & Simpson 1978). The initial experiments utilized a haplogranitic glass produced from sol–gel (mix HGS1, Table 1), whose composition is $Ab_{47}Or_{24}Qtz_{29}$ (Table 1); 25 wt.% of the same starting pollucite was added to the HGS1 glass. The methodological change from this glass to the mineral mixture HGS4 above was prompted by the need for a composition closer to the 200 MPa $H_2O$ minimum in the hydrous haplogranite system ($Ab_{38}Or_{28}Qtz_{34}$: Tuttle & Bowen 1958), and for holocrystalline starting materials in runs to locate the solidus (also HGS4). The experiments with glass HGS1, however, are valid for the purposes cited below. For both HGS1 and HGS4, Ca, Mg, Fe, Ti, and Rb are below the detection limit, and hence are not reported in Table 1. Mixture HGS4 contains <0.1 wt.% BaO imparted from the starting adularia.

In all runs, the mineral (or mineral–glass) mixtures were sealed with a slight excess of $H_2O$ (needed to saturate the melt at pressure and temperature) into 20 × 3 mm Au capsules (with powder mix confined to a central 5 × 3 mm portion of capsule). Experiments were pressurized cold then run to temperature. Forward experiments (F, Tables 1–3) were taken directly to run temperature. Reverse experiments (R, Tables 1–3) were preconditioned for 72 hr at 750°–850°C before being set to the final run temperature. The purpose of the reverse experiments was to use the high temperature to oversaturate the melt in the Pol component relative to its concentration in melt at the final run temperature, and hence to precipitate pollucite on the retrograde cycle. Because melt tended to persist metastably in this and similar reverse experiments with haplogranitic compositions, the composition of melt closest to equilibrium with crystalline phases [albite, K-feldspar (Kfs), quartz, and pollucite where saturated] was studied mostly by forward experiments using the crystalline HGS4 starting mixes. Most experiments were 4–6 weeks in duration (Table 3). Capsules were run subhorizontally in water-pressurized cold-seal René-41® and NIMONIC 105® vessels at 200 MPa. Pressure was measured with a factory-calibrated Heise bourdon tube gauge, with fluctuations of <5 MPa over the course of experiments. Temperature was monitored by an internal Chromel–Alumel thermocouple, with a measured total uncertainty of less than or equal to ±5°C. Oxygen fugacity was not controlled, but the combined intrinsic oxygen fugacity of these vessels, filler rods, and the water pressure medium with a hydrocarbon rust inhibitor is <0.5 log units below the

TABLE 1. COMPOSITIONS OF STARTING GLASS AND QUENCHED EXPERIMENTAL MELTS

| run | HGS4 | GCs-19 | GCs-18 | GCs-11 | GCs-13 | GCs-15 | GCs-14 |
|---|---|---|---|---|---|---|---|
| T | | 750F | 750R | 700F | 700F | 700F | 675F |
| starting mix | HGS4 | HGS4+25% Pol | HGS4+25% Pol | HGS4+5% Pol | HGS4+10% Pol | HGS4+15% Pol | HGS4+15% Pol |
| wt.% | | | | | | | |
| $SiO_2$ | 72.32 [0.82] | 65.05 [0.46] | 65.34 [0.27] | 71.48 [0.64] | 69.93 [0.42] | 68.37 [0.37] | 69.09 [0.30] |
| $Al_2O_3$ | 11.65 [0.39] | 12.96 [0.15] | 13.01 [0.14] | 11.47 [0.25] | 11.70 [0.13] | 11.94 [0.12] | 11.40 [0.18] |
| $Na_2O$ | 4.14 [0.20] | 4.17 [0.12] | 4.22 [0.13] | 3.74 [0.15] | 3.80 [0.12] | 3.64 [0.13] | 3.35 [0.13] |
| $K_2O$ | 4.50 [0.14] | 3.34 [0.12] | 3.39 [0.09] | 3.64 [0.11] | 3.53 [0.10] | 3.29 [0.08] | 3.01 [0.12] |
| $Cs_2O$ | 0.00 [0.00] | 5.74 [0.07] | 5.90 [0.07] | 1.62 [0.04] | 3.21 [0.04] | 4.73 [0.05] | 5.21 [0.04] |
| Sum Ox | 92.61 | 91.26 | 91.86 | 91.95 | 92.17 | 91.97 | 92.06 |
| norm Ab | 37.83 | 38.67 | 38.88 | 34.42 | 34.89 | 33.49 | 30.79 |
| norm Or | 28.72 | 21.63 | 21.81 | 23.39 | 22.63 | 21.14 | 19.32 |
| norm Pol | 0.00 | 13.92 | 14.21 | 3.90 | 7.71 | 11.38 | 12.52 |
| norm Qtz | 33.49 | 25.33 | 24.81 | 37.43 | 34.27 | 33.25 | 36.55 |
| K* [1] | 41.70 | 34.51 | 34.58 | 39.04 | 37.94 | 37.29 | 37.15 |
| ASI [2] | 1.00 | 1.03 | 1.02 | 1.07 | 1.04 | 1.06 | 1.07 |
| norm Ab' [3] | 37.83 | 44.92 | 45.32 | 35.81 | 37.80 | 37.79 | 35.20 |
| norm Or' [3] | 28.72 | 25.13 | 25.43 | 24.34 | 24.52 | 23.86 | 22.09 |
| norm Qtz' [3] | 33.49 | 29.43 | 28.92 | 38.95 | 37.13 | 37.52 | 41.78 |

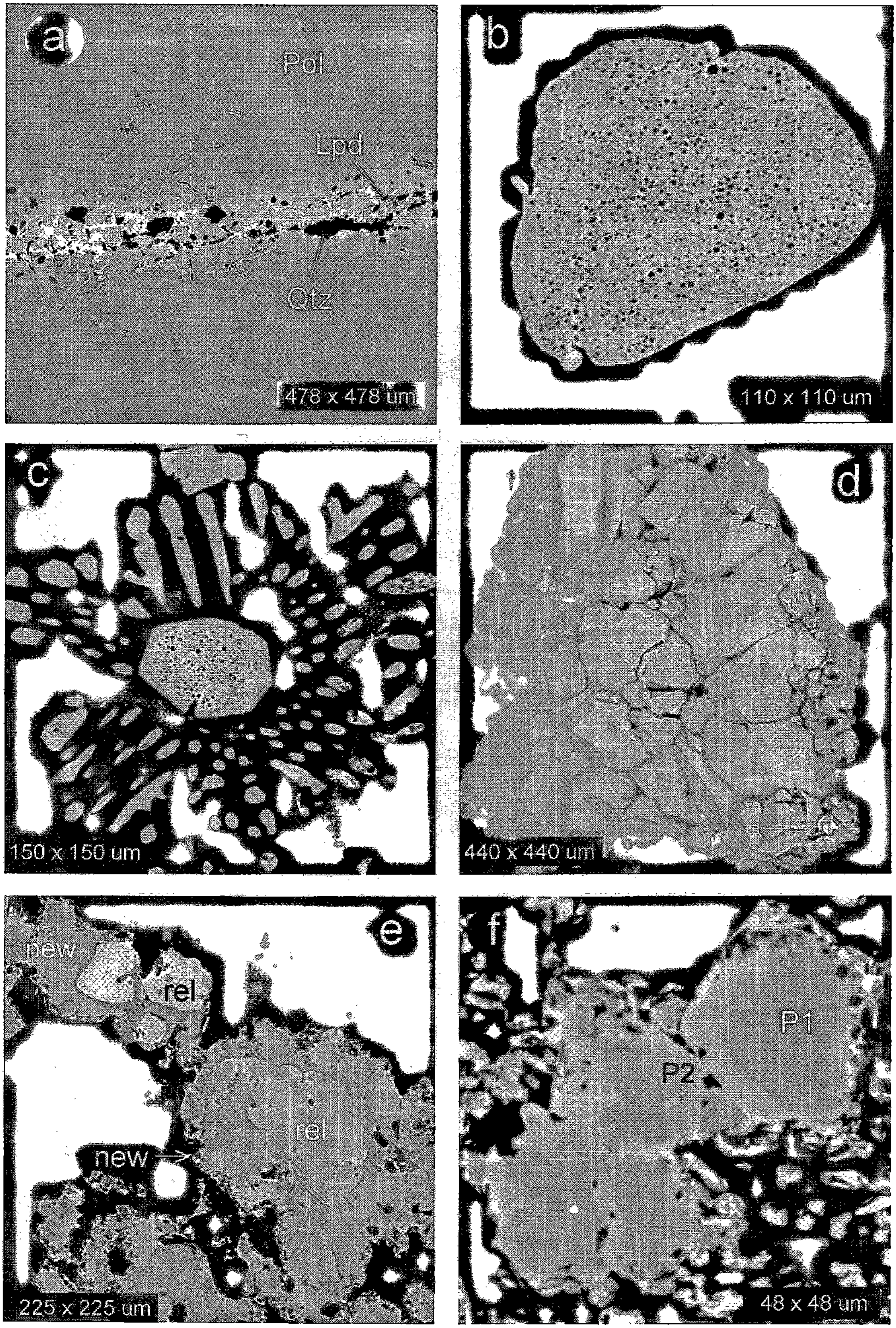
[1] K* = 100 mol K/(K + Na); [2] ASI = mol $Al_2O_3$/(mol $Na_2O$ + $K_2O$ + $Cs_2O$); [3] normative composition normalized to Ab, Or, and Qtz components only (haplogranite projection)

TABLE 2. COMPOSITIONS OF STARTING POLLUCITE AND EXPERIMENTAL PRODUCTS

| run | TNO Pol | TNO Pol | GCs-8 | GCs-19 | GCs-18 | GCs-3 | GCs-3 |
|---|---|---|---|---|---|---|---|
| T | | | 650F | 750F | 750R | 650R | 650R |
| phase | main | high BSE | relict | new | new | new | relict |
| wt.% | | | | | | | |
| $SiO_2$ | 44.69 | 40.78 | 45.07 [0.96] | 43.61 [0.55] | 43.27 [0.57] | 47.81 [0.74] | 46.20 [0.50] |
| $Al_2O_3$ | 15.98 | 16.18 | 16.18 [0.21] | 16.88 [0.13] | 16.76 [0.22] | 15.79 [0.07] | 16.18 [0.10] |
| $Na_2O$ | 1.41 | 0.64 | 0.60 [0.05] | 1.02 [0.01] | 0.93 [0.06] | 1.89 [0.07] | 1.81 [0.07] |
| $K_2O$ | 0.00 | 0.00 | 2.25 [0.04] | 2.20 [0.12] | 2.27 [0.07] | 1.91 [0.06] | 1.99 [0.05] |
| $Cs_2O$ | 31.87 | 37.17 | 32.02 [0.68] | 31.46 [0.60] | 32.15 [0.77] | 27.32 [0.32] | 27.94 [0.21] |
| Sum Ox | 93.95 | 94.77 | 96.14 | 95.17 | 95.38 | 94.72 | 94.12 |
| CRK cat [1] | 0.83 | 0.93 | 0.93 | 0.89 | 0.90 | 0.79 | 0.80 |
| Anl cat [2] | 0.13 | 0.06 | 0.06 | 0.09 | 0.09 | 0.17 | 0.16 |
| Lct cat [3] | 0.00 | 0.00 | 0.14 | 0.13 | 0.14 | 0.11 | 0.12 |
| Si/Al: | 2.37 | 2.14 | 2.36 | 2.22 | 2.19 | 2.57 | 2.42 |
| mole % Pol | 83.25 | 92.74 | 77.20 | 73.71 | 74.47 | 65.63 | 66.33 |
| mole % Lct | 0.00 | 0.00 | 16.23 | 15.42 | 15.73 | 13.73 | 14.13 |
| mole % Anl | 16.75 | 7.26 | 6.58 | 10.87 | 9.80 | 20.64 | 19.54 |

| run | GCs-2 | GCs-2 | GCs-1 | GCs-1 | GCs-1 | GCs-1 |
|---|---|---|---|---|---|---|
| T | 550R | 550R | 450R | 450R | 450R | 450R |
| phase | low BSE | high BSE | relict | main new | low BSE | high BSE |
| wt.% | | | | | | |
| $SiO_2$ | 48.89 [0.34] | 45.92 [0.44] | 44.94 [0.19] | 46.00 [0.83] | 49.98 [0.26] | 42.75 [0.44] |
| $Al_2O_3$ | 15.18 [0.21] | 15.77 [0.24] | 15.85 [0.23] | 15.66 [0.29] | 14.98 [0.29] | 15.91 [0.24] |
| $Na_2O$ | 1.99 [0.07] | 1.62 [0.05] | 2.31 [0.21] | 2.09 [0.19] | 2.59 [0.12] | 1.34 [0.05] |
| $K_2O$ | 0.86 [0.02] | 0.90 [0.01] | 0.59 [0.06] | 0.47 [0.04] | 0.41 [0.03] | 0.48 [0.01] |
| $Cs_2O$ | 27.39 [0.31] | 30.58 [0.22] | 29.90 [0.22] | 30.75 [0.53] | 25.82 [0.20] | 35.16 [0.22] |
| Sum Ox | 93.91 | 94.79 | 93.59 | 94.97 | 93.78 | 95.64 |
| CRK cat [1] | 0.77 | 0.82 | 0.75 | 0.77 | 0.70 | 0.86 |
| Anl cat [2] | 0.17 | 0.15 | 0.21 | 0.19 | 0.22 | 0.13 |
| Lct cat [3] | 0.05 | 0.05 | 0.04 | 0.03 | 0.02 | 0.03 |
| Si/Al: | 2.73 | 2.47 | 2.41 | 2.49 | 2.83 | 2.28 |
| mole % Pol | 70.21 | 75.25 | 70.91 | 73.81 | 66.51 | 82.36 |
| mole % Lct | 6.60 | 6.63 | 4.19 | 3.38 | 3.16 | 3.36 |
| mole % Anl | 23.19 | 18.12 | 24.91 | 22.81 | 30.33 | 14.27 |

[1] molar (Cs + K)/(Cs + K + Na); [2] moles Na (analcime component) per 6 O; [3] moles K (leucite component) per 6 O


a
Pol
Lpd
Qtz
478 x 478 um
b
110 x 110 um
c
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440 x 440 um
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new
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225 x 225 um
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P2
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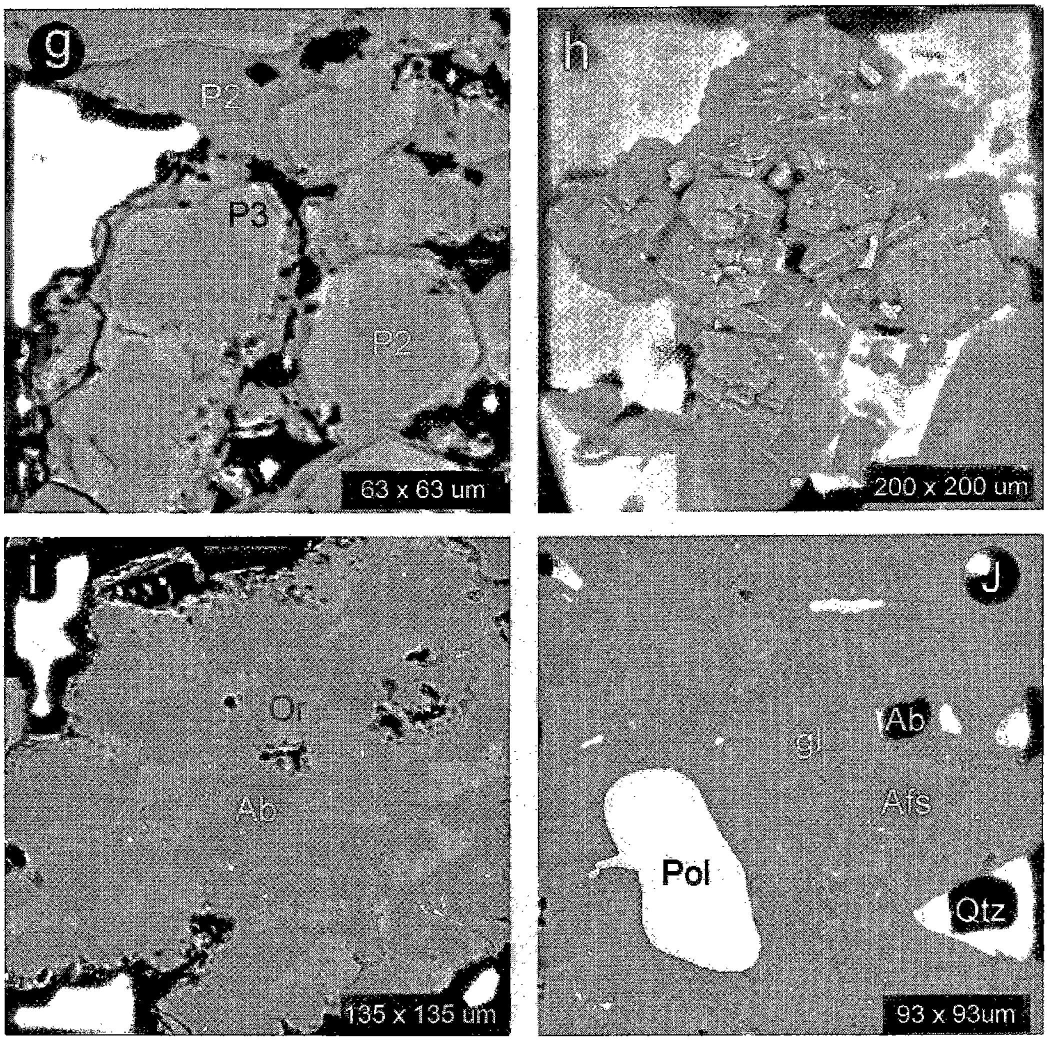

FIG. 1. Back-scattered electron (BSE) images of starting pollucite and GCs run products: (a) starting pollucite from Tanco, showing the main phase (Pol, also TNO Pol main, Table 2), a veinlet of high-Cs pollucite, and dark spots of quartz and lepidolite (Lpt); (b) relict pollucite, GCs–8, 850°C, in glass; holes in relict pollucite are filled with glass; (c) relict pollucite (spongy core) with overgrowth (rim and radial skeletal growth), GCs–3, 650°C; (d) aggregate of pollucite crystals, GCs–2, 550°C; (e) relict pollucite (rel) and overgrowths (new), GCs–2, 550°C; (f) growth of new pollucite, P1 (low BSE, Table 2) and P2 (main new, Table 2), GCs–1, 450°C; (g) growth of new pollucite, P2 (main new, Table 2) and overgrowth of P3 (high BSE, Table 2), GCs–1, 450°C; note that there are two generations of P2, *i.e.*, oscillatory growth-zoning about P3; (h) alkali feldspar crystal aggregate, GCs–2, 550°C; crystal in lower left is pollucite; (i) alkali feldspar, patchy intergrowths, GCs–2, 550°C; (j) high-Ba rim on relict alkali feldspar (Afs) and relict pollucite (Pol), GCs–14, 675°C.

NNO buffer (*e.g.*, Huebner 1971). Runs were quenched isobarically in air (5–10°C/s). Capsules were reweighed to test for leaks; all experiments gain weight as Ni from the reaction vessel dissolves into the precious metal tubing (systematic with run time and temperature). Upon puncture of capsules, the pH of quench solutions was measured using pHydrion™ multirange indicating paper.

Chemical analyses were obtained by wavelength-dispersion spectrometry (WDS) on a Cameca SX–50 electron microprobe (EMPA) using crystalline standards with TAP, PET, and LiF diffraction crystals. Glasses were analyzed with two beam conditions: (1) 20 kV, 2 nA regulated beam, 20 μm spot size, 30 s on peak and backgrounds for Na, K, Al, and Si, followed by (2) 20 kV, 20 nA regulated beam, 20 μm spot

TABLE 3. EXPERIMENTAL RUNS [1]

| | starting mix | Pol wt% | F (forward) R (reverse) [2] | T, °C | t, hrs | Products [3] |
|---|---|---|---|---|---|---|
| | glass | | | | | |
| GCs-1 | HGS1 | 25 | R | 450 | 720 | quartz, feldspar, pollucite |
| GCs-4 | HGS1 | 25 | F | 450 | 625 | quartz, feldspar, pollucite |
| GCs-2 | HGS1 | 25 | R | 550 | 720 | quartz, feldspar, pollucite |
| GCs-6 | HGS1 | 25 | F | 550 | 625 | quartz, feldspar, pollucite |
| GCs-3 | HGS1 | 25 | R | 650 | 720 | pollucite, glass |
| GCs-5 | HGS1 | 25 | F | 650 | 625 | pollucite, glass |
| GCs-7 | HGS1 | 25 | R | 650 | 480 | pollucite, glass |
| GCs-8 | HGS1 | 25 | F | 850 | 95 | pollucite, glass |
| GCs-9 | HGS1 | 25 | R | 650 | 525 | pollucite, glass |
| | crystalline | | | | | |
| GCs-16 | HGS4 | 15 | F | 600 | 120 | quartz, feldspar, pollucite |
| GCs-17 | HGS4 | 15 | F | 650 | 120 | quartz, feldspar, pollucite, glass |
| GCs-10 | HGS4 | 5 | F | 675 | 960 | quartz, feldspar, glass |
| GCs-12 | HGS4 | 10 | F | 675 | 960 | feldspar, glass |
| GCs-14 | HGS4 | 15 | F | 675 | 960 | quartz, feldspar, pollucite, glass |
| GCs-12 | HGS4 | 5 | F | 700 | 960 | quartz, feldspar, glass |
| GCs-13 | HGS4 | 10 | F | 700 | 960 | feldspar, glass |
| GCs-15 | HGS4 | 15 | F | 700 | 960 | quartz, feldspar, glass |
| GCs-18 | HGS4 | 25 | R | 750 | 765 | pollucite, glass |
| GCs-19 | HGS4 | 25 | F | 750 | 765 | pollucite, glass |
| GCs-20 | HGS4 | 25 | R | 750 | 960 | pollucite, glass |

[1] all experiments at 200 MPa $H_2O$; [2] preconditioned at 850°C for 48 hours, quenched in air, then run to temperature indicated; [3] stable products are in contact in contact with glass; does not include relict pollucite armored by feldspar

size for Ca (30 s), Fe (30 s), and Cs (45 s). The low beam-current minimized volatilization of the mobile elements, especially Na (*e.g.*, Morgan & London 1996). Analyses of minerals (pollucite and feldspar) were conducted mostly at 20 kV, 10 nA regulated beam, and 3 µm spot size. The PAP correction procedure was used (Pouchou & Pichoir 1985). Natural crystalline standards were used for all elements, including Tanco pollucite (B12–226.2, Černý & Simpson 1978) for Cs.

## RESULTS

### *Effects of Cs (as pollucite) on liquidus relations*

Forward experiments using crystalline starting materials of HGS4 (*e.g.*, GCs–17, Table 3) contained glass at temperatures ≥650°C (Fig. 1, Table 3); hence, the addition of Cs by the melting of pollucite lowers the solidus temperature of the 200 MPa $H_2O$ haplogranite system (680°C: Tuttle & Bowen 1958) by more than 30°C. Using digital back-scattered electron (BSE) images, the glass (melt) fraction in these forward experiments extrapolates to zero at (the minimum melting temperature of) 640°C. Experiments with sufficient melt to analyze accurately (≥675°C) showed no consistent change in the K* (= 100 K/[K + Na], molar ratio) of melt (Table 1). Compared to HGS4 and the haplogranite minimum reported by Tuttle & Bowen (1958), the minimum melt produced in the pollucite-saturated system is slightly more siliceous. The glass in the forward experiment GCs–14 at 675°C, which is the lowest-temperature experiment with sufficient glass to analyze, contains ~3% more normative Qtz component, even with dilution by 12.52 wt.% Pol, than the starting (minimum haplogranite) mix HGS4 (Table 1). The effect of dilution alone *via* the dissolution of pollucite (a feldspathoid) into melt should lower the normative Qtz component relative to HGS4.

The pH of the aqueous fluid was ~6 in experiments quenched from above the solidus; this is a typical value for quenched aqueous solutions derived from metaluminous granite experiments. In two subsolidus experiments (450° and 550°C), the pH increased to ~10–11.

### *The Cs content of melt at pollucite saturation*

Forward dissolution experiments (with relict pollucite in contact with glass, *e.g.*, GCs–14, Table 3) and reverse experiments in which pollucite grew (*e.g.*, runs GCs–3, –7, –9, and –14, Table 3) bracket the Cs content of melt between 4.4 and 5.2 wt.% $Cs_2O$ at pollucite saturation between 650° and 675°C (Table 1). This corresponds to ~12 wt.% of a normative Pol component in melt. Experiments starting with ≤10 wt.% pollucite were found to contain no new or relict

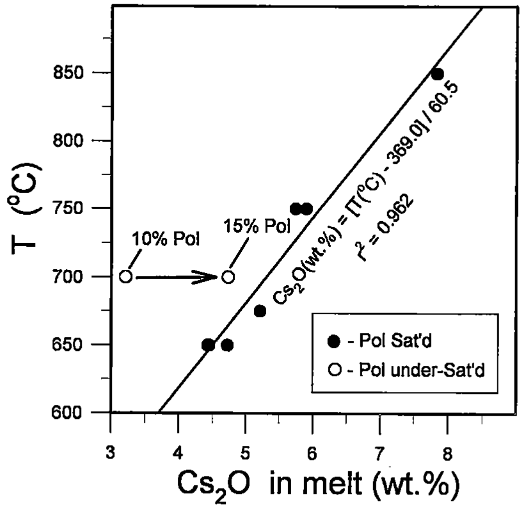

FIG. 2. $Cs_2O$ content of melt *versus* temperature.

pollucite in contact with glass. The Cs content of melt increased with temperature (Fig. 2), as the bulk compositions of most mixes were intentionally skewed well toward the pollucite composition.

### *The composition of relict and new pollucite*

Back-scattered electron images and EMPA of random grain-mounts of the starting pollucite from the Tanco mine revealed that it consists mostly of one homogeneous phase (TNO Pol main, Table 2), with ~10 vol.% of veins containing Cs-richer domains (TNO Pol high BSE, Table 2), plus traces of quartz and lepidolite (Fig. 1a). The sample is representative of primary material from Tanco and other pegmatites in its modest Na content (the phase is sodian pollucite in the nomenclature of Černý 1974), low Rb and Li, and negligible K. The $H_2O$ content estimated by difference of EMPA oxide totals from 100% is larger than the expected range of $2y \geq 1\text{–}x \geq y$ (Černý 1974). This error or uncertainty runs systematically through the analytical results in Table 2. Comparison of EMPA results for standard pollucite B12–226.2 to the results of the wet-chemical analysis (bulk sample) reported by Černý & Simpson (1978) gives EMPA values for Si that are low by ~2 wt.% $SiO_2$; EMPA results reported by others (*e.g.*, Teertstra *et al.* 1992) also are higher by approximately the same percentage of $SiO_2$. We note, however, that B12–226.2 is a bulk sample veined by secondary minerals including quartz, and that most of the available EMPA were performed at 20 nA beam current (Faraday cup), with the possibility of Si "grow-in" as a result of densification of low-density hydrous structures, which include glass (*e.g.*, Morgan & London 1996) and possibly zeolites. We regard the $H_2O$ contents of pollucite listed in Table 2 as unknown at present.

In these experiments, relict starting pollucite displays a rounded and embayed morphology, which we interpret as a feature of dissolution. Most relict pollucite has a distinctly spongy internal texture (Fig. 1b), with pore space filled by melt in supersolidus experiments or with vapor in subsolidus runs. Overgrowths of new pollucite (and in rare cases, an armoring rim of Kfs: Fig. 1c) were distinguished from the relict phase principally by the absence of a spongy texture and by skeletal to euhedral growth-habits. The relict pollucite in all experiments underwent a substantial degree of chemical exchange of Pol, Anl, and Lct components (Table 2, Fig. 3) toward the composition of the new pollucite. This complicated the distinction between the two phases, and in some cases the distinction between relict and new pollucite was ambiguous. The preconditioning step dissolved most of the 25 wt.% natural pollucite added; remnant pollucite constitutes only ~5 vol.% of the 850°C control run GCs–8. Although some reversed runs contain pollucite intergrowths and overgrowths that resemble the starting materials (see Fig. 1), they lacked the spongy texture, and the high abundance of pollucite in these reverse runs helped to distinguish it as new growth rather than the relict phase.

Relict pollucite in the forward control experiment GCs–8 to 850°C re-equilibrated in all components, but most notably in a high Lct content compared to the starting composition (Table 2, Fig. 3). Both relict (forward experiment GCs–19) and new (reverse experiment GCs–18, and replicate experiment GCs–20) pollucite at 750°C possess virtually identical compositions (Table 2), which are similar in all respects to the relict pollucite at 850°C.

Pollucite precipitated from melt at 650°C (reverse runs GCs–3, –7, –9, Table 3) as a rim on relict pollucite and as new, skeletal crystals in melt. These crystals possess a weak chemical zonation that is visible in BSE images (*e.g.*, Fig. 1c); cores of skeletal crystals have slightly lower BSE signal intensity than the rims. The individual grains or rims of new pollucite were too narrow to allow separate analyses of the two domains, and the composition reported in Table 2 represents an average. As in the experiments at higher temperature, the CRK occupancy and Anl content of the new-growth pollucite are similar to those of the starting Tanco material, but the Pol component is substantially lower because of the incorporation of K (mostly) for Cs. The Pol content of both new and relict pollucite at 650°C is also lower than at 750° and 850°C (Table 2, Fig. 3).

A reversed experiment at 550°C (run GCs–2, Tables 2, 3) yielded euhedral crystals of quartz, feldspar, and pollucite that were deposited through vapor by the dissolution of quenched melt. The pollucite morphology is dominated by the {211} trapezohedral form (Fig. 1d), typical of crystallization from solutions at high

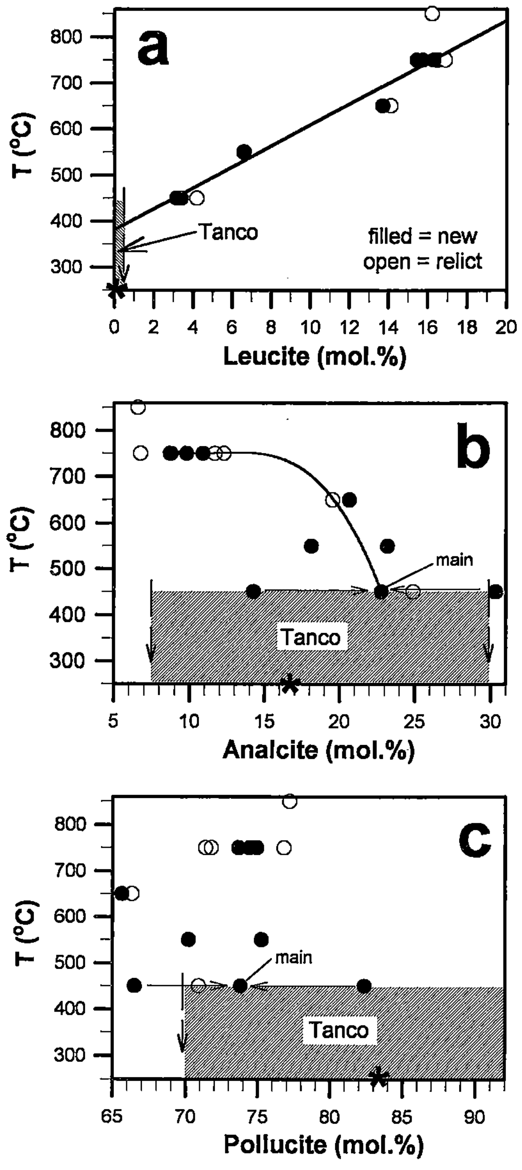

FIG. 3. Variations of pollucite composition as a function of temperature. Mole % of leucite (a), analcime (b), and pollucite (c) components. Filled circles: new synthetic pollucite, open circles: relict starting pollucite; large asterisk: starting Tanco pollucite, main phase of Table 2; shaded box: range of pollucite from Tanco, as reported by Černý & Simpson (1978) and from compositions of the starting Tanco pollucite used in these experiments (includes high-BSE phase, Table 2). Linear regressions of data are first-order in 3a, third-order for main and relict phases in 3b.

temperature or high pH (Teertstra & Černý 1992). In cross section, most euhedral crystals of pollucite possess a core of what appears to be relict starting material that is overgrown by the new euhedral phase (Fig. 1e). The overgrowth phase, however, contains a patchy to skeletal intergrowth of two different domains of pollucite. The phase with the higher BSE signal contains higher CRK, higher Pol, identical Lct, and similar Anl components compared to the lower-BSE phase (Table 2). Compared to the new pollucite at 650°C, the two domains of pollucite grown at 550°C possess higher Pol, lower Lct, and similar Anl contents.

A reversed experiment to 450°C (run GCs–1, Tables 2, 3) contains the same crystalline phases as GCs–2: euhedral quartz, euhedral trapezohedral pollucite that displays patchy zonation in cross section, and euhedral alkali feldspar that also shows patchy intergrowth in cross section. Though some rounded relics of starting pollucite are present, most pollucite seems to represent new growth. The zonation in pollucite is complex, but seems to be oscillatory; the first phase of new growth has a high Anl component and, consequently, low CRK (phase P1, Fig. 1f). This is followed by the dominant phase (phase P2, Figs. 1f, g) with higher Pol component (lower Anl), succeeded by a phase with the highest Pol and lowest Anl (phase P3, Figs. 1f, g), and finally a regrowth of the dominant phase P2. The Lct component of all pollucite in this experiment is minor and essentially constant; BSE signal variation is caused by changes in Pol–Anl components only.

### *Feldspars*

The rim of new crystals of alkali feldspar that precipitated onto relict St. Gotthard adularia at 675° and 700°C (runs GCs–14 and –15, Tables 3, 4, Fig. 1j) shows a higher BSE signal intensity than the relict cores. The high BSE signal intensity of these rims is imparted principally by Ba (derived from the starting adularia), which partitions strongly into the small fraction of new alkali feldspar (Icenhower & London 1996a). With the substitution of Ba for K (Icenhower & London 1996a) and the equilibration of the feldspar with haplogranitic melt, the K* of the new alkali feldspar is lower than that of the starting St. Gottard material (Table 4).

Feldspar crystals in the reversed runs at 550° and 450°C possess euhedral forms of a single alkali feldspar phase (Fig. 1h). Sections of the crystals reveal a patchy intergrowth (Fig. 1i) of Kfs- and Ab-rich domains, identical to those produced by rapid growth *via* undercooling in other granitic compositions (*e.g.*, London *et al.* 1989). The feldspar compositions at 550°C (Table 4) lie on the Or–Ab solvus at 200 MPa $H_2O$ (Luth & Tuttle 1966), which corresponds to a strain-free solvus (heterogeneous nucleation of two phases). In both experiments, the Kfs-rich phase

TABLE 4. COMPOSITIONS OF STARTING K-FELDSPAR AND EXPERIMENTAL FELDSPAR PRODUCTS

| run | St. Gottard | GCs-15 | GCs-2 | GCs-2 | GCs-1 | GCs-1 |
|---|---|---|---|---|---|---|
| T | adularia | 700F | 550R | 550R | 450R | 450R |
| starting mix | | HGS4 | HGS1 | HGS1 | HGS1 | HGS1 |
| wt.% | | | | | | |
| $SiO_2$ | 64.11 [0.33] | 64.38 [0.00] | 69.46 [0.43] | 66.26 [0.54] | 68.85 [0.57] | 66.22 [1.12] |
| $Al_2O_3$ | 18.96 [0.20] | 18.86 [0.06] | 19.27 [0.29] | 18.64 [0.25] | 19.42 [0.47] | 18.19 [0.47] |
| CaO | 0.02 [0.01] | 0.01 [0.00] | 0.00 [0.00] | 0.00 [0.00] | 0.00 [0.00] | 0.00 [0.00] |
| BaO | 0.32 [0.05] | 2.01 [0.02] | nd | nd | nd | nd |
| $Na_2O$ | 1.25 [0.02] | 3.91 [0.02] | 10.46 [0.22] | 3.25 [0.20] | 11.68 [0.34] | 1.60 [0.48] |
| $K_2O$ | 14.84 [0.07] | 9.94 [0.10] | 1.56 [0.30] | 11.64 [0.23] | 0.50 [0.30] | 13.69 [0.53] |
| $Cs_2O$ | nd | nd | 0.02 [0.01] | 0.29 [0.04] | 0.06 [0.05] | 0.16 [0.16] |
| Sum Ox | 99.50 | 99.11 | 100.76 | 100.08 | 100.51 | 99.86 |
| norm wt. % Ab | 10.76 | 36.03 | 90.56 | 28.56 | 97.10 | 14.34 |
| norm wt. % Or | 89.24 | 63.97 | 9.44 | 71.44 | 2.90 | 85.66 |

nd = not determined

contains Cs above detection level (Table 4), though Cs remains highly incompatible in the alkali feldspars (Icenhower & London 1995a).

## DISCUSSION

### *Effects of Cs on phase relations*

Cesium has a strong affinity for silica-rich melts (*e.g.*, Watson 1976) and stabilizes silicate melt or glass structures (*e.g.*, Roy & Navrotsky 1984). Not surprisingly, then, the addition of Cs as pollucite (the likely Cs-saturating phase for granitic magmas) to haplogranitic melt promotes a large depression of the solidus temperature and a small change of melt composition toward increasing silica content, as first reported by Henderson & Manning (1984). Together with other components such as B, P, or F, the accumulation of Cs in the wt.% range permits a substantial fraction of melt to persist to low temperatures in granitic pegmatites (*e.g.*, London 1996). Note, however that the components F, B, and P shift the (projections of) haplogranitic melt compositions away from Qtz (*e.g.*, Manning 1981, Pichavant 1987, London *et al.* 1993). The simultaneous increase of Cs and these other components would foster a tendency toward two-phase liquid (melt) immiscibility; London (1986) proposed liquid immiscibility as a possible explanation of zoning in the Tanco pegmatite, which is highly enriched in Cs among other fluxing lithophile components (Černý 1982).

In the preliminary experiments to this study, Icenhower & London (1996b) reported an unusually large shift of melt composition away from the haplogranite minimum toward the Ab–Qtz join with the addition of Cs as a pollucite component. Though that was indeed the case, an explanation has emerged. The earlier runs were conducted by the "sandstone method", with a large fraction of coarse-grained seeding material (pollucite in this case) and a small fraction of melt. This method normally optimizes the attainment of crystal–melt equilibrium and gives a large enough volume of glass for analysis. In these experiments, however, the equilibration of starting Tanco pollucite entailed $KNa_{-1}$ exchange with melt: K diffused into the pollucite (at the Cs site) and concomitantly displaced some $H_2O$ and Na out of the structure and into melt. This process accounts for the drop in K* in the early experiments that contained a large fraction (35%) of relict pollucite; hence, it is an artifact of the cation exchange of the pollucite but is not intrinsic to Cs-bearing granitic melts. It does, however, corroborate extensive Pol–Lct miscibility at high temperature that is not known from natural samples. In these more recent experiments with little or no remnant pollucite, there is no change in K* of the melt.

### *The Cs content of melt at pollucite saturation*

Near the solidus at ~640°C, the Cs content of melt must reach ~5 wt.% $Cs_2O$ to be saturated in pollucite solid-solution. This is equivalent to ~12 wt.% normative Pol. The results here are consistent with the absence of pollucite in the experiments reported by Henderson & Manning (1984), though their bulk compositions must have been close to pollucite saturation.

The high content of Cs needed to stabilize pollucite in the melt explains the rarity of this phase in nature and begs the question of what combination of source and process can generate melts with several wt.% $Cs_2O$? London (1995) suggested that anatectic melts anomalously rich in Cs (and Li) could be generated by (1) low-temperature anatexis of muscovite-rich protoliths (*e.g.*, mica schists), which can produce only a small fraction of melt at incipient hydrous anatexis,

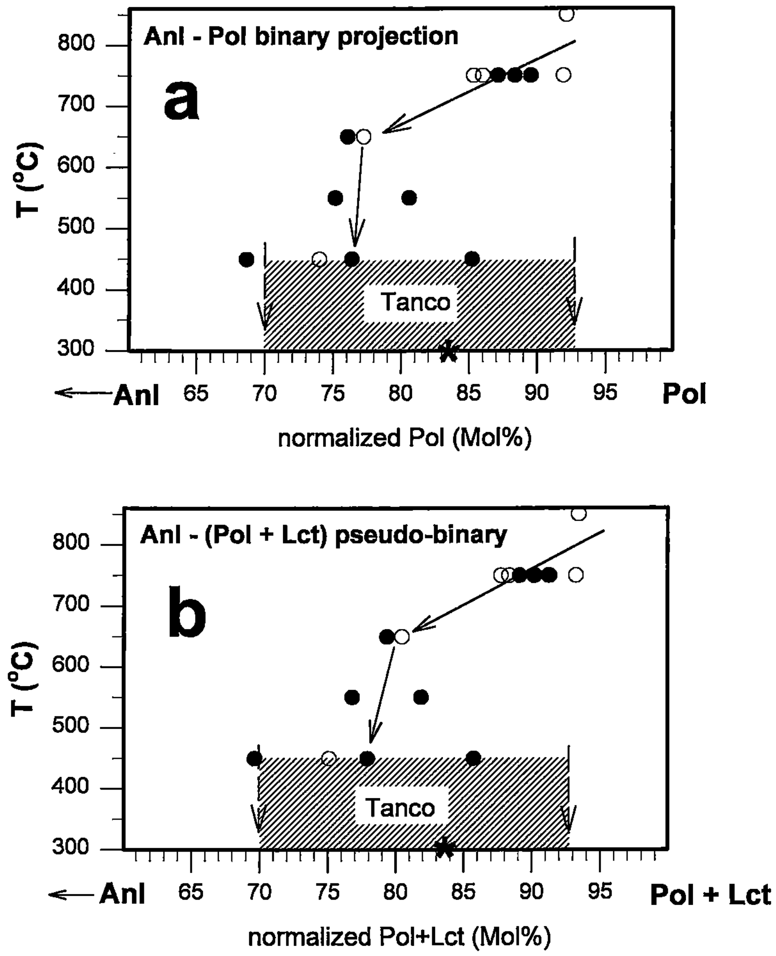

FIG. 4. Plot of temperature *versus* the compositions of new and relict experimental pollucite (a) normalized to Pol + Anl = 100 (projection through Lct), and (b) plotted on the pseudobinary Anl – (Pol + Lct). Solid arrows show the general trend of pollucite composition (main or average phase compositions). Asterisk and shaded box correspond to Tanco pollucite as described in Figure 3.

followed by (2) the breakdown of muscovite to alkali feldspar + corundum or aluminosilicate at higher temperature. In this way, most of the Cs in white mica could be transferred to a small volume of melt. As long as biotite (Bea *et al.* 1994, Icenhower & London 1995) or cordierite (Icenhower & London 1996a) remains stable in the source, however, a large fraction of Cs is retained in these residual minerals and would be parceled out to melt over a wide range of increasing temperature. Though poorly constrained by a lack of data, the Cs contents of mica schists appear to be in the $10^0$–$10^1$ ppm range (*e.g.*, Moss *et al.* 1995). A further enrichment of Cs by $10^3$–$10^4$ in melt is apparently necessary to reach pollucite saturation.

### *Synthetic versus natural pollucite*

The most notable difference between the synthetic pollucite grown in these experiments (650° and 750°C supersolidus, 550° and 450°C subsolidus) and that from nature (for which pollucite from Tanco is typical and representative) is the large leucite component of the experimental products at magmatic temperatures, whereas leucite is a negligible component of the natural phase. We reiterate that the high Lct component of the pollucite in these experiments is not an artifact of unusually rapid growth of new crystals of pollucite, because the starting pollucite that is clearly relict at the end of the experiments has fully equilibrated with the composition of the main new pollucite phase in each of the experiments. In addition, complete miscibility among Pol and Lct components has been reported from other synthesis experiments (*e.g.*, Martin & Lagache 1979).

Figure 3a, which illustrates the variation in Lct component of the pollucite with temperature, shows that a first-order regression through the experimental data intercepts zero leucite component at 385°C. With decreasing temperature, both the Anl component and the range of Anl contents of pollucite domains increase (Fig. 3b). The variation of Pol component of the new and relict pollucite with temperature (Fig. 3c) shows no simple or systematic variation, and only partly overlaps the field of natural compositions from the Tanco pegmatite (Černý & Simpson 1978). However, when the pollucite compositions are normalized to the Pol–Anl binary only (projected through Lct), then the changes of Pol component with temperature appear to be more systematic and overlap the natural Tanco compositions to a larger degree (Fig. 4a). The projection in Figure 4a emphasizes the importance of the large Lct component in pollucite, especially in experiments such as GCs–3 (compare Fig. 3c). A plot of the experimental compositions on the pseudobinary join (Pol + Lct) – Anl (Fig. 4b) shows similar relations and illustrates the increasing dominance of the Anl component (substitution of $H_2O$ for Cs) over Pol (Lct become negligible) with decreasing temperature. Figure 4 reveals that the amount of Pol component of the main or average compositions of pollucite decreases with decreasing temperature, although the maximum Pol content of domains increases. Taking these observations as a whole, we propose that (1) there is substantial miscibility between Pol and Lct components in pollucite that crystallizes from high-temperature granitic melts; (2) the Lct and Anl components vary inversely in pollucite solid-solution as a function of temperature, such that (3) the mean Anl and the maximum Anl and Pol components of the pollucite solid-solution increase with decreasing temperature, and (4) natural and experimental pollucite equilibrates readily with melt or aqueous solutions and completely loses the Lct component *via* exchange with aqueous vapor (and coexisting alkali feldspars) at temperatures below ~400°C. The inverse variations in Lct and Anl components with temperature (point 2) follow logically from the instability of the hydrous Anl component (as opposed to the anhydrous Lct component) with increasing temperature. As a consequence of point (4), the temperature of pollucite crystallization cannot be deduced from its Lct component, though variation in Lct content with temperature is the most consistent compositional parameter in these experiments.

There are few good constraints on the temperature of pollucite crystallization in pegmatites. Pollucite forms coarse to giant crystalline masses that are intergrown with equally coarse-grained K-feldspar, spodumene or petalite, and quartz in most pegmatite occurrences (*e.g.*, Tanco, Manitoba: Černý & Simpson 1978; Bikita, Zimbabwe: Cooper 1964); such pollucite appears to have formed prior to complete crystallization of the silicate melt. In addition, pollucite or cesian analcime is associated with lepidolite, elbaite, cookeite, calcite, and other low-temperature minerals indicative of subsolidus hydrothermal growth (*e.g.*, Černý 1972). Thus, the formation of pollucite in granitic pegmatites seems to occur at the transition from magmatic to hydrothermal conditions. In the Tanco deposit, London (1986) observed a pollucite – cesian analcime solid solution as a component of an assemblage of daughter minerals in fluid–solid inclusions that were entrapped as a hydrous silicate melt at ~450°–475°C (estimated from melting phenomena), which represents the inferred transition from magmatic to subsolidus conditions in the pegmatite. Based on these experiments, pollucite formed at those conditions should have contained slightly less than 0.5 wt.% $K_2O$. In fact, the natural pollucite from Tanco contains ≤0.5 wt.% $K_2O$ (Černý & Simpson 1978), but most analyzed values are within this same order of magnitude. The significance of Pol–Lct miscibility, then, may be moot if pollucite, in general, crystallizes at temperatures <450°C; its Lct component will be negligible from the start.

The range of Pol and Anl components in pollucite from Tanco is large, almost as great as the variations found over the entire interval of temperatures in these experiments (Fig. 3). However, the range of Pol and Anl components in these experiments also increases (greater heterogeneity) with decreasing temperature, and an even wider spread of compositions might be expected at the low temperatures, at which we think most natural pollucite equilibrates. It is still not clear what drives this separation of pollucite compositions into distinct domains, though in the experiment at 450°C the extremes comprise only ~20 vol.% of the pollucite. The bulk of new pollucite has a restricted range of intermediate composition, and starting Tanco pollucite re-equilibrates toward this intermediate composition. We do not know how this observation (volumetric proportion *versus* range of composition) compares in detail with natural settings such as Tanco, but Černý & Simpson (1978) noted that most of the pollucite from Tanco is rather uniform in composition, but a considerable percentage of samples covers the range of about $Pol_{83}Anl_{17} – Pol_{70}Anl_{30}$.

### *Immiscibility in pollucite – analcime solid solutions*

Patchy intergrowths of the alkali feldspars in these and similar experiments (*e.g.*, London *et al.* 1989) that entail rapid growth from melt or vapor represent simultaneous crystallization of solvus-controlled pairs of alkali feldspars within a single host crystal. For example, the compositions of the patchy intergrowths from the experiment GCs–6 at 550°C lie precisely on the alkali feldspar solvus of Luth & Tuttle (1966). The question has been raised, however, of a miscibility gap in the pollucite – analcime system based on the appearance of coexisting blebs or domains of different Pol–Anl content in natural pollucite (*e.g.*, Teertstra *et al.* 1992). Lagache (1995, Lagache *et al.* 1995) reported complete miscibility in the Pol–Anl system to low temperatures (330°C); the run products were characterized by X-ray diffraction rather than EMPA. Beyond its geological relevance, the question is germane to the stability of synthetic pollucite as a host repository for radiogenic $^{137}Cs$ (*e.g.*, Černý 1979) and to retention of Cs in analcime that might be produced as a reaction product of silicate glasses used for radionuclide storage.

The high mass contrast seen in BSE images between domains within natural pollucite (*e.g.*, Teertstra *et al.* 1992) and synthetic pollucite (Fig. 1) can be misleading of the actual compositional differences because the substitutions of heavy CRK cations for $H_2O$ and Na entail a large change in the mean atomic number of the phase. The compositions of the domains in these experiments, however, diverge with decreasing temperature to span more than 15 mol.% of Pol or Anl component at 450°C (Table 2, Figs. 3, 4), as would be expected of a miscibility gap in the system. In experiment GCs–2 at 550°C, the new pollucite consists of two sharply delineated domains that are patchy or radial from a nucleation center; these resemble the patchy intergrowths of the solvus-controlled alkali feldspars. In experiment GCs–1 at 450°C, however, the dominant new pollucite ("main", Fig. 3) is intermediate to the extremes ("main new", Table 2), and it constitutes ~80 vol.% of the pollucite phase. In GCs–1, the zonation of pollucite is concentric and oscillates about the main composition (P2 in Figs. 1f, g). Relict pollucite in experiments at 450° and 650°C approaches the intermediate composition of the "main new" pollucite, not the extremes. In these experiments, the intermediate "main new" pollucite appears to be stable, whereas the extremes that might be construed as solvus pairs are evidently metastable. In total, we conclude that the observed zoning in the experimental pollucite is more consistent with the kinetic effect of rapid growth far from equilibrium in closed systems (*e.g.*, Watson 1996, Shore & Fowler 1996) than with the existence of a miscibility gap in the Pol–Anl system (*e.g.*, Teertstra *et al.* 1992). Though the trends in pollucite–analcime compositions are similar between the natural and experimental regimes, the conditions of rapid crystallization and short run-times in the experiments do not closely mimic the slower cooling of natural plutonic rocks; therefore, we cannot strictly equate the patchy texture of the experimental products to the fine-scale heterogeneities found in natural pollucite.

### *Cation mobility and subsolidus relations of pollucite*

We have observed that alkalis, in particular K, are fully exchanged between pollucite and melt or aqueous vapor down to temperatures of 450°C in these experiments. We cannot be specific about the diffusion coefficients for the alkalis through pollucite because the relict pollucite is fully re-equilibrated and because changes in grain shape and porosity with dissolution changed the net diffusion-distance over the course of the experiments. We can state, however, that compared to any other alkali aluminosilicate systems we have studied, the exchange of alkalis and $H_2O$ between pollucite and melt or vapor is very rapid.

A potentially important aspect of the rapid and extensive cation-exchange described in this experimental study concerns the possible mobility of radiogenic isotopes of Cs out of the pollucite structure. Because the compositions of the synthetic pollucite approach those of the starting material with decreasing temperature, these experiments shed little light on the mobility of Cs through pollucite at the low temperatures likely in radionuclide waste-containment media. The equilibration described above occurs at the structural site occupied by Cs. At high temperature, the equilibration of a natural Cs-rich pollucite with melt does entail $KCs_{-1}$ exchange. With decreasing temperature, however, the cation exchange is primarily limited to $KNa_{-1}$ (increasing Anl, decreasing Lct) and does not appear to involve Cs.

As a complement to the investigations of Lagache (1995, Lagache *et al.* 1995, Sebastian & Lagache 1990) on the composition of aqueous vapor in equilibrium with pollucite-bearing assemblages, we have explored the composition and fine-scale zoning of pollucite at subsolidus temperatures, but not the composition of the fluid phase. Lagache (1995, Lagache *et al.* 1995) reported an increase in the ratio Cs/(Na + Cs) in aqueous vapor at all temperatures as the Pol component of pollucite increased. This fact alone, however, does not clearly explain why the pH of the quench solution in our experiments increases dramatically from the supersolidus (pH $\simeq$ 6) to the subsolidus conditions (pH $\simeq$ 10–11). We speculate that the change in pH is related to a proportional increase in the ratio of Cs ion (a weaker acid) to other alkali ions (smaller, hence stronger acids) in the solution with decreasing temperature, and to the fact that the solutions in these experiments were not buffered by a large mass of solute components (nothing added to vapor but the alkali aluminosilicate components that dissolved from melt or crystalline phases).

## CONCLUDING REMARKS

Pollucite is an unlikely magmatic phase because the Cs content of granitic melt at saturation in pollucite must exceed 4 wt.% $Cs_2O$, several orders of magnitude over likely starting quantities in anatectic melts. Such extreme fractionation does, apparently, occur in some of the most evolved granite and pegmatite deposits. The high solubility of pollucite in granitic melts has corollary significance for efforts to dispose of $^{137}$Cs in silicate glasses: whatever the initial entry phase, a pollucite component is very soluble in the melt and hence the glass.

Leucite (Lct) forms a large component of pollucite solid solutions at normal magmatic temperatures (>650°C). The Lct content drops with temperature, and pollucite should contain essentially no Lct below ~400°C. Most natural pollucite contains a slightly lower Lct component than would be expected by crystallization from a silicate melt, even exotic melts that may persist to very low temperatures of 450°–500°C. We infer that primary natural pollucite mostly crystallizes in this range of temperature, but continues to lose K *via* exchange with aqueous vapor to yet lower temperatures.

As the Lct component falls with decreasing temperature, the Anl content increases and the range of compositions, or small-scale heterogeneity of pollucite, also increases. Only a small fraction, generally ≤20 vol.% of the pollucite, deviates from the composition of the dominant phase. The products of the experimental system at low temperature (450°C) are similar to the natural system (Tanco) in these respects: the pollucite solid-solution is dominated by the components Pol and Anl, and although there is a large range of composition, the majority of pollucite is intermediate to the extremes. The dominance of the intermediate compositions provides good though not final evidence of complete miscibility in Pol–Anl (or Pol–Lct) solid solutions. The resolution of this question will require a slightly different experimental approach than the one used here. The low-temperature experiments cited in this study, however, entail the devitrification of silicate glasses by dissolution in a hydrothermal medium. The observed crystalline Cs-bearing phases are therefore relevant to the actual if not equilibrium phases that would be produced by the devitrification of industrial silicate glasses containing $^{137}$Cs.

## ACKNOWLEDGEMENTS

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## REFERENCES

BEA, F., PEREIRA, M.D., CORRETGÉ, L.G. & FERSHTATER, G.B. (1994): Differentiation of strongly peraluminous, perphosphorus granites: the Pedrobernardo pluton, central Spain. *Geochim. Cosmochim. Acta* **58**, 2609-2627.

BEALL, G.H. & RITTLER, H.L. (1982): Glass-ceramics based on pollucite. *In* Nucleation and Crystallization of Glasses (J.H. Simmons, D.R. Uhlmann & G.H. Beall, eds.). American Ceramic Society, Inc., Columbus, Ohio (301-312).

BEGER, R.M. (1969): The crystal structure and chemical composition of pollucite. *Z. Kristallogr.* **129**, 280-302.

ČERNÝ, P. (1972): The Tanco pegmatite at Bernic Lake, Manitoba. VIII. Secondary minerals from the spodumene-rich zones. *Can. Mineral.* **11**, 714-726.

________ (1974): The present status of the analcime – pollucite series. *Can. Mineral.* **12**, 334-341.

________ (1979): Pollucite and its alteration in geological occurrences and in deep-burial radioactive waste disposal. *In* Scientific Basis for Nuclear Waste Management **1** (G.J. McCarthy, ed.). Plenum, New York, N.Y. (231-236).

________ (1982): The Tanco pegmatite at Bernic Lake, Manitoba. *In* Granitic Pegmatites in Science and Industry (P. ern , ed.). *Mineral. Assoc. Can., Short-Course Handbook* **8**, 527-543.

________ (1991): Fertile granites of Precambrian rare-element pegmatite fields: is geochemistry controlled by tectonic setting or source lithologies? *Precamb. Res.* **51**, 429-468.

________ & BURT, D.M. (1984): Paragenesis, crystallochemical characteristics, and geochemical evolution of micas in granite pegmatites. *In* Micas (S.W. Bailey, ed.). *Rev. Mineral.* **13**, 257-297.

________ & SIMPSON, F.M. (1978): The Tanco pegmatite at Bernic Lake, Manitoba. X. Pollucite. *Can. Mineral.* **16**, 325-333.

COOPER, D.G. (1964): The Geology of the Bikita pegmatite. *In* Geology of Some Ore Deposits in Southern Africa (S.H. Haughton, ed.). *Geol. Soc. S. Afr., Monogr.* **2**, 441-461.

DRYSDALE, D.J. (1992): The pollucite – analcime series, 1974–1990. *Papers of the Department of Earth Sciences, University of Queensland* **12**, 317-324.

HENDERSON, C.M.B. & MANNING, D.A.C. (1984): The effect of Cs on phase relations in the granite system: stability of pollucite. *In* Progress in Experimental Petrology, sixth progress report of research supported by N.E.R.C., 1981–1984. *Nat. Env. Res. Council (UK) Publ. Ser. D* **25**, 41-42.

HUEBNER, J.S. (1971): Buffering techniques for hydrostatic systems at elevated pressures. *In* Research Techniques for High Pressure and High Temperature (G.C. Ulmer, ed.). Springer-Verlag, New York, N.Y. (123-177).

Icenhower, J.P. & London, D. (1995): An experimental study of element partitioning between biotite, muscovite and coexisting peraluminous granitic melt at 200 MPa ($H_2O$). *Am. Mineral.* **80**, 1229-1251.

________ & ________ (1996a): Experimental partitioning of Rb, Cs, Sr, and Ba between alkali feldspars and peraluminous melt. *Am. Mineral.* **81**, 719-734.

________ & ________ (1996b): Stability of pollucite in granitic melts at 600°–750°C, 200 MPa $H_2O$. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.* **21**, 46.

Lagache, M. (1995): New experimental data on the stability of the pollucite – analcime series: application to natural assemblages. *Eur. J. Mineral.* **7**, 319-323.

________, Dujon, S.-C. & Sebastian, A. (1995): Assemblages of Li–Cs pegmatite minerals in equilibrium with a fluid from their prù/ary crystallization until their hydrothermal alteration: an experimental study. *Mineral. Petrol.* **55**, 131-143.

London, D. (1986): The magmatic–hydrothermal transition in the Tanco rare-element pegmatite: evidence from fluid inclusions and phase equilibrium experiments. *Am. Mineral.* **71**, 376-395.

________ (1995): Geochemical features of peraluminous granites, pegmatites, and rhyolites as sources of lithophile metal deposits. *In* Magmas, Fluids, and Ore Deposits (J.F.H. Thompson, ed.). *Mineral. Assoc. Can., Short-Course Handbook* **23**, 175-202.

________ (1996): Granitic Pegmatites. *Trans. R. Soc. Edinburgh Earth Sci.* **87**, 305-319.

________, Morgan, G.B., VI, Babb, H. A. & Loomis, J. L. (1993): Behavior and effects of phosphorus in the system $Na_2O–K_2O–Al_2O_3–SiO_2–P_2O_5–H_2O$ at 200 MPa($H_2O$). *Contrib. Mineral. Petrol.* **113**, 450-465.

________, ________ & Hervig, R.L. (1989): Vapor-undersaturated experiments in the system macusanite–$H_2O$ at 200 MPa, and the internal differentiation of granitic pegmatites. *Contrib. Mineral. Petrol.* **102**, 1-17.

Luth, W.C. & Tuttle, O.F. (1966): The alkali feldspar solvus in the system $Na_2O–K_2O–Al_2O_3–SiO_2–H_2O$. *Am. Mineral.* **51**, 1359-1373.

Manning, D.A.C. (1981): The effect of fluorine on liquidus phase relationships in the system Qz–Ab–Or with excess water at 1 kb. *Contrib. Mineral. Petrol.* **76**, 206-215.

Martin, R.F. & Lagache, M. (1975): Cell edges and infrared spectra of synthetic leucites and pollucites in the system $KAlSi_2O_6$ – $RbAlSi_2O_6$ – $CsAlSi_2O_6$. *Can Mineral.* **13**, 275-281.

Morgan, G.B., VI & London, D. (1996): Optimizing the electron microprobe analysis of hydrous alkali aluminosilicate glasses. *Am. Mineral.* **81**, 1176-1185.

Moss, B.E., Haskin, L.A., Dymek, R.F. & Shaw, D.M. (1995): Redetermination and reevaluation of compositional variations in metamorphosed sediments of the Littleton Formation, New Hampshire. *Am. J. Sci.* **295**, 988-1019.

Pichavant, M. (1987): Effects of B and $H_2O$ on liquidus phase relations in the haplogranite system at 1 kbar. *Am. Mineral.* **72**, 1056-1070.

Pouchou, J.L. & Pichoir, F. (1985): "PAP" ( $\phi\rho Z$) correction procedure for improved quantitative microanalysis. *In* Microbeam Analysis (J.T. Armstrong, ed.), San Francisco Press, San Francisco, California (104-106).

Roy, B.N. & Navrotsky, A. (1984): Thermochemistry of charge coupled substitutions in silicate glasses: the systems $M^{n+}_{1/n}AlO_2–SiO_2$ (M = Li,Na,K,Rb,Cs,Mg,Ca,Sr,Ba,Pb). *J. Am. Ceram. Soc.* **67**, 606-610.

Sebastian, A. & Lagache, M. (1990): Experimental study of the equilibrium between pollucite, albite, and hydrothermal fluid in pegmatitic systems. *Mineral. Mag.* **54**, 447-454.

Shore, M. & Fowler, A.D. (1996): Oscillatory zoning in minerals: a common phenomenon. *Can. Mineral.* **34**, 1111-1126.

Teertstra, D.K. & Černý, P. (1992): Controls on morphology of analcime – pollucite in natural minerals, synthetic phases, and nuclear waste products. *Cryst. Res. Technol.* **27**, 931-939.

________, ________ & Chapman, R. (1992): Compositional heterogeneity of pollucite from High Grade dyke, Maskwa Lake, southeastern Manitoba. *Can. Mineral.* **30**, 687-697.

Tuttle, O.F. & Bowen, N.L. (1958): Origin of granite in the light of experimental studies in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–$SiO_2$–$H_2O$. *Geol. Soc. Am., Mem.* **74**.

Watson, E.B. (1976): Two liquid partition coefficients: experimental data and geochemical implications. *Contrib. Mineral. Petrol.* **56**, 119-134.

________ (1996): Surface enrichment and trace-element uptake during crystal growth. *Geochim. Cosmochim. Acta* **60**, 5013-5020.

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