

## PHOSPHORUS IN ALKALI FELDSPARS OF RARE-ELEMENT GRANITIC PEGMATITES

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### ABSTRACT

The abundance and distribution of phosphorus were determined in plagioclase and K-feldspar samples from 59 localities of nine types and subtypes of rare-element pegmatites. The incorporation of phosphorus in natural feldspars is represented by the coupled exchange  $\text{Al}^{3+} + \text{P}^{5+} = 2 \text{Si}^{4+}$ . For optically inclusion-free samples, the phosphorus content of feldspars varies inversely with calcium, which indicates that submicroscopic inclusions of apatite are not the cause of phosphorus enrichment. The distribution of P within individual samples is commonly variable within and among associated feldspar grains. In associated K-feldspar + plagioclase pairs, phosphorus is slightly enriched in the K-feldspar. As expected, feldspars from gadolinite-type pegmatites (A-type affinity) contain < 0.15 wt.%  $\text{P}_2\text{O}_5$ , and commonly below detection limit (0.002 wt.%  $\text{P}_2\text{O}_5$  by spectrophotometry, 0.01 wt.%  $\text{P}_2\text{O}_5$  by EMPA). Feldspars from all other types of pegmatite (generally S-type affinity) range from below detection limit to 1.20 wt.%  $\text{P}_2\text{O}_5$ , with approximately 60% of the data indicating greater than 0.30 wt.%. For the cases studied, the mean phosphorus content increases from early to late generations of primary feldspars within individual pegmatites. Phosphate-rich peraluminous pegmatites generally have the most phosphorus-enriched feldspars (Hagendorf, Peerless, Black Mountain, White Picacho district). Except for the uniformly low phosphorus contents of feldspars from gadolinite-type pegmatites, few other systematic differences are evident among the other different pegmatite types, or among different subtypes of cogenetic pegmatites within a given field. The abundance of phosphorus in source lithologies, activity of apatite or other phosphates in parental and derivative granitic magmas, and the aluminum saturation of the magmas are important factors in controlling the phosphorus content of pegmatite feldspars. The phosphorus content of pegmatites and related granitic rocks generally increases with bulk peraluminosity, as reflected by high whole-rock  $\text{P}_2\text{O}_5$ , and an abundance of phosphates other than apatite. An increase in the solubility of apatite in the melt with increasing Al content, and a decreasing Ca/P ratio in the melt, caused by plagioclase fractionation, may promote high P contents of alkali feldspars.

**Keywords:** pegmatite, feldspars, phosphorus, geochemistry.

### SOMMAIRE

Nous avons déterminé l'abondance et la distribution du phosphore dans le plagioclase et le feldspath alcalin d'échantillons de 59 exemples de pegmatites granitiques, subdivisés en neuf types et sous-types. L'incorporation du phosphore dans les feldspaths naturels résulte de l'échange couplée  $\text{Al}^{3+} + \text{P}^{5+} = 2\text{Si}^{4+}$ . Dans le cas des échantillons limpides, sans inclusions, la teneur en P varie inversement avec la teneur en Ca, ce qui prouve que ce ne sont pas des micro-inclusions d'apatite qui causent l'enrichissement en P. La distribution du P est généralement variable à l'intérieur d'un seul grain ou d'un grain à l'autre. Dans un couple plagioclase – feldspath alcalin, le P favorise légèrement le feldspath alcalin. Comme prévu, les feldspaths de pegmatites de type gadolinite (à affinité avec les granites de type A) contiennent moins de 0.15% de  $\text{P}_2\text{O}_5$ , et couramment moins que le seuil de détection, soit 0.002% de  $\text{P}_2\text{O}_5$  (poids) par spectrophotométrie, ou 0.01% par microsonde électronique. Les feldspaths de toute autre variété de pegmatite granitique, en général à affinité avec les granites de type S, ont des teneurs variables, de moins que le seuil de détection à 1.20% en  $\text{P}_2\text{O}_5$ ; dans environ 60% des cas, la teneur dépasse 0.30% en  $\text{P}_2\text{O}_5$ . Dans les exemples étudiés, la teneur moyenne augmente d'une génération précoce de feldspaths à une génération tardive. Les pegmatites hyperalumineuses riches en phosphates (e.g., celles des districts de Hagendorf, Peerless, Black Mountain et White Picacho) possèdent les feldspaths les plus enrichis en P. Sauf pour les faibles teneurs des pegmatites à gadolinite, il n'y a pas de généralisations à faire parmi les autres types de pegmatites, ou parmi les sous-types cogénétiques de pegmatites d'une région. L'abondance du phosphore à la source, l'activité de l'apatite ou d'autres phosphates dans les magmas granitiques primaires ou dérivés, et la saturation des magmas en aluminium seraient des facteurs importants pour expliquer la teneur d'un feldspath en P. La teneur en P des pegmatites et des roches granitiques affiliées augmente généralement avec le degré d'hyperaluminosité du système, comme le révèlent un niveau élevé de  $\text{P}_2\text{O}_5$  dans la roche globale et la proportion élevée de phosphates autres que l'apatite. Une augmentation dans la solubilité de l'apatite dans le magma avec enrichissement de celui-ci en Al, ainsi qu'une diminution dans le rapport Ca/P du magma due au fractionnement du plagioclase, pourraient promou-

voir l'incorporation de quantités importantes de P dans le feldspath alcalin.

(Traduit par la Rédaction)

**Mots-clés:** pegmatite granitique, feldspaths, phosphore, géochimie, systèmes hyperalumineux.

## INTRODUCTION

In basic to intermediate magmas, the relative abundance of Ca (in the presence of F, H<sub>2</sub>O and Cl) promotes the crystallization of apatite, such that the activity of phosphorus in residual melts is buffered at low and decreasing values. Watson & Capobianco (1981) demonstrated experimentally that the solubility of phosphorus in metaluminous felsic melts (as controlled by apatite saturation) decreases with the normal trend of fractionation toward increasing silica content of melt.

It is significant, therefore, that certain types of highly differentiated, Ca-poor silicic igneous rocks, in particular peraluminous leucogranites and their derivative pegmatites, possess high whole-rock phosphorus contents (sometimes in excess of 1.0 wt. % P<sub>2</sub>O<sub>5</sub>), and that the phosphorus content of these rocks increases with differentiation to the point that normal silicate assemblages (e.g., of lithium aluminosilicates, garnet) are replaced by analogous phosphate assemblages (e.g., amblygonite-montebrazite, Fe-Mn phosphates, *etc.*: London & Burt 1982b). By implication, the activity of apatite in highly fractionated, Ca-poor peraluminous melts is strongly reduced from the early stages of their crystallization. In such evolved melts, phosphorus (along with H<sub>2</sub>O, B and F) may exert a significant influence on bulk phase-equilibria, liquid lines of descent, and abundances and distributions of trace elements. Some preliminary data on the network-modifying role of phosphorus, its possible interaction with alkalis, H<sub>2</sub>O, and various other incompatible lithophile trace elements, and other aspects of its behavior in differentiated silicic magmas, are provided by Ryerson & Hess (1980), Mysen *et al.* (1981), London (1987, 1990a), Gan & Hess (1989), and London *et al.* (1988, 1989, 1990).

At the high phosphorus contents evident in many leucogranitic and pegmatitic rocks, it is reasonable to expect that an increasing chemical activity of phosphorus should lead to incorporation of this element into crystalline phases that otherwise do not contain it in significant amounts. In glasses and minerals, phosphorus forms distorted tetrahedral PO<sub>4</sub><sup>3-</sup> oxyanions with mean P-O bond lengths of 1.54 Å (a resonant structure of three singly bonded and one doubly bonded oxygen atoms with a high degree of covalent bond character: Corbridge 1985). Thus, PO<sub>4</sub> might be expected to substitute for other tetra-

hedrally coordinated species (Al, Si, possibly Fe) in silicate minerals. The most likely charge-balanced mechanism for phosphorus substitution in aluminosilicates is  $Al^{3+} + P^{5+} = 2 Si^{4+}$ . Although solid solutions between quartz (SiO<sub>2</sub>) and isostructural berlinite (AlPO<sub>4</sub>) have not been observed or well studied, Simpson (1977) demonstrated experimentally that this mechanism of substitution leads to complete miscibility between alkali feldspars and their phosphorus analogues, NaAl<sub>2</sub>PSiO<sub>8</sub> and KAl<sub>2</sub>PSiO<sub>8</sub>, at geologically relevant conditions of elevated fluid pressures.

The structural details of phosphorus substitution in feldspars are not known. Simpson (1977) noted that the unit-cell dimensions of P-substituted alkali feldspars are greater than those of albite and K-feldspar of the same structural state. An increase in unit-cell volumes can be rationalized by the substitution of the slightly larger AlO<sub>4</sub> for SiO<sub>4</sub> tetrahedra, and by distortion caused by the one doubly bonded oxygen atom in each PO<sub>4</sub> tetrahedron. Although the feldspars possess fully polymerized structures that contain four-coordinate tetrahedra, note that the existence of a P = O double bond formally limits PO<sub>4</sub> coordination to not more than three other cationic species (forming sheet structures) and thus precludes framework structures. Some of the data presented here suggest preliminarily that the  $Al^{3+} + P^{5+} = 2 Si^{4+}$  substitution may not be strictly stoichiometric.

Because of extensive solid-solution with P-bearing analogues, feldspars should be useful monitors of phosphorus activity in melt, once the partition coefficients for phosphorus between feldspar and melt are known for compositions of varying silica content, aluminum saturation index (ASI), and Ca content. As a complement to a current experimental study of phosphorus in granites and feldspars (London *et al.* 1990), this paper serves to document the abundance and distribution of phosphorus in natural alkali feldspars from granitic pegmatites. The new analytical data presented here corroborate the experimental evidence of London *et al.* (1989) in showing that the phosphorus content of natural alkali feldspars in pegmatites is not negligible, and that feldspars may in fact represent the principal reservoirs of phosphorus in many such rocks. This paper, expanded from the initial study of Pan (1988, Pan & Černý 1989), provides the first reconnaissance assessment of phosphorus in feldspars from a broad spectrum of pegmatite types from a variety of localities.

## PREVIOUS WORK

A survey of the literature reveals only scanty information on the phosphorus content of feldspars. The few data available indicate, however, that pegmatite feldspars are significantly enriched in phospho-

rus relative to those of mafic and intermediate plutonic rocks. Plagioclase of mafic rocks contains 0.001 to 0.140 wt.%  $P_2O_5$ ; plagioclase and K-feldspar (including anorthoclase and sanidine) of intermediate to granitic rocks carry 0.01–0.18 and 0.01–0.21 wt.%  $P_2O_5$ , respectively (Corlett & Ribbe 1967, Smith 1974, 1983, Mason 1982, Mason *et al.* 1982, unpubl. data of Petr Černý). In contrast, albite from granitic pegmatites has been reported to contain up to 0.89 wt.%  $P_2O_5$  (Corlett & Ribbe 1967, Strunz *et al.* 1975), and pegmatitic K-feldspar, up to 0.86 wt.%  $P_2O_5$  (Strunz *et al.* 1975). In feldspars from Bavarian granites that spawned rare-element pegmatites, Strunz *et al.* (1975) reported 0.34 to 0.65 wt.%  $P_2O_5$ . The enhanced phosphorus contents of the few samples of feldspars from pegmatites examined to date, and the general lack of a meaningful data-base, indicate a need for systematic study.

#### PEGMATITES EXAMINED

Appendix 1 lists localities from which feldspars were sampled for this study. They were selected to represent all types and subtypes of the rare-element class of granitic pegmatites, from a broad range of geographic locations and geological environments. In total, data on feldspars from 59 localities of nine pegmatite types and subtypes are presented here. Because of the complexities and variations inherent in rare-element pegmatites, however, this should not be construed as a large or necessarily representative data-set.

The gadolinite type of pegmatite is characterized by an alkaline to metaluminous signature and enrichment in Nb, Y, F (Ti, REE, Zr, U, Th); it is commonly associated with post-tectonic to anorogenic A-type granites, locally with a probable mantle component (Černý 1990a, b). The Lövböle pegmatite belongs to a hybrid pegmatite group transitional into the beryl-columbite-phosphate subtype. The Crystal Peak pegmatites are properly classified into the shallow-seated miarolitic class, but their geochemical features and genetic affiliation rank them with the gadolinite type (*cf.* the South Platte pegmatites of Simmons & Heinrich 1980, Simmons *et al.* 1987).

The beryl type of pegmatite is the least fractionated of the granitic pegmatites found in association with late- to post-tectonic peraluminous granites. The beryl-columbite and beryl-columbite-phosphate subtypes represent a more advanced stage of evolution, which culminates in precipitation of triphylite as the first Li-bearing mineral.

The complex pegmatite type is characterized by substantial contents of lithium minerals. The spodumene subtype represents a high-pressure, low-temperature counterpart to the low-pressure, high-temperature petalite subtype, as shown by Stewart

(1978) and London (1984). The amblygonite subtype is generated under conditions of high activity of phosphorus, such that lithium aluminosilicates are unstable with respect to amblygonite-montebrazite *via* equilibria such as  $LiAlSi_3O_6 + PO_2(OH,F) = LiAlPO_4(OH,F) + 2 SiO_2$  (London & Burt 1982b). The lepidolite subtype requires high activity of LiF and KF at relatively low acidity, with low  $\mu KF/\mu HF$  stabilizing topaz also (London 1982). Extreme "end-member" bulk compositions are, of course, rather uncommon: spodumene and petalite subtypes routinely contain amblygonite-montebrazite or lepidolite-enriched units, or both (*e.g.*, Harding, Tanco, Varuträsk, Utö), whereas amblygonite and lepidolite subtypes are occasionally enriched in lepidolite and amblygonite, respectively (*e.g.*, Peerless, Bob Ingersoll, Riber). Consequently, the classification shown in Appendix 1 is based on the volumetrically dominant Li-bearing phase.

By comparison to the zoned complex subtypes, the albite-spodumene type is nearly homogeneous, high in bulk Li content but usually rather poor in Be, Nb-Ta and Sn (*e.g.*, Heinrich 1978, Solodov 1971). The three localities to be examined here contain apatite, minor altered triphylite, or other secondary phosphates.

Pegmatites of the albite type also tend to be homogeneous, composed dominantly of saccharoidal to tabular albite with minor K-feldspar or lithium minerals, and occasionally prominent Be, Sn, Nb-Ta or Ti mineralization. The Tin Dyke is rich in apatite, but the other two pegmatites of this type listed in Appendix 1 are poor in this mineral.

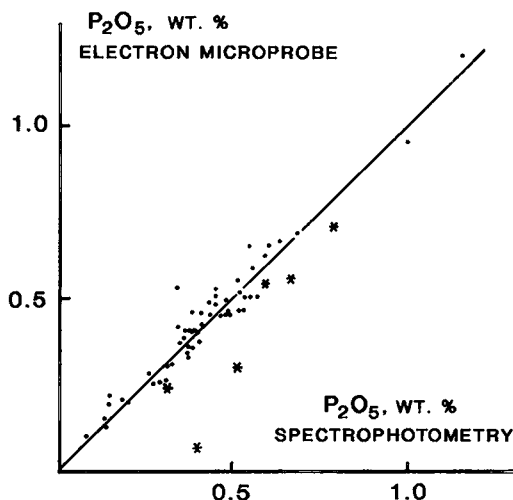


FIG. 1. Comparison of analytical data obtained by electron microprobe and spectrophotometry, University of Manitoba. Stars denote feldspars containing perceptible quantities of microscopic inclusions of apatite.

Further details of the general features of the above types and subtypes of rare-element pegmatites are discussed in Černý (1989a, b).

### SAMPLING AND ANALYTICAL METHODS

Where possible, blocky K-feldspar from cores, core-margins, or other late-stage internal units were used in the present study to facilitate meaningful comparisons among different localities. For all analyses of K-feldspar, the samples chosen and areas analyzed were free of perthitic albite lamellae. Some K-feldspar and albite samples from a given pegma-

tite come from the same textural-paragenetic zone, but are not necessarily paired in mutual contact. In many samples, albite (commonly with Li-micas, tourmaline, apatite, *etc.*) is interstitial to blocky K-feldspar, and hence may not be strictly cogenetic with the megacrystic K-feldspar phase. Consequently, these K-feldspar - albite pairs are designated as associated rather than coexisting feldspars. A number of albite samples come from saccharoidal to coarse-grained albitic units with no directly associated K-feldspar. Representation of more-or-less complete sequences of crystallization was attempted only in a few cases, to further explore changes in phosphorus content during crystallization of individual pegmatite bodies (as examined initially by Černý *et al.* 1984). Finally, note that the frequency distribution of feldspars sampled for this study is not weighted to the relative abundance of different types and subtypes of pegmatite in nature. Were they so weighted, there would probably be more values for the more common types of pegmatite (*e.g.*, beryl-columbite and complex-spodumene categories) and fewer data for less widespread types of pegmatite (*e.g.*, gadolinite type, amblygonite and albite subtypes).

Analyses conducted at the University of Manitoba utilized a UNICAM Sp 500 series 2 spectrophotometer for colorimetric determination of phosphorus

TABLE 1. SUMMARY OF THE  $P_2O_5$  CONTENTS OF FELDSPARS SPECTROPHOTOMETRIC ANALYSES\*

Locality	K-feldspar N	x(wt.%)	range(wt.%)	plagioclase N	x(wt.%)	range(wt.%)
<b>GADOLINITE SUBTYPE:</b>						
Shatford Lake	7	0.012	bd1 -0.015	4	0.010	bd1 -0.010
Huron Claim	8	0.124	0.11 -0.14	3	0.081	0.060-0.110
Rode Ranch	-	bd1	-	-	bd1	-
Ytterby	4	0.013	0.012-0.014	3	0.013	0.010-0.021
Lövöbblé	4	0.116	0.078-0.148	2	0.111	0.096-0.126
Crystal Peak	4	0.006	0.001-0.013	3	0.003	0.001-0.006
<b>BERYL-COLUMBITE SUBTYPE:</b>						
Greer Lake	10	0.066	0.022-0.075	5	0.058	0.025-0.081
Bill	2	0.569	0.541-0.597	-	-	-
Plex	5	0.159	0.124-0.185	3	0.122	0.104-0.141
Vezna	6	0.074	0.054-0.101	5	0.104	0.087-0.146
<b>BERYL-COLUMBITE-PHOSPHATE SUBTYPE:</b>						
Cross Lake #22	4	1.051	0.861-1.203	-	-	-
Dan Patch	4	0.439	0.382-0.523	-	-	-
Bull Moose	5	0.442	0.371-0.536	3	0.379	0.360-0.410
Big Chief	5	0.429	0.310-0.542	-	-	-
Hagendorf-Süd	6	0.636	0.554-0.782	3	0.373	0.24 -0.51
Doñi Bory	6	0.387	0.304-0.455	5	0.355	0.306-0.410
Peg	4	0.507	0.402-0.562	-	-	-
<b>COMPLEX - SPODUMENE SUBTYPE:</b>						
Bet	3	0.555	0.510-0.584	-	-	-
Helen Beryl	4	0.152	0.092-0.181	2	0.110	0.080-0.141
Tin Mountain	4	0.545	0.486-0.603	2	0.426	0.420-0.433
Etta	4	0.340	0.270-0.433	2	0.301	0.280-0.323
Tip Top	3	0.336	0.292-0.400	1	0.268	-
Harding	3	0.091	0.073-0.108	-	-	-
Kamatwi	7	0.563	0.065-0.732	-	-	-
<b>COMPLEX - PETALITE SUBTYPE:</b>						
Tanco	4	0.518	0.450-0.610	2	0.323	0.280-0.367
Hirvikallio	5	0.325	0.264-0.378	2	0.263	0.220-0.306
Luomäki	3	0.435	0.408-0.481	2	0.363	0.356-0.370
Varuträsk	12	0.490	0.364-0.590	4	0.341	0.316-0.371
Utö	5	0.472	0.389-0.532	2	0.320	-
<b>COMPLEX - LEPIDOLITE SUBTYPE:</b>						
High Grade Dike	2	0.063	0.028-0.099	-	-	-
Riber	1	0.33	-	-	-	-
Bob Ingersoll	3	0.501	0.440-0.542	2	0.350	0.315-0.385
Radkovic	2	0.413	0.412-0.414	-	-	-
Biskupice	1	0.669	-	-	-	-
<b>COMPLEX - AMBLYGONITE SUBTYPE:</b>						
Peerless	3	0.567	0.402-0.677	2	0.310	0.300-0.320
Vitaniemi	5	0.409	0.327-0.482	3	0.283	0.256-0.311
<b>ALBITE - SPODUMENE TYPE:</b>						
Violet	4	0.071	0.063-0.088	-	-	-
Nite	3	0.413	0.364-0.445	-	-	-
<b>ALBITE TYPE:</b>						
Tin Dyke	-	-	-	3	0.01	-
Odd	-	-	-	3	0.447	0.410-0.470
Hengshan	-	-	-	3	0.317	0.240-0.370

\* no analyses: - ; below detection: bd1; University of Manitoba

TABLE 2. SUMMARY OF THE  $P_2O_5$  CONTENT OF FELDSPARS ELECTRON MICROPROBE ANALYSES\*

Locality	K-feldspar N	x(wt.%)	range(wt.%)	plagioclase N	x(wt.%)	range(wt.%)
<b>BERYL-COLUMBITE SUBTYPE:</b>						
Case	-	-	-	3	bd1	bd1 -0.051
Gotta-Apple Orchard	3	0.107	bd1 -0.173	7	bd1	bd1 -0.117
Hale	1	0.129	-	7	0.068	bd1 -0.052
White Rocks	2	0.083	bd1 -0.196	5	bd1	bd1 -0.148
<b>BERYL-COLUMBITE-PHOSPHATE SUBTYPE:</b>						
Palermo	-	-	-	2	0.227	bd1 -0.585
<b>COMPLEX - SPODUMENE SUBTYPE:</b>						
Bennet	-	-	-	3	0.061	bd1 -0.107
Black Mountain	8	0.417	0.318-0.509	35	0.201	bd1 -0.557
Branchville	3	bd1	bd1 -0.068	10	0.114	bd1 -0.398
Etta	-	-	-	2	0.103	bd1 -0.352
Gotta-Walden	-	-	-	6	0.066	bd1 -0.142
Helen Beryl	-	-	-	2	bd1	bd1
Harding	1	bd1	bd1	7	bd1	bd1 -0.147
Homestead	-	-	-	6	0.153	bd1 -0.427
Midnight Owl	2	0.398	0.334-0.470	1	bd1	bd1 -0.044
Strickland	3	0.157	bd1 -0.257	8	0.066	bd1 -0.175
Tin Mountain	-	-	-	2	0.055	bd1 -0.125
White Ridge	2	0.359	0.196-0.428	3	0.100	bd1 -0.355
<b>COMPLEX - PETALITE SUBTYPE:</b>						
Tanco	1	bd1	bd1	7	0.171	bd1 -0.443
<b>COMPLEX - LEPIDOLITE SUBTYPE:</b>						
Swanson	-	-	-	8	0.178	bd1 -0.570
Bob Ingersoll	-	-	-	3	0.312	bd1 -0.443
Himalaya/S. Diego	-	-	-	12	bd1	bd1 -0.215
Little Three	-	-	-	5	bd1	bd1 -0.166
Stewart	-	-	-	3	0.142	bd1 -0.203
<b>ALBITE - SPODUMENE TYPE:</b>						
Kings Mountain	3	0.336	0.010-0.601	9	0.169	bd1 -0.491

\* no analyses: - ; below detection: bd1; University of Oklahoma

as molybdenum blue (Jeffery & Hutchison 1981). Dissolution of 0.5 to 1.0 g of powdered feldspar, manually separated from 1–3 mm chips under a binocular microscope, was achieved by acid digestion. A calibration curve was constructed from readings on standards prepared from a  $\text{KH}_2\text{PO}_4$  stock solution. The detection limit proved to be 0.002 wt.%  $\text{P}_2\text{O}_5$ .

For comparative purposes, these same feldspars were analyzed by electron microprobe (EMP); the analyses were performed on a MAC-5 instrument in wavelength-dispersion mode, with 120 seconds counting time at 15 kV accelerating potential and 0.04 nA sample current. Taylor Wilberforce apatite was used as the phosphorus standard, calibrated against orthoclase or albite background. The detection limit was found to be close to 0.01 wt.%  $\text{P}_2\text{O}_5$  at two standard deviations above mean background. Because of phosphorus variability from point to point, multiple points were analyzed and averaged for each grain to facilitate a comparison with the results of spectrophotometry.

Figure 1 compares the results obtained by the two methods. The match is in general very good, except for a few samples that proved to contain relatively abundant microinclusions of apatite. Optical microscopic checks of samples plotting close to the 1:1 reference line showed only traces of apatite or its total absence.

Additional electron-microprobe analyses (EMPA) of feldspars from other localities were performed on a CAMECA SX-50 microprobe at the University of Oklahoma. Beam conditions were 15 kV, beam current of 10 nA, spot size of 5  $\mu\text{m}$ . Apatite from Durango was used as the phosphorus standard, with a live counting time of 120 seconds on samples. Data were reduced by the PAP procedure (Pouchou & Pichoir 1985). The detection threshold for phosphorus, taken conservatively as three standard deviations above mean background, was 0.04 wt.%  $\text{P}_2\text{O}_5$ .

The analytical results are summarized in Tables 1 and 2. Again to facilitate comparisons, the EMPA results listed in Table 2 and used in subsequent figures (except where noted) represent averages of multiple points on individual grains. Complete listings of all data condensed here may be obtained at nominal cost from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

## RESULTS AND DISCUSSION

### *Phosphorus distributions within individual grains*

The results of EMPA reveal that the distribution of phosphorus in individual grains (1–2 mm portions of larger crystals) is commonly patchy (also see Corlett & Ribbe 1967), and may vary from near

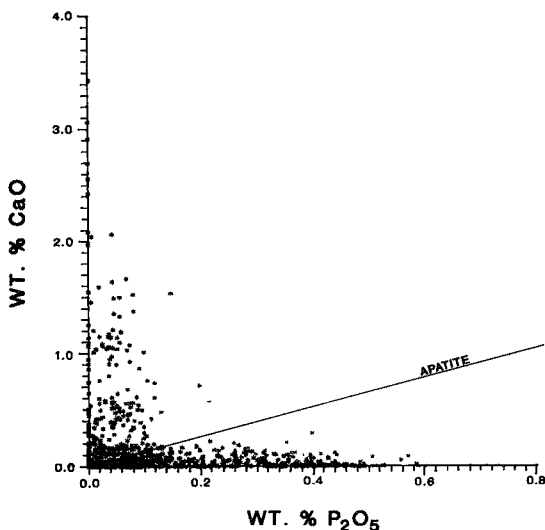


FIG. 2. Comparison of CaO content versus  $\text{P}_2\text{O}_5$  content in feldspars (EMPA, all data from Table 2), University of Oklahoma.

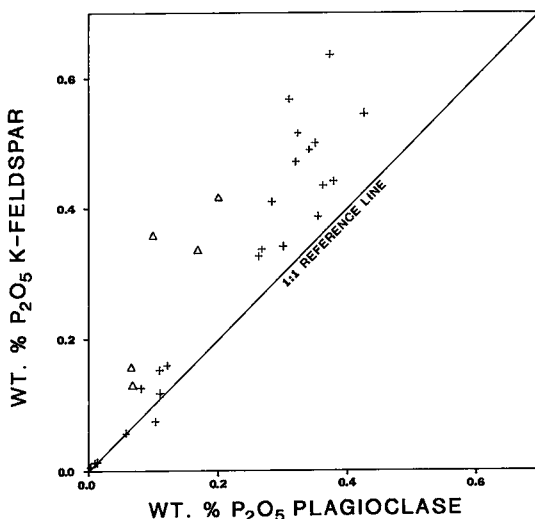


FIG. 3. The  $\text{P}_2\text{O}_5$  contents of associated K-feldspar and plagioclase, showing slight preference for incorporation of P in the K-feldspar. Results of spectrophotometric analyses (+) from Table 1, University of Manitoba; EMPA results ( $\Delta$ ) from Table 2, University of Oklahoma.

detection to  $>0.5$  wt.%  $\text{P}_2\text{O}_5$ . There is no positive correlation of phosphorus with Ca, indicating that microinclusions of apatite are not responsible for this variability (Fig. 2). Also, the  $\text{P}_2\text{O}_5$  contents of some grains are internally homogeneous, but different by

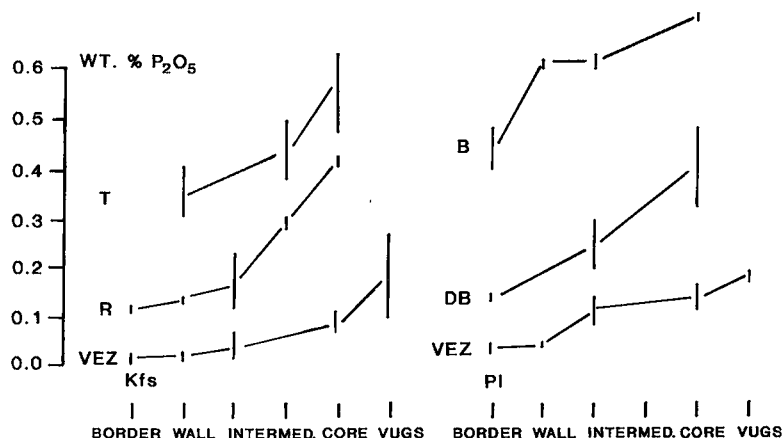


FIG. 4. Increase in  $P_2O_5$  content in crystallization sequences of K-feldspar in the Tanco (T), Biskupice (B), Radkovice (R) and Dolni Bory pegmatites (DB), and in the K-feldspar and plagioclase sequences of the Vezna (VEZ) pegmatite (from Černý *et al.* 1984).

TABLE 3. THE PHOSPHORUS CONTENT IN FELDSPAR CRYSTALLIZATION SEQUENCES

PEGMATITE ZONE	N	x	range
<b>TANCO (K-Feldspar)</b>			
wall	3	0.355	0.291 - 0.394
intermediate	5	0.340	0.363 - 0.483
core	4	0.516	0.450 - 0.610
<b>BISKUPICE (K-Feldspar)</b>			
border	2	0.426	0.390 - 0.462
wall	1	0.550	-
intermediate	2	0.592	0.580 - 0.604
core	1	0.669	-
<b>RADKOVICE (K-Feldspar)</b>			
border	1	0.111	-
wall	1	0.133	-
intermediate	2	0.150	0.112 - 0.209
intermediate	2	0.281	0.281 - 0.281
core	2	0.413	0.413 - 0.414
<b>DOLNI BORY (K-Feldspar)</b>			
border	1	0.110	-
intermediate	2	0.225	0.182 - 0.268
core	6	0.387	0.304 - 0.455
<b>VEZNA (K-Feldspar)</b>			
wall	3	0.011	0.006 - 0.019
intermediate	5	0.012	0.007 - 0.018
graphic	4	0.037	0.008 - 0.064
core	6	0.074	0.054 - 0.101
vugs	2	0.172	0.092 - 0.251
adularia	1	0.078	-
<b>VEZNA (Plagioclase)</b>			
wall	4	0.024	0.023 - 0.026
intermediate	2	0.027	0.024 - 0.029
graphic	5	0.097	0.076 - 0.118
core	5	0.104	0.087 - 0.146
vugs	2	0.157	0.146 - 0.168
border with apatite	4	0.022	0.018 - 0.026

more than an order of magnitude from other grains taken several millimeters away in the same sample. Patchy, heterogeneous distributions of phosphorus within and among associated feldspars could arise

from: (i) rapid, disequilibrium growth of feldspars (*e.g.*, Černý *et al.* 1984, London *et al.* 1989); (ii) local gradients in concentration in the melt stemming from chemical potential gradients induced by crystallization of phosphates; or (iii) localized gain or loss of phosphorus as a result of sporadic but extensive feldspar re-equilibration along cleavage or fracture surfaces. The variability observed in this study points to a complex but potentially very informative behavior of phosphorus in feldspars of differentiated granite-pegmatite systems.

The EMPA data represented in Table 2 show close conformity to the  $Al + P = 2 Si$  substitution mechanism, *i.e.*,  $XP/(XAl - 1) \approx 1$  for most samples, but exceptions appear to exist. Specifically, the ratio  $XP/(XAl - 1)$  tends to be slightly greater than 1 for K-feldspar (those data summarized in Table 2), which tends to be richest in phosphorus, with consequently good X-ray counting statistics. Experimentally grown P-rich alkali feldspars with 1 to 3 wt. %  $P_2O_5$  consistently show  $XP/(XAl - 1)$  greater than 1 (London & Loomis, unpubl. data). Given that distorted  $PO_4$  tetrahedra with one  $P=O$  bond are not truly isostructural with  $SiO_4$  or charge-balanced  $AlO_4$  tetrahedra, the structural incorporation of phosphorus in feldspars could involve vacancy- or other defect-generating schemes that promote other substitutions in addition to the isovalent  $Al + P = 2 Si$  substitution.

#### Partitioning of phosphorus between K-feldspar and plagioclase

Figure 3 shows data averaged for associated K-feldspar + plagioclase pairs, indicating a slightly to

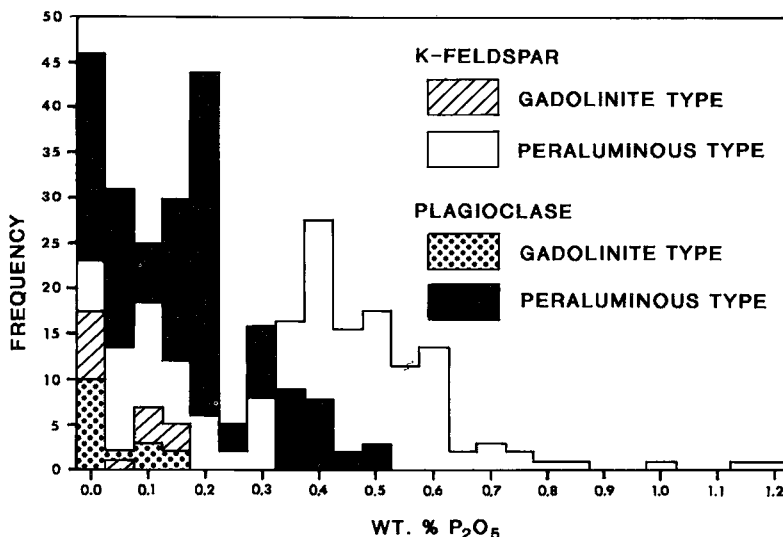


FIG. 5. Frequency of  $P_2O_5$  contents in plagioclase and K-feldspar, combined data of Tables 1 and 2. Frequency bars are superimposed, not stacked. Values of wt. %  $P_2O_5$  are given in 0.05% increments, centered at X.Y0 and X.Y5 values.

distinctly preferential incorporation of phosphorus into the K-feldspar structure. This is in agreement with previous results obtained on truly coexisting feldspars, including perthitic exsolution pairs (*e.g.*, Smith 1974, 1983, Mason 1982). In most samples studied, however, albite is interstitial to the blocky K-feldspar, and hence is paragenetically later than the substrate K-feldspar megacrysts. Preliminary experimental results fail to show fractionation of phosphorus between potassic and sodic feldspars in appropriately constructed comparisons (London *et al.* 1990).

#### *Internal evolution within individual pegmatites*

Figure 4 and Table 3 show  $P_2O_5$  contents in K-feldspar crystallization sequences from four pegmatites, and in K-feldspar and plagioclase sequences from the Vezna pegmatite, taken from Černý *et al.* (1984). With progress of pegmatite consolidation, the  $P_2O_5$  content of the feldspars invariably increases. However, two deviations from this trend are not illustrated in Figure 4. Firstly, feldspars coprecipitated with abundant apatite can be severely depleted in phosphorus, as shown by Černý *et al.* (1984) on an oligoclase + apatite pair of the Vezna pegmatite, generated locally by reaction with serpentinite wallrock and not easily correlated with the internal zoning sequence illustrated in Figure 4. This oligoclase contains only 0.018–0.026 wt. %  $P_2O_5$ . Secondly, late low-temperature K-feldspar of secondary origin is commonly poor in phosphorus, as shown by the Vezna adularia (Černý *et al.* 1984:

0.078 wt. %  $P_2O_5$ ), and by other samples of adularia from granitic pegmatites (Černý & Chapman 1984).

#### *Range and frequency*

Figure 5, which includes data from all pegmatite types and subtypes, shows that the  $P_2O_5$  contents of plagioclase range from below detection to 0.57 wt. %, and those of K-feldspar from below detection to 1.20 wt. %.

Frequency distributions of  $P_2O_5$  contents of both K-feldspar and plagioclase are distinctly bimodal. Both histograms in Figure 5 contain a prominent mode at or slightly above detection level. The mean values of modes corresponding to higher  $P_2O_5$  contents lie near 0.45 wt. %  $P_2O_5$  for K-feldspar, and 0.20 wt. %  $P_2O_5$  for plagioclase. The lower mean value for plagioclase may stem partly from incomplete sampling (*i.e.*, a lack of plagioclase data from pegmatites with the highest  $P_2O_5$  contents in K-feldspar).

As shown below, the mode at low phosphorus values is populated by feldspars from gadolinite-type pegmatites, with a substantial proportion of the data from the peraluminous types and subtypes (Fig. 5). In contrast, the high- $P_2O_5$  mode consists solely of feldspar data from peraluminous pegmatites.

#### *Feldspars of pegmatites of the gadolinite type*

The data for feldspars from the gadolinite pegmatites, condensed within the  $P_2O_5$ -poor maxima of Figure 5, are spread out and subdivided in Figure

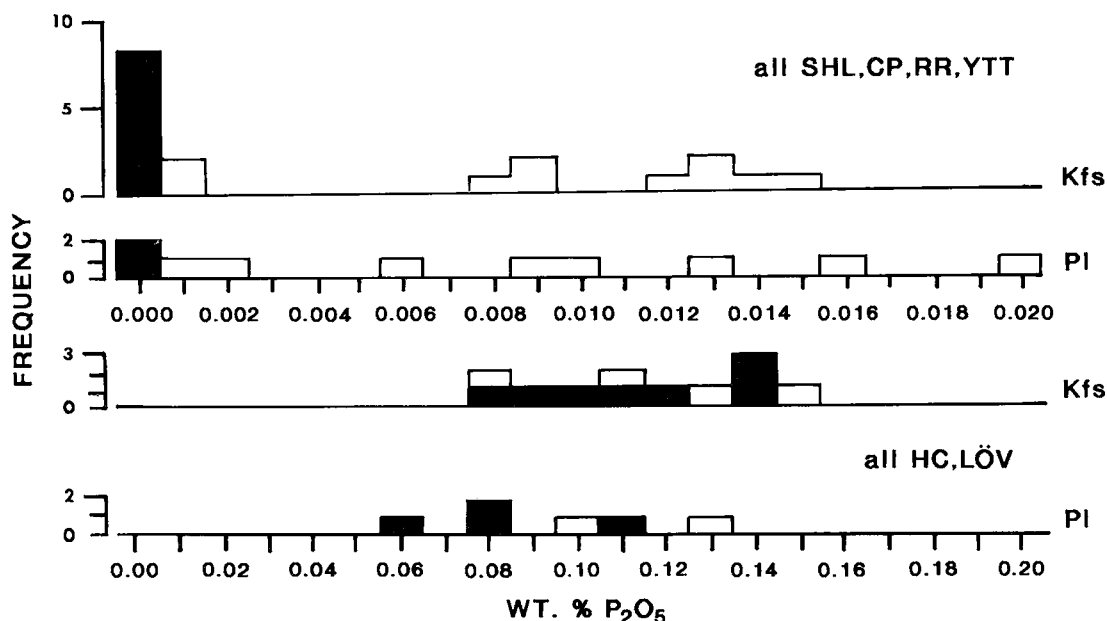


FIG. 6. Frequency of  $P_2O_5$  contents in plagioclase and K-feldspar from the gadolinite subtype of rare-element pegmatites, data from Table 1. Upper part: total of Shatford Lake (SHL), Crystal Peak (CP), Rode Ranch (RR) and Ytterby (YTT) data, with black bars representing data below detection limit. Lower part: data for Huron Claim (HC, black bars) and Lövböle (LOV, white bars). Note the difference in scales between the upper and lower parts.

6. All feldspars from four typical pegmatites or pegmatite groups of this type contain less than 0.02 wt. %  $P_2O_5$ , and most are near or below the detection limit. The only feldspars with higher concentrations of  $P_2O_5$  (0.06–0.15 wt. %) come from the Huron Claim pegmatite (the most fractionated and mineralized member of the Shatford Lake Group, Manitoba), and from the Lövböle pegmatite, Finland, which belongs to a group of atypical pegmatites transitional into Li-enriched peraluminous members. In general, it appears that the  $P_2O_5$  contents of feldspars in gadolinite pegmatites are consistently low relative to those in other types or subtypes.

#### *Feldspars of the peraluminous pegmatites*

With very few but significant exceptions, mean  $P_2O_5$  contents of these feldspars are much higher than those of the gadolinite category. Internally, however, they are much more variable.

Figure 7 shows a broad spread of  $P_2O_5$  values among feldspars of virtually all subtypes of peraluminous pegmatites. For the existing data, mean values of  $P_2O_5$  in alkali feldspars appear to be lowest for the beryl–columbite subtype, highest for the beryl–columbite–phosphate and all complex categories, then decreasing again for albite–spodumene and albite subtypes (Table 4). Some overlap between populations exists, however, at the 1σ

deviation about mean values (Table 4). Also, the histograms for the albite–spodumene and albite subtypes are so sharply bimodal that statistical averages for these data appear to be meaningless in the absence of more data. In addition to the unbalanced sample-base for this study, other factors present problems for such general comparisons of pegmatite subtypes. There may be (and in fact are) significantly different degrees of fractionation among individual pegmatite bodies within the same subtype. Also, the absolute abundance of phosphorus (as manifested by phosphate minerals) varies dramatically for similar types of pegmatites from different pegmatite fields. Thus, only limited conclusions can be drawn, and interesting features pointed out, from the present data.

In general, the phosphorus content of feldspars is low in pegmatites that contain abundant apatite as the only or principal phosphate phase. This is to be expected from the fact that continuous crystallization of apatite (in rare-element pegmatites that are anomalously enriched in Ca) should buffer the phosphorus content of residual melts at low and decreasing values (Watson & Capobianco 1981). Apatite abundance is moderately to remarkably high in the Harding, Violet and Tin Dyke pegmatites. These pegmatites are conspicuous by the very low abundances of P in their feldspars relative to their counterparts in their respective categories. However, the phospho-



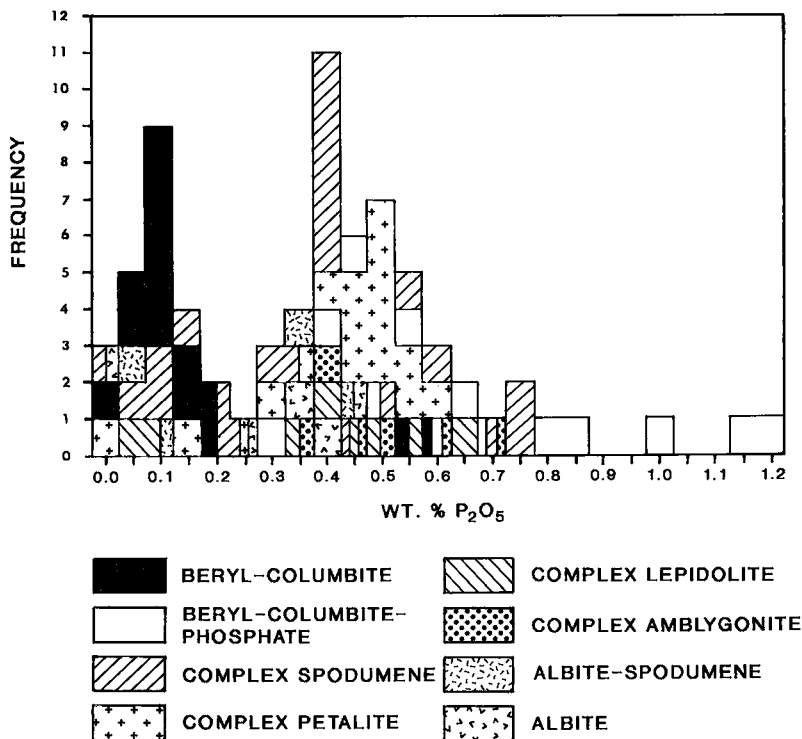


FIG. 7. Frequency of  $P_2O_5$  contents of K-feldspar from different types and subtypes of peraluminous rare-element pegmatites, combined data of Tables 1 and 2. Frequency bars are superimposed, not stacked. Some bars have been split to show all pegmatite types represented at the same frequency. Values of wt. %  $P_2O_5$  are given in 0.05% increments, centered at X.Y0 and X.Y5 values.

rus content of feldspars is uniformly higher in leucogranites and associated pegmatites that contain apatite or other phosphates than in granites that contain no phosphates at all. In the Winnipeg River district, Manitoba, the Greer Lake leucogranite and its pegmatite aureole are extremely depleted in phosphorus, whereas the neighboring Osis Lake and Bernic Lake systems (represented in this study by the Tanco pegmatite) are enriched in phosphorus in all their members (Černý *et al.* 1981, Goad & Černý 1981). In the first case, apatite is extremely rare, no other phosphates were encountered, and phosphorus contents of feldspars are negligible. In the other intrusive suites, apatite is present with other phosphates in both the leucogranite and pegmatites of all types or subtypes, and the phosphorus content of feldspars is moderate to high. Within a single deposit, feldspars that coprecipitated with phosphates may contain more phosphorus than in similar but phosphate-absent assemblages. For example, tabular albite crystals intergrown with phosphates (triphylite, amblygonite-montebrazite) from Black Mountain,

TABLE 4. MEAN CONCENTRATION AND STANDARD DEVIATION FOR PHOSPHORUS IN FELDSPARS FROM PERALUMINOUS PEGMATITES (SEE FIGURE 7)

pegmatite types/subtypes	X	1 S.D.
beryl-columbite	0.137	0.148
beryl-columbite-phosphate	0.592	0.229
complex spodumene	0.352	0.204
complex petalite	0.422	0.130
complex lepidolite	0.383	0.197
complex amblygonite	0.475	0.120
albite-spodumene	0.255	0.171
albite	0.250	0.197

Maine, contain significantly higher phosphorus contents than does albite from phosphate-free, albite-rich portions of the pegmatite (albite-lepidolite-tourmaline masses interstitial to spodumene). Fine-grained, saccharoidal albite from this pegmatite contains more phosphorus than do coarse-grained, tabular crystals from the same unit with the same mineralogical assemblage and mode.

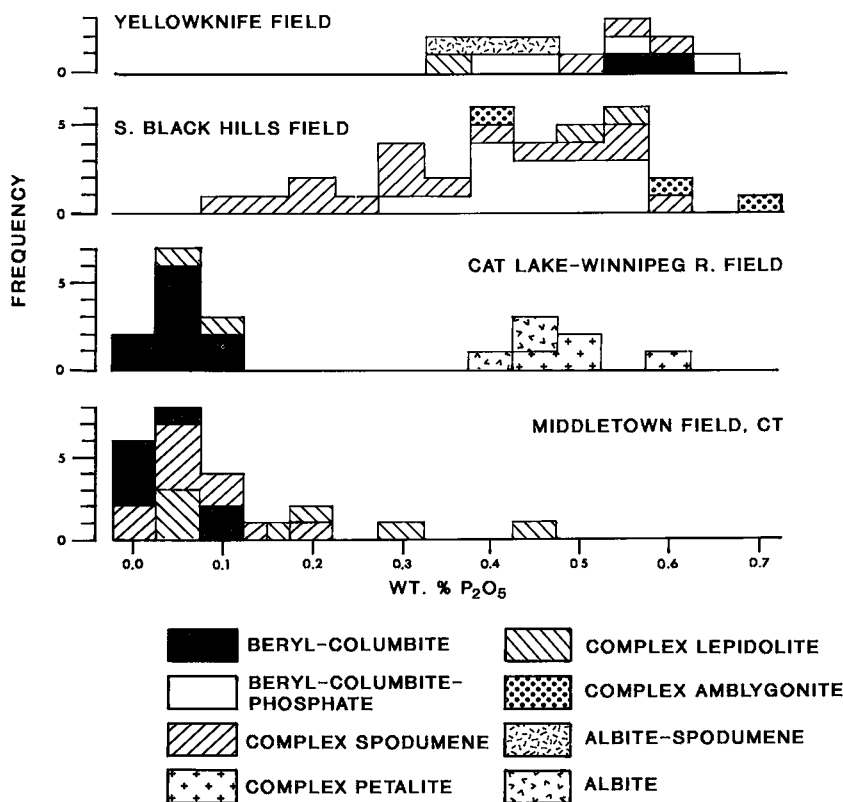


FIG. 8. Comparison of total ranges of  $P_2O_5$  contents of feldspar from four pegmatite fields, subdivided internally by pegmatite types and subtypes. Histograms for Yellowknife field, Southern Black Hills field, and Cat Lake - Winnipeg River fields are for K-feldspar from Table 1; the histogram for the Middletown field is for plagioclase from Table 2.

TABLE 5. MEAN AND STANDARD DEVIATIONS FOR PHOSPHORUS IN PLAGIOCLASE FROM PEGMATITES OF THE MIDDLETOWN FIELD (SEE FIGURE 8)

pegmatites	$\bar{X}$	1 S.D.
White Rocks	0.060	0.082
Case, Hale, Gotta-Apple Orchard	0.047	0.051
Strickland, Gotta-Walden	0.064	0.041
Swanson	0.181	0.141

#### *Comparisons among cogenetic pegmatites within the same field*

Different but cogenetic pegmatites from the same field may provide more meaningful comparisons than the groupings by pegmatite type or subtypes discussed above. The variability of  $P_2O_5$  contents of feldspars is extensive even in genetically constrained

populations. Three of the four fields illustrated in Figure 8 show broad overlaps among the different categories of pegmatite, with no consistent shifts from one to another. One possible exception is the Yellowknife field, which shows a relatively restricted range. This probably results from the rather simple array of pegmatite types and subtypes in this field and its overall geochemical uniformity (Meintzer 1987). In the Middletown pegmatite field, Connecticut, average phosphorus contents of plagioclase appear to be similar (Table 5), from the source pegmatitic granite (White Rocks) through a group of weakly to modestly differentiated complex pegmatite bodies (Hale, Case, Gotta Apple Orchard, and Gotta-Walden and Strickland, the latter two of which contain minor spodumene and traces of lithium phosphates). However, the  $P_2O_5$  content of albite from the Swanson pegmatite, a complex lepidolite subtype and the most differentiated pegmatite in the field, is conspicuously higher than the

rest. Interestingly, the Swanson body is also one of the most phosphate-rich pegmatites in this field, and albite from this pegmatite is clearly cogenetic with very abundant apatite and minor triplite.

#### SUMMARY

The extreme variability of phosphorus in feldspars at all scales of examination (individual small grains to pegmatite fields) points to a very complex history and behavior of phosphorus in rare-element pegmatites. With additional analytical and experimental data, however, the phosphorus content of feldspars from pegmatites and compositionally similar leucogranites has the potential for revealing much information on many facets of crystallization, melt differentiation, and trace-element fractionation (especially for the *REE*) in evolved silicic melts.

The distinctly low  $P_2O_5$  content of feldspars from the gadolinite-type pegmatites may result from cumulative effects of protolith composition, "orthomagmatic" crystallization of apatite, and approximately subaluminous chemistry of the pegmatites, for the following reasons:

(i) Metamorphic protoliths of A-type granites, which typically yield the gadolinite pegmatites, are depleted in mobile components that are lost to granitic melts generated by preceding anatexis event(s) (e.g., Collins *et al.* 1982, Jackson *et al.* 1984, Whalen *et al.* 1987). In addition to the rare alkalis and other elements, this depletion also applies to phosphorus. The A-type melts are commonly regarded as dry (Collins *et al.* 1982), in which case diffusivity of phosphorus and incorporation of the apatite components into the  $H_2O$ -poor melts might be commensurately slow (Harrison & Watson 1984). However, the relatively high abundance of F in A-type melts would compensate for  $H_2O$  by enhancement of diffusivity of cations (Johnson *et al.* 1974).

(ii) Importantly, the relative enrichment of A-type melts in Ca and F promotes crystallization of apatite during early plutonic crystallization, further reducing the abundance of phosphorus in residual melts (e.g., Simmons *et al.* 1987). Relatively high levels of Ca promoting precipitation of apatite also are characteristic of M-type melts (e.g., Whalen 1985, Whalen *et al.* 1987), which may contribute to the composition of postorogenic to anorogenic granites that generate gadolinite pegmatites (e.g., Fowler & Doig 1983, Baadsgaard *et al.* 1984).

(iii) The traces of phosphorus surviving the early stages of granite crystallization tend to form phosphates of Y, *REE* (e.g., xenotime and monazite) in derivative pegmatites. As phosphorus rather than *REE* appears to be the limiting component (i.e., the *REE* are sufficiently abundant to attain saturation in *REE* silicates and fluorides), the comparatively low solubility of *REE* phosphates (e.g., Ellison &

Hess 1988, Rapp & Watson 1986) should buffer the phosphorus content of the residual melt at low values.

(iv) Perhaps most importantly, the Al-poor compositions of these melts will necessarily limit the extent of the  $Al + P = 2 Si$  substitution in feldspars.

In contrast, feldspars from peraluminous pegmatites are largely enriched in P because of favorable circumstances: phosphorus-bearing protoliths, reduced importance of "orthomagmatic" precipitation of apatite, and peraluminous compositions that favor the  $Al + P = 2 Si$  exchange:

(i) Metamorphic country rocks yielding peraluminous fertile granitic melts are generally undepleted in mobile elements (Černý & Meintzer 1988, Černý 1990b). The hydrous nature of anatexis generating these melts facilitates dissolution of apatite and diffusion of phosphorus (Harrison & Watson 1984).

(ii) The melts are Ca-poor throughout most of their crystallization. Incipient crystallization of abundant plagioclase effectively decreases the Ca/P ratio of residual peraluminous melts [Černý & Meintzer 1988, Sawka, 1989, see London *et al.* (1989) for partition coefficients of Ca and P between plagioclase and melt]. The chemical activity of F is probably also lower than in the A-type melts, at least relative to that of  $H_2O$ . Regardless of the mechanisms, London *et al.* (1989) have shown experimentally that crystallization of apatite is suppressed in chemically differentiated peraluminous melts, and that in the absence of apatite, P is highly compatible in alkali feldspars.

(iii) An increase in the compatibility and hence solubility of P in peraluminous melts may be explained by the formation of  $AlPO_4$  melt species (Mysen *et al.* 1981). Such speciation would decrease the activity of apatite in melt, and would serve to enhance the incorporation of P in feldspars.

(iv) Consequently, phosphorus is available in relatively high concentrations for incorporation into feldspars, its entry facilitated by the availability of Al in excess of the normal feldspar stoichiometry. Mineralogy, bulk chemistry and  $P_2O_5$  contents of feldspars (0.45–0.75 wt. %  $P_2O_5$ ) in experiments with Macusani glass (equivalent of highly fractionated rare-element pegmatite magmas) are in full agreement with this interpretation (London *et al.* 1989).

Significant exceptions to the generally high  $P_2O_5$  contents in feldspars of peraluminous pegmatites clearly do exist. These variations are undoubtedly controlled by combinations of source-rock composition, nature and degree of anatexis involving phosphates in the protoliths, and trends of crystal fractionation in derivative granites and pegmatites (especially with regard to phases that may modify the concentrations of Ca, P, Al, volatile contents,

and the ASI of residual melts). This heterogeneity in phosphorus abundance exists among broadly related but geochemically distinctive granite + pegmatite subsystems within a single field (e.g., Black Hills, South Dakota), and among spatially associated but compositionally distinct leucogranites and their pegmatite aureoles (e.g., Winnipeg River district, Manitoba).

#### CONCLUDING REMARKS

This reconnaissance study demonstrates that the phosphorus content of alkali feldspars, especially in P-rich peraluminous leucogranites and related pegmatites, is not negligible, and in fact that feldspars may represent the principal reservoirs of phosphorus in such systems. Moreover, high phosphorus content is not restricted to the alkali feldspar of pegmatites, but is found in other geochemically similar systems. Kontak & Strong (1988) found more than 1 wt.%  $P_2O_5$  in feldspars from the South Mountain Batholith, Nova Scotia. Phosphorus contents of alkali feldspar from granites of Cornwall, England, average 0.4 to 0.7 wt.%  $P_2O_5$ , those from the ambygonite-bearing Beauvoir granite, France, range from 0.4 to 1.0 wt.%  $P_2O_5$ , and sanidine from the peraluminous Moroccala rhyolite province, Bolivia, also shows marked enrichment in phosphorus (London 1990b).

We hope that this survey stimulates our colleagues working in similar granite-pegmatite systems to pursue more detailed studies of phosphorus contents and distributions in the feldspars, and ultimately the fate of phosphorus from anatexis of protoliths, through crystallization of the felsic melt, and eventual production of pegmatites. These studies are important not just for an understanding of feldspar chemistry, but potentially for a very effective means of rock correlation, a modeling of differentiation paths, and an assessment of the timing and consequences of phosphate-buffered *versus* unbuffered evolution of peraluminous silicic melts. As an important corollary, we caution others that normative whole-rock calculations, in which  $P_2O_5$  is removed first as apatite, may be erroneous for these rock types. Among other inaccuracies, such removal may lead to overestimation of the modal abundance of apatite and to increase of the ASI values in subsequent numerical modeling. The implications of phosphorus in feldspars are particularly great for modeling REE fractionation in evolved silicic systems.

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#### REFERENCES

- ANDERSON, A.J. (1984): *Geochemistry, Mineralogy and Petrology of the Cross Lake Pegmatite Field, Manitoba*. M.Sc. thesis, Univ. Manitoba, Winnipeg, Manitoba.
- BAADSGAARD, H., CHAPLIN, C. & GRIFFIN, W.L. (1984): Geochronology of the Glosseheia pegmatite, Froland, southern Norway. *Nor. Geol. Tidsskr.* **64**, 111-119.
- BRUSH, G.J. & DANA, E.S. (1878): On a new and remarkable mineral locality in Fairfield County, Connecticut, with a description of several new species occurring there. *Am. J. Sci.* **116**, 33-46, 114-123.
- CAMERON, E.N. and others (1954): Pegmatite investigations, 1942-45, New England. *U.S. Geol. Surv. Prof. Pap.* **255**.
- ČERNÝ, P. (1982): The Tanco pegmatite at Bernic Lake, southeastern Manitoba. In *Granitic Pegmatites in Science and Industry* (P. Černý, ed.). *Mineral. Assoc. Can., Short Course Handbook* **8**, 527-543.
- \_\_\_\_ (1989a): Characteristics of pegmatite deposits of tantalum. In *Lanthanides, Tantalum and Niobium* (P. Möller, P. Černý & F. Saupé, eds.). Springer-Verlag, Berlin (192-236).
- \_\_\_\_ (1989b): Exploration strategy and methods for pegmatite deposits of tantalum. In *Lanthanides, Tantalum and Niobium* (P. Möller, P. Černý & F. Saupé, eds.). Springer-Verlag, Berlin (271-299).
- \_\_\_\_ (1990a): Distribution, affiliation and derivation of rare-element granitic pegmatites in the Canadian Shield. *Geol. Rundschau* **79**, 183-226.
- \_\_\_\_ (1990b): Fertile granites of Precambrian rare-element pegmatite fields: is geochemistry controlled by tectonic setting or source region? *Precamb. Res.* (in press).
- \_\_\_\_ & CHAPMAN, R. (1984): Paragenesis, chemistry

- and structural state of adularia from granitic pegmatites. *Bull. Minéral.* **107**, 369-384.
- \_\_\_\_\_, & MACEK, J. (1974): Petrology of potassium feldspars in two lithium-bearing pegmatites. In *The Feldspars* (W.S. MacKenzie & J. Zussman, eds.). Manchester University Press, Manchester, U.K. (615-628).
- \_\_\_\_\_, & MEINTZER, R.E. (1988): Fertile granites in the Archean and Proterozoic fields of rare-element pegmatites: crustal environment, geochemistry and petrogenetic relationships. In *Recent Advances in the Geology of Granite-related Mineral Deposits* (R.P. Taylor & D.F. Strong, eds.). *Can. Inst. Min. Metall., Spec. Vol.* **39**, 170-207.
- \_\_\_\_\_, SMITH, J.V., MASON, R.A. & DELANEY, J.S. (1984): Geochemistry and petrology of feldspar crystallization in the Vezna pegmatite, Czechoslovakia. *Can. Mineral.* **22**, 631-651.
- \_\_\_\_\_, & TRUEMAN, D.L. (1990): The PLEX pegmatite at Generator Lake, central Baffin Island. *Contrib. Geol. Northwest Terr.* (in press).
- \_\_\_\_\_, ZIEHLKE, D.V., GOAD, B.E. & PAUL, B.J. (1981): The Cat Lake - Winnipeg River and the Wekusko Lake pegmatite fields, Manitoba. *Manitoba Dep. Energy & Mines, Min. Res. Div., Econ. Geol. Rep.* **ER80-1**.
- CHACKOWSKY, L.E. (1987): *Mineralogy, Geochemistry and Petrology of Pegmatitic Granites and Pegmatites at Red Sucker Lake and Gods Lake, North-eastern Manitoba*. M.Sc. thesis, Univ. Manitoba, Winnipeg, Manitoba.
- COLLINS, W.J., BEAMS, S.D., WHITE, A.J.R. & CHAPPELL, B.W. (1982): Nature and origin of A-type granites with particular reference to southeastern Australia. *Contrib. Mineral. Petrol.* **80**, 189-200.
- CORBRIDGE, D.E.C. (1985): *Phosphorus: An Outline of its Chemistry, Biochemistry, and Technology* (3rd ed.). Elsevier, New York.
- CORLETT, M. & RIBBE, P.H. (1967): Electron probe microanalysis of minor elements in plagioclase feldspars. *Schweiz. Mineral. Petrogr. Mitt.* **47**, 317-332.
- EHLMANN, A.J., WALPER, J.L. & WILLIAMS, J. (1964): A new, Barringer-Hill-type, rare-earth pegmatite from the Central Mineral Region, Texas. *Econ. Geol.* **59**, 1348-1360.
- ELLISON, A.J.G. & HESS, P.C. (1988): Peraluminous and peralkaline effects upon "monazite" solubility in high-silica liquids. *Trans. Am. Geophys. Union* **69**, 498 (abstr.).
- ERCIT, T.S., ANDERSON, A.J., ČERNÝ, P. & HAWTHORNE, F.C. (1986): Bobfergusonite: a new primary phosphate mineral from Cross Lake, Manitoba. *Can. Mineral.* **24**, 559-604.
- EWING, R.C. & EHLMANN, A.H. (1973): Yttrialite and uraninite, additional minerals from the Rode Ranch pegmatite, Central Mineral Region, Texas. *Am. Mineral.* **58**, 545-547.
- FOORD, E.E. (1982): Amazonite-bearing pegmatites of the Lake George intrusive center. *Geol. Assoc. Can. - Mineral. Assoc. Can., Field Trip Guidebook* **12**, 51-56.
- FOWLER, A.D. & DOIG, R. (1983): The age and origin of Grenville Province uraniferous granites and pegmatites. *Can. J. Earth Sci.* **20**, 92-104.
- GAN, H. & HESS, P.C. (1989): Phosphorus effects upon the structure of potassium aluminosilicate glasses: inference from Raman and NMR. *Trans. Am. Geophys. Union* **70**, 1375 (abstr.).
- GOAD, B.E. & ČERNÝ, P. (1981): Peraluminous pegmatitic granites and their pegmatite aureoles in the Winnipeg River district, southeastern Manitoba. *Can. Mineral.* **19**, 177-194.
- HARRISON, T.M. & WATSON, E.B. (1984): The behavior of apatite during crustal anatexis: equilibrium and kinetic considerations. *Geochem. Cosmochim. Acta* **48**, 1467-1477.
- HEINRICH, E.W. (1978): Mineralogy and structure of lithium pegmatites. *J. Mineral., Recife* **7**, 59-65.
- JACKSON, N.J., WALSH, J.N. & PEGRAM, E. (1984): Geology, geochemistry and petrogenesis of late Precambrian granitoids in the Central Hijaz Region of the Arabian Shield. *Contrib. Mineral. Petrol.* **87**, 205-219.
- JAHS, R.H. (1979): Gem-bearing pegmatites of San Diego County, California: the Stewart mine, Pala district, and the Himalaya mine, Mesa Grande district. In *Mesozoic Crystalline Rocks: Peninsular Ranges Batholith and Pegmatites*, Point Sal Ophiolite (P.L. Abbott & V.R. Todd, eds.). Manuscripts and road logs prepared for Geological Society of America National Meeting, San Diego, California, 1979. Published by Department of Geological Sciences, San Diego State University, San Diego (1-38).
- \_\_\_\_\_, & EWING, R.C. (1976): The Harding mine, Taos County, New Mexico. In *New Mexico Geol. Soc., 27th Field Conf., Guidebook* (R.C. Ewing & B.S. Kies, eds.), 263-276.
- JEFFERY, P.G. & HUTCHISON, D. (1981): *Chemical Methods of Rock Analysis* (3rd ed.). Pergamon Press, New York.
- JOHNSON, R.F., STARK, R.A. & TAYLOR, J. (1974): Diffusion in liquid slags. *Ironmak. Steelmak.* **1**, 220-227.
- JOLLIFF, B.L., PAPIKE, J.J. & SHEARER, C.K. (1987): Fractionation trends in mica and tourmaline as indi-

- cators of pegmatite internal evolution: Bob Ingersoll pegmatite, Black Hills, South Dakota. *Geochim. Cosmochim. Acta* **51**, 519-534.
- KESLER, T.L. (1961): Exploration of the Kings Mountain pegmatites. *Mining Engineering* **13**, 1063-1068.
- KONTAK, D.J. & STRONG, D.F. (1988): Geochemical studies of alkali feldspars in lithophile element-rich granitic suites from Newfoundland, Nova Scotia and Peru. *Geol. Assoc. Can. - Mineral. Assoc. Can., Abstr. Program* **13**, A68.
- LAHTI, S. (1981): On the granitic pegmatites of the Eräjärvi area in Orivesi, southern Finland. *Geol. Surv. Finland, Bull.* **314**.
- LONDON, D. (1979): *Occurrence and Alteration of Lithium Minerals, White Picacho Pegmatites, Arizona*. M.S. thesis, Arizona State Univ., Tempe, Arizona.
- \_\_\_\_\_. (1982): Stability of spodumene in acidic and saline fluorine-rich environments. *Carnegie Inst. Wash., Ann. Rep.* **81**, 331-334.
- \_\_\_\_\_. (1984): Experimental phase equilibria in the system  $\text{LiAlSi}_4\text{O}_{10}$ - $\text{SiO}_2$ - $\text{H}_2\text{O}$ : a petrogenetic grid for lithium-rich pegmatites. *Am. Mineral.* **69**, 995-1004.
- \_\_\_\_\_. (1985): Pegmatites of the Middletown District, Connecticut. In *Guidebook for Fieldtrips in Connecticut and Adjacent Areas of New York and Rhode Island* (R.J. Tracy, ed.). *State Geol. & Natural History Survey of Connecticut, Guidebook* **6**, 509-533.
- \_\_\_\_\_. (1987): Internal differentiation of rare-element pegmatites: effects of boron, phosphorus, and fluorine. *Geochim. Cosmochim. Acta* **51**, 403-420.
- \_\_\_\_\_. (1990a): Internal differentiation of rare-element pegmatites: a synthesis of recent research. In *Ore-Bearing Granite Systems; Petrogenesis and Mineralizing Processes* (H.J. Stein & J.L. Hannah, eds.). *Geol. Soc. Am., Spec. Pap.* **246**, in press.
- \_\_\_\_\_. (1990b): The berlinite substitution,  $\text{AlP} = 2 \text{ Si}$ , in alkali feldspars from differentiated peraluminous igneous rocks (granites, pegmatites, and rhyolites). *Geol. Soc. Am., Program Abstr.* **22**, (in press).
- \_\_\_\_\_. & BURT, D.M. (1982a): Alteration of spodumene, montebrasite and lithiophilite in pegmatites of the White Picacho District, Arizona. *Am. Mineral.* **67**, 97-113.
- \_\_\_\_\_. & \_\_\_\_\_. (1982b): Chemical models for lithium aluminosilicate stabilities in pegmatites and granites. *Am. Mineral.* **67**, 494-509.
- \_\_\_\_\_. HERVIG, R.L. & MORGAN, G.B., VI (1988): Melt-vapor solubilities and elemental partitioning in peraluminous granite - pegmatite systems: experimental results with Macusani glass at 200 MPa. *Contrib. Mineral. Petrol.* **99**, 360-373.
- \_\_\_\_\_. LOOMIS, J.T., HUANG, W., & MORGAN, G.B., VI (1990): Behavior and effects of phosphorus in the system  $\text{Ab-Or-Qz-H}_2\text{O}$  at 200 MPa( $\text{H}_2\text{O}$ ). *Geol. Soc. Am., Program Abstr.* **22**, in press..
- \_\_\_\_\_. MORGAN, G.B., VI & HERVIG, R.L. (1989): Vapor-undersaturated experiments with Macusani glass +  $\text{H}_2\text{O}$  at 200 MPa, and the internal differentiation of granitic pegmatites. *Contrib. Mineral. Petrol.* **102**, 1-17.
- MASON, R.A. (1982): Trace element distributions between the perthite phases of alkali feldspars from pegmatites. *Mineral. Mag.* **45**, 101-106.
- \_\_\_\_\_. SMITH, J.V., DAWSON, J.B. & TREVES, S.B. (1982): A reconnaissance of trace elements in anorthoclase megacrysts. *Mineral. Mag.* **46**, 7-11.
- MEINTZER, R.E. (1987): *The Mineralogy and Geochemistry of the Granitoid Rocks and Related Pegmatites of the Yellowknife Pegmatite Field, Northwest Territories*. Ph.D. thesis, Univ. Manitoba, Winnipeg, Manitoba.
- MYSEN, B.O., RYERSON, F.J. & VIRGO, D. (1981): The structural role of phosphorus in silicate melts. *Am. Mineral.* **66**, 106-117.
- NEUVONEN, K.J. & VESASALO, A. (1960): Pollucite from Luolamäki, Somero, Finland. *Comm. Géol. Finlande Bull.* **188**, 133-148.
- NORDENSKJÖLD, J. (1908): Der Pegmatit von Ytterby. *Geol. Inst. Uppsala Bull.* **9**, 183-228.
- NORTON, J.J. and others (1964): Geology and mineral deposits of some pegmatites in the southern Black Hills, South Dakota. *U.S. Geol. Surv., Prof. Pap.* **297-E**.
- PAN, J.J. (1988): *The Geochemistry and Mode of Occurrence of Phosphorus in Pegmatite Feldspars*. B.Sc. thesis, Univ. Manitoba, Winnipeg, Manitoba.
- \_\_\_\_\_. & ČERNÝ, P. (1989): Phosphorus in feldspars of rare-element granitic pegmatites. *Geol. Assoc. Can. - Mineral. Assoc. Can., Abstr. Program* **14**, A82.
- PAUL, B.J. (1984): *Mineralogy and Geochemistry of the Huron Claim Pegmatite, Southeastern Manitoba*. M.Sc. thesis, Univ. Manitoba, Winnipeg, Manitoba.
- PEHRMAN, G. (1945): Die Granitpegmatite von Kimito (S.W. Finland) und ihre Minerale. *Acta Acad. Aboen., Mat. Phys.* **15**.
- POUCHOU, J.L. & PICHOR, F. (1985): "PAP" ( $\phi - \rho - Z$ ) procedure for improved quantitative microanalysis. In *Microbeam Analysis* (J.T. Armstrong, ed.). San Francisco Press, San Francisco (104-106).

- QUENSEL, P. (1956): The paragenesis of the Varuträsk pegmatite. *Ark. Mineral. Geol.* **2**, 9-125.
- RAPP, R.P. & WATSON, E.B. (1986): Monazite solubility and dissolution kinetics: implications for the thorium and light rare earth chemistry of felsic magmas. *Contrib. Mineral. Petrol.* **94**, 304-316.
- RIJKS, H.R.P. & VAN DER VEEN, A.H. (1972): The geology of the tin-bearing pegmatites in the eastern part of the Kamativi district, Rhodesia. *Miner. Deposita* **7**, 383-395.
- ROBERTS, W.C., CAMPBELL, T.C., MACLEOD, R.J. & FRENCH, G.McN. (1982): The pegmatite field of the southern Black Hills. Description of pegmatites. *Geol. Assoc. Can. - Mineral. Assoc. Can., Field Trip Guidebook* **12**, 8-23.
- RYERSON, F.J. & HESS, P.C. (1980): The role of  $P_2O_5$  in silicate melts. *Geochim. Cosmochim. Acta* **44**, 611-624.
- SAWKA, W.N. (1989): Highly fractionated S-type granites from western Tasmania, chemical differences with highly fractionated A-type granites. *Trans. Am. Geophys. Union* **70**, 491 (abstr.).
- SHEARER, C.K., PAPIKE, J.J. & LAUL, J.C. (1985): Chemistry of potassium feldspars from three zoned pegmatites, Black Hills, South Dakota: implications concerning pegmatite evolution. *Geochim. Cosmochim. Acta* **49**, 663-673.
- SHERIDAN, D.M., STEPHENS, H.G., STAATZ, M.H. & NORTON, J.J. (1957): Geology and beryl deposits of the Peerless pegmatite, Pennington County, South Dakota. *U.S. Geol. Surv., Prof. Pap.* **297-A**.
- SIMMONS, W. B. & HEINRICH, E.W. (1980): Rare-earth pegmatites of the South Platte District, Colorado. *Colo. Geol. Surv. Res. Ser.* **11**.
- , LEE, M.T. & BREWSTER, R.H. (1987): Geochemistry and evolution of the South Platte granite-pegmatite system, Jefferson County, Colorado. *Geochim. Cosmochim. Acta* **51**, 455-471.
- SIMPSON, D.R. (1977): Aluminum phosphate variants of feldspars. *Am. Mineral.* **62**, 351-355.
- SMEDS, S.A. & ČERNÝ, P. (1989): Pollucite from the Proterozoic petalite-bearing pegmatites of Utö, Stockholm Archipelago, Sweden. *Geol. Fören. Stockholm Förh.* **111**, 361-372.
- SMITH, J.V. (1974): *Feldspar Minerals. 2. Chemical and Textural Properties*. Springer Verlag, New York.
- (1983): Some chemical properties of feldspars. In *Feldspar Mineralogy* (2nd edition, P.H. Ribbe, ed.). *Rev. Mineral.* **2**, 281-296.
- SOLODOV, N.A. (1971): *Scientific Principles of Perspective Evaluation of Rare-Element Pegmatites*. Nauka, Moscow (in Russ.).
- STAATZ, M.H., PAGE, L.R., NORTON, J.J. & WILMARTH, V.R. (1963): Exploration for beryllium at the Helen Beryl, Elkhorn and Tin Mountain pegmatites, Custer County, South Dakota. *U.S. Geol. Surv., Prof. Pap.* **297-C**.
- STANEK, J. (1954): Petrography and mineralogy of the pegmatite veins at Dolní Bory, Czechoslovakia. *Acta Acad. Sci. Cechosl. Basis Brunensis* **26**, 1-43.
- STERN, L.A., BROWN, G.E., JR., BIRD, D.K., JAHNS, R.H., FOORD, E.E., SHIGLEY, J.E. & SPAULDING, L.B., JR. (1986): Mineralogy and geochemical evolution of the Little Three pegmatite-aplite layered intrusive, Ramona, California. *Am. Mineral.* **71**, 406-427.
- STEWART, D.B. (1978): Petrogenesis of lithium-rich pegmatites. *Am. Mineral.* **63**, 970-980.
- STRUNZ, H., FORSTER, H. & TENNYSON, C. (1975): Die Pegmatite in der nördlichen Oberpfalz. A. Geologie und Genese. B. Mineralführung. *Der Aufschluss* **26**, 117-189.
- VESASALO, A. (1959): On the petalite occurrences of Tammela, southwest Finland. *Comm. Géol. Finlande Bull.* **184**, 59-74.
- WALKER, R.J., HANSON, G.N., PAPIKE, J.J., O'NEIL, J.R. & LAUL, J.C. (1986): Internal evolution of the Tin Mountain pegmatite, Black Hills, South Dakota. *Am. Mineral.* **71**, 440-459.
- WATSON, E.B. & CAPOBIANCO, C.J. (1981): Phosphorus and the rare earth elements in felsic magmas: an assessment of the role of apatite. *Geochim. Cosmochim. Acta* **45**, 2349-2358.
- WHALEN, J.B. (1985): Geochemistry of an island-arc plutonic suite: the Uasilau - Yau Yau intrusive complex, New Britain, P.N.G. *J. Petrol.* **26**, 603-632.
- , CURRIE, K.L. & CHAPPELL, B.W. (1987): A-type granites: geochemical characteristics, discrimination and petrogenesis. *Contrib. Mineral. Petrol.* **95**, 407-419.
- WISE, M.A. (1987): *Geochemistry and Crystal Chemistry of Nb, Ta and Sn Minerals from the Yellowknife Pegmatite Field, N.W.T.* Ph.D. thesis, Univ. Manitoba, Winnipeg, Manitoba.

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## APPENDIX 1. SAMPLE LOCALITIES

**SADOLINITE SUBTYPE:**

Shatford Lake, Manitoba	(SHL)	Černý et al. (1981)
Huron Claim, Manitoba	(HC)	Paul (1984), Černý et al. (1981)
Rode Ranch, Texas	(RR)	Ehmann et al. (1964), Ewing & Ehmann (1973)
Ytterby, Sweden	(YTT)	Nordenskiöld (1908)
Lövböle, Finland	(LOV)	Pehrman (1945)
Crystal Peak, Colorado	(CP)	Ford (1982)

**BERYL-COLUMBITES SUBTYPE:**

Greer Lake, Manitoba	(GL)	Černý et al. (1981)
Bill, Yellowknife, NWT	(YKF-BL)	Meintzer (1987), Wise (1987)
Plex, Baffin Island, NWT	(PX)	Černý & Trueman (1990)
Vezna, Czechoslovakia	(VEZ)	Černý et al. (1984)
White Rocks, Connecticut	(WRX)	London (1985)
Case, Connecticut	(CAS)	Cameron et al. (1954)
Hale, Connecticut	(HAL)	London (1985)
Gotta-Apple Orchard, Conn.	(GAO)	London (1985)

**BERYL-COLUMBITES-PHOSPHATE SUBTYPE:**

Cross Lake #22, Manitoba	(CL)	Anderson (1984), Ercit et al. (1986)
Dan Patch, S. Dakota	(DP)	Norton et al. (1964)
Bull Moose, S. Dakota	(BM)	Shearer et al. (1985)
Big Chief, S. Dakota	(BCH)	Morton et al. (1964)
Hagendorf-Süd, Bavaria	(HAG)	Strunz et al. (1975)
Dolní Bory, Czechoslovakia	(DB)	Stánek (1954)
Peg, Yellowknife, NWT	(YKF-PEG)	Meintzer (1987), Wise (1987)
Palermo, New Hampshire	(PMO)	Cameron et al. (1954)

**COMPLEX - SPODUMENE SUBTYPE:**

Bet, Yellowknife, NWT	(YKF-BET)	Meintzer (1987), Wise (1987)
Heien Beryl, S. Dakota	(HB)	Roberts et al. (1982), Staats et al. (1963)
Tin Mountain, S. Dakota	(TM)	Walker et al. (1986)
Etta, S. Dakota	(ETT)	Norton et al. (1964)
Tip Top, S. Dakota	(TT)	Shearer et al. (1985)
Harding, N. Mexico	(HD)	Jahns & Ewing (1976)
Kamatiwi, Zimbabwe	(KAM)	Rijks & v.d. Voort (1972)
Bennet, Maine	(BNT)	Cameron et al. (1954)
Gotta-Walden, Connecticut	(GW)	Cameron et al. (1954)
Strickland, Connecticut	(STK)	Cameron et al. (1954)
Branchville, Connecticut	(BVL)	Brush & Dana (1878)
Black Mountain, Maine	(BN)	Cameron et al. (1954)
Homestead, Arizona	(HOM)	London (1978)
Midnight Owl, Arizona	(MNO)	London & Burt (1982a)
White Ridge, Arizona	(WHR)	Jahns (1979)
		London & Burt (1982a)
		London (1979)
		London & Burt (1982a)

**COMPLEX - PETALITE SUBTYPE:**

Tanco, Manitoba	(TC)	Černý (1982)
Hirvikallio, Finland	(HVK)	Vesasalo (1958)
Luolamäki, Finland	(LUO)	Neuvonen & Vesasalo (1960)
Varuträsk, Sweden	(VAR)	Quensel (1956)
Utö, Sweden	(UT)	Smeds & Černý (1989)

**COMPLEX - LEPIDOLITE SUBTYPE:**

High Grade Dike, Manitoba	(HGD)	Černý et al. (1981)
Riber, Yellowknife, NWT	(YKF-RIB)	Meintzer (1987), Wise (1987)
Bob Ingersoll, S. Dakota	(BI)	Jolliff et al. (1987)
Radkovice, Czechoslovakia	(R)	Černý & Macek (1974)
Biskupice, Czechoslovakia	(BSTC)	Černý & Macek (1974)
Swanson, Connecticut	(SWN)	Cameron et al. (1954)
		London (1985)
Himalaya/San Diego, CA	(HIM-SDG)	Jahns (1979)
Little Three, California	(LT3)	Stern et al. (1986)
Stewart, California	(STW)	Jahns (1979)

**COMPLEX - AMBLYGONITE SUBTYPE:**

Peerless, S. Dakota	(PRL)	Sheridan et al. (1957)
Viitaniemi, Finland	(VIT)	Lahti (1981)

**ALBITE - SPODUMENE TYPE:**

Violet, Manitoba	(VT)	Černý et al. (1981)
Nite, Yellowknife, NWT	(YKF-NT)	Meintzer (1987), Wise (1987)
Kings Mountain, NC	(KGM)	Kesler (1961)

**ALBITE TYPE:**

Yin Dyke, Manitoba	(TD)	Chackowsky (1987)
Odd, Manitoba	(OD)	Černý et al. (1981)
Hengshan, China	(HN)	Černý (1989a)