

## Alteration of spodumene, montebrasite and lithiophilite in pegmatites of the White Picacho District, Arizona

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### Abstract

The crystallization sequence and metasomatic alteration of spodumene ( $\text{LiAlSi}_2\text{O}_6$ ), montebrasite ( $\text{LiAlPO}_4(\text{OH},\text{F})$ ), and lithiophilite ( $\text{Li}(\text{Mn},\text{Fe})\text{PO}_4$ ) are described for nine zoned lithium pegmatites in the White Picacho district, Arizona. The observed crystallization trends suggest a progressive increase in the activities of lithium species (spodumene follows microcline as the principal alkali aluminosilicate), as well as an increase in the activities of the acidic volatiles phosphorus and fluorine (montebrasite succeeds spodumene as the stable primary lithium phase). Much of the lithiophilite occurs with columbite, apatite, beryl, zircon, and tourmaline in cleavelandite complexes that formed in part at the expense of quartz-spodumene pegmatite. Fracture-controlled pseudomorphic alteration of the primary lithium minerals is widespread and apparently is the result of subsolidus reactions with residual pegmatitic fluids. Spodumene has been replaced by eucryptite, albite, and micas. Alteration products of montebrasite include low-fluorine secondary montebrasite, crandallite (tentative), hydroxylapatite, muscovite, brazilianite, augelite (tentative), scorzalite, kulanite, wyllieite, and carbonate-apatite. Secondary phases identified in altered lithiophilite include hureaulite, triploidite, eosphorite, robertsite, fillowite, wyllieite, dickinsonite, fairfieldite, Mn-chlorapatite, and rhodochrosite. Initial subsolidus metasomatism of the lithium minerals took place in an alkaline environment, as evidenced by albitization of spodumene and calcium metasomatism of the phosphates. The formation of secondary micas in spodumene, montebrasite, tourmaline, and much feldspar reflects a change from alkaline to relatively acidic postmagmatic fluids, as (K+H)-metasomatism produced greisen-like or sericitic alteration. The abundance of minerals containing Li, Be, Mn, Nb, Ta, and Bi indicate that these pegmatites originated from a highly differentiated granitic source. These pegmatites were not fluorine-rich, as evidenced by the low fluorine contents of primary and secondary montebrasite, by the formation of OH- and Cl-apatites, and by the absence of topaz and the rarity of lepidolite, triplite, and fluorite.

### Introduction

The White Picacho pegmatite district lies near the southeast end of the Arizona pegmatite belt (Jahns, 1952; see Fig. 1). The district, which is located mostly on the Red Picacho 7.5' topographic quadrangle map (U.S. Geological Survey, 1964), contains several hundred pegmatites. These pegmatites intrude low- to medium-grade Precambrian schists, gneisses, and amphibolites that Jahns (1952) tentatively correlated with the Yavapai Series in the Jerome and Prescott areas (Jagger and Palache, 1905; Anderson *et al.*, 1971). The pegmatites are

also Precambrian (Laughlin, 1969), although a precise age has not been established.

Only nine lithium pegmatites have been identified in the district. Most of these were mapped and described by R. H. Jahns (1952), and his work provided a foundation for subsequent studies by us (Burt, London, and Smith, 1977; London, Bandy, and Kealy, 1978; London and Burt, 1978; London, 1979). At present, most of Jahns' maps are still usable, inasmuch as only minor mining and development have been carried out in the district over the past thirty years. Additional maps of the region and of the pegmatites are available in London and Burt (1978) and in London (1979).

In the White Picacho pegmatites, as at many

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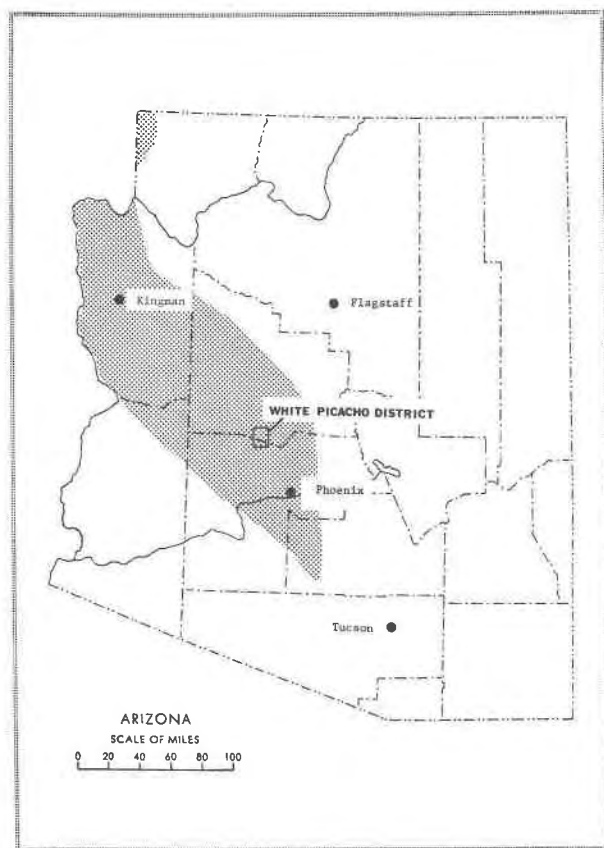


Fig. 1. Map showing the location of the White Picacho district in the Arizona pegmatite belt (stippled area) as defined by Jahns (1952).

other localities, the lithium minerals have been metasomatically altered to a large number of rare and mineralogically complex phases (Table 1). This cleavage-controlled pseudomorphic replacement of the primary lithium minerals is pervasive at most of the pegmatites and apparently is the result of sub-solidus reactions with residual aqueous pegmatitic fluids. The sporadic distribution of alteration within individual pegmatites and even within single undeformed crystals suggests that the replacement was not produced by regional metamorphism or by local hydrothermal alteration related to brittle deformation.

This mainly descriptive paper focuses on the mineralogy of replacement assemblages observed in primary spodumene, montebrasite, and lithiophilite from the White Picacho pegmatites. Although metasomatic replacement features such as those that occur in the White Picacho pegmatites have received considerable attention from mineralogists (e.g., Brush and Dana, 1878, 1879a, 1879b, 1880;

Moore, 1971, 1972; 1973, 1974), the significance of these replacements as indicators of pegmatite chemistry and evolution remains poorly understood. In the White Picacho lithium pegmatites, the paragenetic sequence of these secondary minerals can be determined for each of the parent lithium minerals. Each paragenesis is interpreted as indicating systematic changes in the geochemistry of the postmagmatic fluids. The central purpose of this paper is to characterize these pseudomorphic replacements and to evaluate their geochemical significance. Seventy-eight representative electron microprobe analyses and refined X-ray powder diffraction data for most of these phases are listed in Appendices 1 and 2, respectively.<sup>1</sup> Some theoretical

<sup>1</sup>To receive copies of these Appendices, order Document AM-82-187 (analyses, Appendix 1) and AM-82-188 (X-ray data, Appendix 2) from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit \$1.00 in advance for each microfiche.

Table 1. Alteration products of spodumene, montebrasite, and lithiophilite in pegmatites of the White Picacho district.

Mineral	Idealized formula*
<u>spodumene</u>	$\text{LiAlSi}_2\text{O}_6$
albite	$\text{NaAlSi}_3\text{O}_8$
eucryptite	$\text{LiAlSiO}_4$
lepidolite	$\text{K}(\text{Li}, \text{Al})_3(\text{Si}, \text{Al})_4\text{O}_{10}(\text{F}, \text{OH})_2$
muscovite	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$
<u>montebrasite</u>	$\text{LiAlPO}_4(\text{OH}, \text{F})$
low-F montebrasite	$\text{LiAlPO}_4(\text{OH}, \text{F})$
crandallite	$\text{CaAl}_3(\text{PO}_4)_2(\text{PO}_3\text{OH})(\text{OH})_6$
hydroxylapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F})$
muscovite	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$
brazilianite	$\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_4$
augelite	$\text{Al}_2(\text{PO}_4)(\text{OH})_3$
scorzalite	$(\text{Fe}^{2+}, \text{Mg})\text{Al}_2(\text{PO}_4)_2(\text{OH})_2$
kulanite	$\text{Ba}(\text{Fe}^{2+}, \text{Mn}, \text{Mg})_2\text{Al}_2(\text{PO}_4)_3(\text{OH})_3$
wyllieite	$(\text{Na}, \text{Ca}, \text{Mn})(\text{Mn}, \text{Fe}^{2+})(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg})\text{Al}(\text{PO}_4)_3$
carbonate-apatite	$\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3(\text{OH}, \text{F})$
<u>lithiophilite</u>	$\text{Li}(\text{Mn}, \text{Fe})\text{PO}_4$
hureaulite	$\text{Mn}_5(\text{PO}_4)_2(\text{PO}_3\text{OH})_2 \cdot 4\text{H}_2\text{O}$
triploidite	$\text{Mn}_2\text{PO}_4(\text{OH})$
eosphorite	$\text{MnAlPO}_4(\text{OH})_2 \cdot \text{H}_2\text{O}$
robertssite	$\text{Ca}_2\text{Mn}_4^{3+}(\text{PO}_4)_4(\text{OH})_6 \cdot 3\text{H}_2\text{O}$
fillowite	$\text{Na}_2\text{Ca}(\text{Mn}, \text{Fe})_7(\text{PO}_4)_6$
dickinsonite	$\text{KNa}_2\text{Ca}(\text{Mn}, \text{Fe})_{14}\text{Al}(\text{OH})_2(\text{PO}_4)_{12}$
wyllieite	$(\text{Na}, \text{Ca}, \text{Mn})(\text{Mn}, \text{Fe}^{2+})(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg})\text{Al}(\text{PO}_4)_3$
fairfieldite	$\text{Ca}_2(\text{Mn}, \text{Fe}^{2+})(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$
Mn-chlorapatite	$(\text{Ca}, \text{Mn})_5(\text{PO}_4)_3(\text{Cl}, \text{OH}, \text{F})$
rhodochrosite	$\text{MnCO}_3$
sicklerite	$\text{Li}(\text{Mn}^{2+}, \text{Fe}^{3+})\text{PO}_4$

models developed in two other papers (London and Burt, 1981a, 1981b) are based in part on observations from the White Picacho pegmatites.

### Geology of the lithium pegmatites

Of the nine known lithium pegmatites in the district, the Homestead, Independence, Midnight Owl, North Morning Star, and White Ridge were chosen for detailed study, as these five pegmatites appear to encompass all variations in general geology and in the occurrence and alteration of primary lithium minerals (see Jahns, 1952, and London, 1979, for index maps and detailed geologic maps and descriptions of the pegmatites). The lithium pegmatites display highly irregular outcrop patterns and usually occur as clusters of small steeply dipping pods or lenses rather than single, isolated bodies. Spodumene ( $\text{LiAlSi}_2\text{O}_6$ ), montebrasite ( $\text{LiAlPO}_4(\text{OH},\text{F})$ ), and lithiophilite ( $\text{Li}(\text{Mn},\text{Fe})\text{PO}_4$ ) are the primary lithium minerals in these pegmatites. Micas generally are not abundant, and true lepidolites occur only as replacements of primary lithium minerals. Green lithium tourmaline (verdelite) occurs at one locality but does not figure prominently in the paragenesis of the lithium minerals.

All of the lithium pegmatites are sharply zoned by grain size and by composition. With few exceptions, the lithium minerals are concentrated in the inner zones and cores of essentially granitic pegmatite. The distribution of zones within each pegmatite is somewhat irregular (nonconcentric), but a general zonation sequence can be established (Fig. 2). Based on the assumption that crystallization proceeded sequentially from borders to core, spodumene was the first lithium mineral to crystallize. Quartz-spodumene pegmatite appears to grade inward into quartz-montebrasite pegmatite, suggesting that montebrasite succeeded spodumene as the stable primary lithium phase. Lithiophilite typically

Table 2. Occurrences of spodumene, montebrasite, and lithiophilite at individual pegmatites in the White Picacho district.\*

Abundances denoted by:			
	X = abundant		
	O = common		
	R = rare		
	A = not reported		
			or observed
Pegmatites	Spodumene	Montebrasite	Lithiophilite
Homestead	O	R	X
Independence	X	O	O
Lone Giant	X	O	R
Lower Jumbo	X	A	A
Midnight Owl	X	X	O
Morning Star	O	A	R
North Morning Star	X	X	A
Picacho View	O	O	A
White Ridge	X	O	R

\*See Jahns (1952) and London (1979) for index maps and geologic maps and descriptions of individual pegmatites.

occurs in the quartz cores and apparently was the last primary lithium mineral to crystallize. Lithiophilite also occurs with columbite, manganian tourmaline, zircon, and manganian apatite in masses of relatively coarse-grained albite (cleavelandite) or cleavelandite + mica. Although lithiophilite nodules are abundant in these complexes at the White Ridge, Homestead, and Midnight Owl pegmatites, the primary phosphate is usually highly altered.

In the White Picacho pegmatites, cleavelandite or cleavelandite + mica complexes usually are located at the margins of quartz-spodumene pegmatite zones; however, they crosscut all other zones at the North Morning Star and Homestead pegmatites, and they are the only units that do so. At the Independence pegmatite, a cleavelandite-lepidolite complex contains rounded relicts of spodumene in a textural relationship similar to that of the "spotted rock" zone at the Harding pegmatite, New Mexico (Jahns and Ewing, 1976). At the Independence, the interior portions of the rounded spodumene relicts have been replaced by fine-grained eucryptite + albite, whereas the rims of these crystal fragments, and medium-grained (5 cm along the *c* axis) secondary spodumene crystals in the complex, have been replaced by mica + albite. These features are sufficient to indicate that the cleavelandite units crystallized late in the history of these pegmatites, and that they formed at least in part at the expense of pre-existing quartz-spodumene pegmatite.

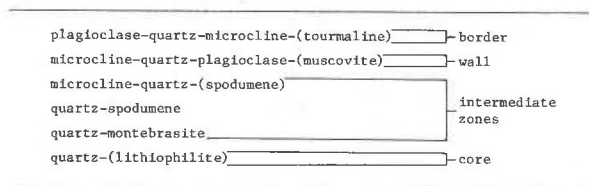


Fig. 2. General sequence of primary crystallization for the White Picacho lithium pegmatites.

### Occurrences of primary spodumene, montebrasite, and lithiophilite

Spodumene is the only primary lithium aluminosilicate present in the district, and it occurs at all of the known lithium pegmatites (Table 2). It usually forms subhedral, prismatic crystals up to two meters in maximum dimension; however, unaltered spodumene is relatively rare.

Montebrasite occurs at most of the pegmatites as blocky, subhedral crystals or rounded nodules up to a meter in dimension. The fluorine content of White Picacho montebrasite was determined using the X-ray technique of Černá *et al.* (1973). Representative samples were analyzed by electron microprobe for Na, K, and Ca, to ensure that no substitutions other than those involving F and OH affected the position of the 20(131) reflection (Černá *et al.*, 1973); in all cases, the contents of Na, K, and Ca in White Picacho montebrasites were at or below the detection limits for these elements (less than 0.10 wt.% as oxides). Table 3 indicates that most primary material examined in this study contains from about 4.5–6.5 wt.% F, corresponding to 30–50 mole % of the amblygonite component. Similar findings for blocky white crystals are reported from the Varutråsk pegmatite, Sweden (Quensel, 1937) and from the Tanco pegmatite, Manitoba, Canada (Černá *et al.*, 1972).

Lithiophilite occurs at several pegmatites as nodules or crude prismatic crystals up to twenty centimeters in dimension. Microprobe analyses of representative samples (Appendix 1) indicate that except for material from the White Ridge pegmatite, most White Picacho lithiophilite is very near the  $\text{LiMnPO}_4$  end member of the lithiophilite–triphylite series. Such iron-free lithiophilite is not common (*cf.* analyses of Palache *et al.*, 1951, p. 666), but comparable material has been described from a few localities (*e.g.*, Thomssen and Anthony, 1977).

### Determination of secondary mineral parageneses

The metasomatic alteration of spodumene, montebrasite, and lithiophilite occurred along cleavages, fractures, and crystal borders of the host primary phases. Veinlets are composed of one or more fine-grained replacement minerals. In some cases, individual veinlets contain two or more discrete assemblages that are bilaterally symmetrical about the center of the veinlet. Individual mineral grains average 25 microns in dimension, and several assemblages, each containing two or three miner-

Table 3. Fluorine contents of montebrasite from the White Picacho pegmatites.

Primary montebrasite		
Sample	20(131)*	Wt% F
MNO 4XX	52.64	6.8
WHR 408a	52.62	6.6
IND 400	52.61	6.5
WHR 406	52.60	6.4
WHR 404	52.56	5.9
WHR 400	52.55	5.8
MNO 400	52.55	5.8
MNO 419	52.55	5.8
WHR 408b	52.51	5.2
HOM 401	52.49	4.9
HOM 400	52.46	4.5
MNO 425	52.43	4.3
Secondary montebrasite		
Sample	20(131)*	Wt% F
WHR 408a	52.41	3.9
WHR 406	52.36	3.3
NMS 400	52.35	3.2
MNO 407	52.35	3.2
HOM 400a	52.32	2.7
MNO 419	52.31	2.6
NMS 401	52.28	2.2
MNO 4XX	52.27	2.1
WHR 408b	52.26	2.0
HOM 400b	52.22	1.4
MNO 400	52.21	1.3
MNO 425	52.11	0.1

\*X-ray data collected on a Philips goniometer, unfiltered  $\text{CuK}\alpha$  radiation, graphite monochromator, at 40 kV, 20mA; scan rate:  $\frac{1}{2}^\circ$  20/min; quartz internal standard.

als, commonly are themselves intimately intergrown. A combination of petrographic, X-ray diffraction, and electron microprobe analyses was required to identify the secondary assemblages. A few secondary phases still are not fully characterized because of a lack of suitable material for study. Nevertheless, most of the secondary minerals have been positively identified, and the crosscutting relationships observed among veinlets indicate the sequence of replacement.

### Alteration of spodumene

The metasomatic alteration of spodumene in these pegmatites has been discussed in several other publications (Burt *et al.*, 1977; London and Burt, 1979, 1980, 1981b), so only a brief description is presented here. At the Independence and Midnight Owl pegmatites, much spodumene in contact

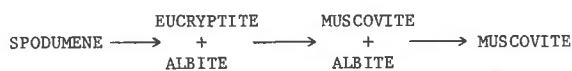


Fig. 3. General alteration sequence for spodumene.

with primary quartz displays a thin reaction rim of fine-grained albite, whereas the interiors of the spodumene crystals are replaced to varying degrees by a very fine-grained, fibrous intergrowth of eucryptite + albite (Fig. 3). This initial replacement produced bilaterally symmetrical veinlets of eucryptite + albite whose long fiber axes are oriented perpendicular to the {110} cleavage of the host spodumene (Fig. 4). In some samples, eucryptite near veinlet centers and spodumene crystal borders has been subsequently altered to muscovite or lepidolite, resulting in the intergrowth of albite + mica called "cymatolite" by Brush and Dana (1880). Finally, remnant spodumene and secondary albite have been converted to lithian muscovite or lepidolite, producing soft, waxy pseudomorphs of nearly pure mica after spodumene (referred to as "killinite" by Julien, 1879). At all of the pegmatites, spodumene also appears to have been converted directly to albite + mica or to pure mica, but the alteration sequence described above and illustrated in Figure 3 represents the most complete history of metasomatic alteration of spodumene at these pegmatites.

#### Alteration of montebrasite

At all of the pegmatites, montebrasite has been replaced by a number of secondary phases (Table 1) in the general sequence illustrated in Figure 5. Incipient alteration of primary montebrasite in-

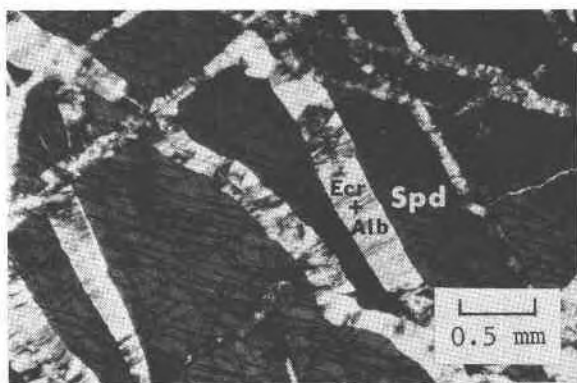


Fig. 4. Photomicrograph showing the cleavage-controlled alteration of spodumene (Spd) to a fibrous intergrowth of eucryptite (Ecr) + albite (Alb). The specimen is from the Midnight Owl pegmatite. Crossed polars.

involved hydroxyl exchange for fluorine, producing low-fluorine, secondary montebrasite along fractures and cleavages in the host primary phase (Fig. 6). Based on values of  $2\theta(131)$ , the secondary montebrasite contains about 1.5–3.5 wt.% F (Table 3). As at the Tanco pegmatite, Manitoba (Černá *et al.*, 1972), replacement by secondary low-fluorine montebrasite is extensive in fresh-appearing material, but the primary and secondary phases are virtually impossible to distinguish in hand specimen. Subsequent alteration of primary and secondary montebrasite produced fine-grained hydroxylapatite, muscovite, and minor amounts of a calcium aluminum phosphate that appears to be crandallite (Fig. 7). Positive identification of crandallite is hampered by the fact that the phase usually is disseminated in and subordinate to apatite and montebrasite; thus it cannot be clearly distinguished in X-ray powder patterns. In addition, its fine grain size requires the use of a narrow (2 micron) beam diameter for microprobe analyses; this results in rapid volatilization and sample destruction. Although these three secondary minerals occur in grain contact with montebrasite, the crandallite invariably occurs at montebrasite borders and probably was the first mineral to crystallize. In a typical specimen (Fig. 8), a thin reaction rim of crandallite at montebrasite borders grades outward into veinlets of grayish-white hydroxylapatite, followed by an intergrowth of apatite + muscovite, and finally fine-grained green muscovite at the centers of replacement veinlets and near the crystal boundaries of the primary phase.

Various combinations of scorzalite, brazilianite, augelite (tentative), wyllieite, and kulanite (Table 3) occur as scattered crystals in the apatite + muscovite replacement intergrowth and also form veinlets that clearly cut the apatite + muscovite assemblage. Thus these rare phosphates formed late in the alteration history of montebrasite (Fig. 5). Based on available samples, augelite, wyllieite, and kulanite are very rare in montebrasite from all of the White Picacho pegmatites, but scorzalite and brazilianite are fairly common. Scorzalite occurs as anhedral disseminated grains that give specimens a light blue tint. Brazilianite forms relatively large (2 mm–1 cm) subhedral yellowish green crystals in specimens from several pegmatites. A few colorless grains of an aluminum phosphate that appears to be augelite have been found in two specimens; this phase is associated with scorzalite, muscovite, and apatite, but positive identification of this aluminum phos-

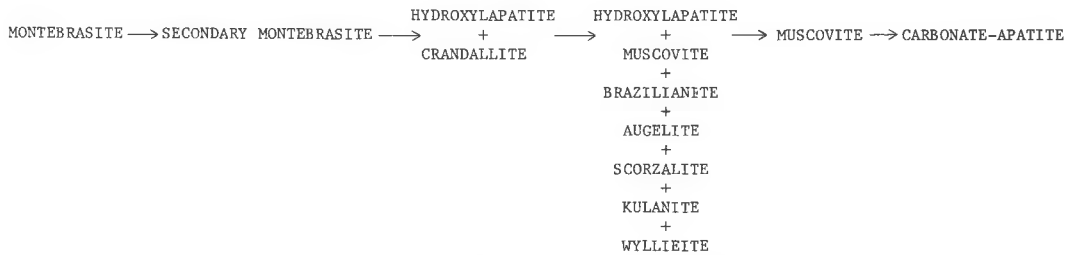


Fig. 5. General alteration sequence for montebrasite.

phate awaits a find of more material. Kulanite also has been found in two specimens as forest green subhedral crystals in association with apatite, muscovite, quartz, and brazilianite. Its composition (analyses 56-58, Appendix 1) is similar to that of the type material (Mandarino and Sturman, 1976), and this represents the second reported occurrence of kulanite. Wyllieite was identified in thin section and by microprobe analyses (analyses 69-72, Appendix 1) as a few grains that occur with scorzalite and brazilianite in one montebrasite specimen. The latest-forming phase in the montebrasite alteration sequence is fine-grained carbonate-apatite that forms banded, colloform rinds that surround montebrasite nodules and veinlets that crosscut all other replacement assemblages (Fig. 9).

#### Alteration of lithiophilite

Lithiophilite displays two different replacement sequences, depending on whether the lithiophilite is embedded in quartz or in albite (Fig. 10 and Table 3). The least-altered crystals occur in quartz (Fig. 11). In this association, the initial replacement involved hydration and removal of lithium to form

intergrowths of hureaulite and triploidite (Fig. 10, Scheme A, and Fig. 12). Along more extensively altered veinlets, hureaulite becomes more birefringent in thin section; this change in optical properties appears to correlate with small but increasing amounts of calcium (analysis 12, Appendix 1). Frequently, calcium-rich hureaulite is associated

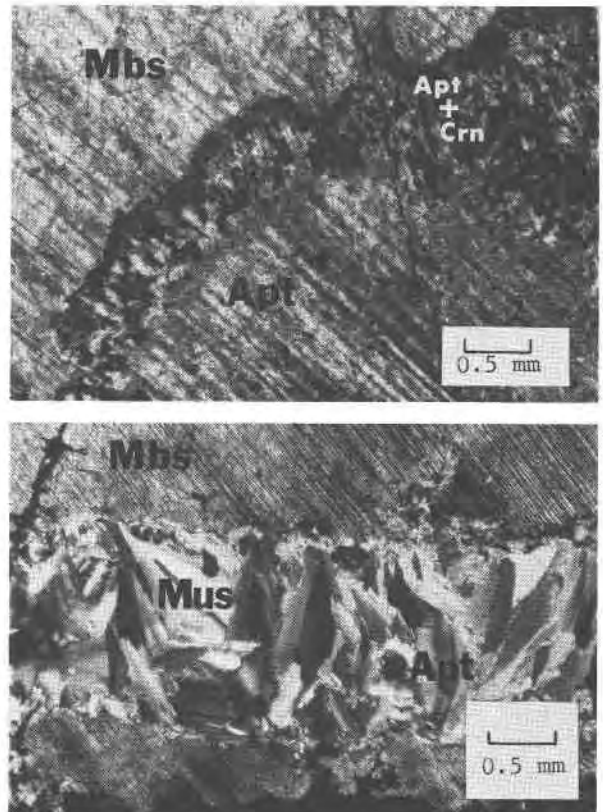


Fig. 7. Photomicrograph (top) showing the replacement of twinned primary montebrasite (Mbs) by a fine-grained aggregate of hydroxylapatite (Apt) with minor crandallite (Crn). Notice in the lower right corner that the twinning present in the host phase has been preserved in the pseudomorphic replacement. Specimen is from the Midnight Owl pegmatite. Crossed polars. Photomicrograph (bottom) showing a veinlet of muscovite (Mus) + apatite (Apt) that cuts twinned primary montebrasite (Mbs). Sample is from the Independence pegmatite. Crossed polars.

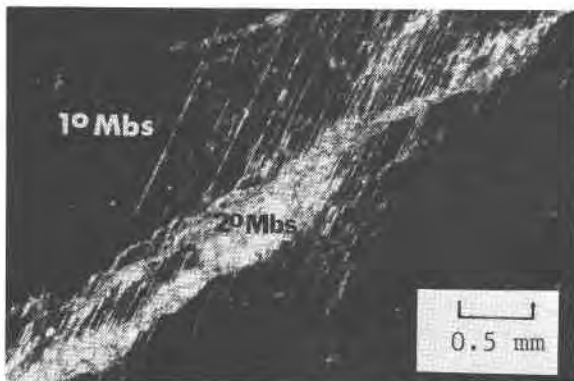


Fig. 6. Photomicrograph showing the replacement of primary montebrasite (1° Mbs) by secondary, low-fluorine montebrasite (2° Mbs). Both phases are polysynthetically twinned. Specimen is from the North Morning Star pegmatite. Crossed polars.



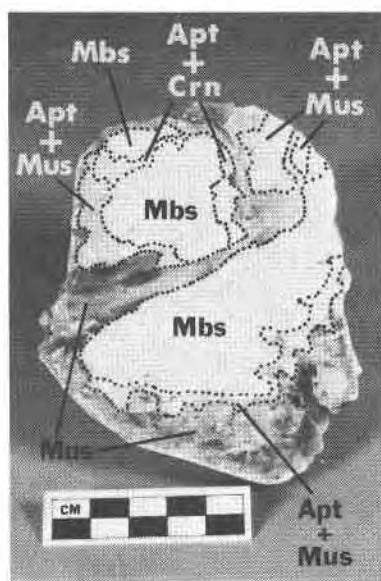


Fig. 8. Arizona State University specimen #3288 from the Midnight Owl pegmatite, showing the typical alteration observed in montebrasite nodules. Phases present in this specimen include primary and secondary montebrasite (Mbs), crandallite (Crn), hydroxylapatite (Apt), muscovite (Mus), and carbonate-apatite (Cpt). The approximate boundaries of assemblages are outlined by dotted lines.

with eosphorite and fairfieldite; identification of eosphorite and fairfieldite was verified by microprobe analysis (numbers 15, 16 and 31-34, Appendix 1). Fairfieldite also forms thin veinlets in close association with dark reddish-brown robertsite; robertsite was identified by its distinctive micaceous habit, by its intense pleochroism in plane-polarized light, and by X-ray and microprobe analyses. This represents the second reported occurrence of robertsite (Moore, 1974). Finally in this association, robertsite and all other earlier-formed replacement phases have been altered to fibrous Mn-rich chlorapatite (Fig. 13).

Relict subhedral lithiophilite crystals in albite display crude prismatic [001] forms, but these crystals are almost completely replaced (Scheme B, Fig. 10). Cores of hureaulite + triploidite and minor lithiophilite are veined and replaced by fillowite, dickinsonite, and wyllieite (Fig. 14). Fillowite has been reported previously only from the pegmatite at Branchville, Connecticut (Brush and Dana, 1879a) and from the Buranga pegmatite, Rwanda (von Knorring, 1963); in the White Picacho district, it occurs abundantly as massive, fine-grained beige crystal aggregates wherever lithiophilite nodules are embedded in albite and was identified on the

basis of optical properties and by X-ray and microprobe analysis. Olive-green dickinsonite and yellowish-brown wyllieite usually occur together and were distinguished principally on the basis of microprobe analyses; both phases commonly are intergrown with fillowite. Fairfieldite commonly forms thin veinlets that clearly cut the fillowite + dickinsonite + wyllieite assemblage. As in the montebrasite alteration sequence, fibrous colloform apatite forms bands that surround lithiophilite nodules and veinlets that cut all other secondary assemblages. This apatite is Mn-rich chlorapatite that contains almost 14 wt.% MnO; the presence of abundant chlorine was determined qualitatively by energy-dispersive microprobe analyses. Along with Mn-chlorapatite, rhodochrosite forms masses and veinlets of pink crystals that represent the latest products of metasomatic alteration of lithiophilite crystals.

Spongy masses of Mn-oxides, purpurite, stewartite, and strengite (Jahns, 1952) also replace lithiophilite, but this assemblage of secondary phases is not present in any freshly mined lithiophilite from subsurface excavations. These oxidized minerals

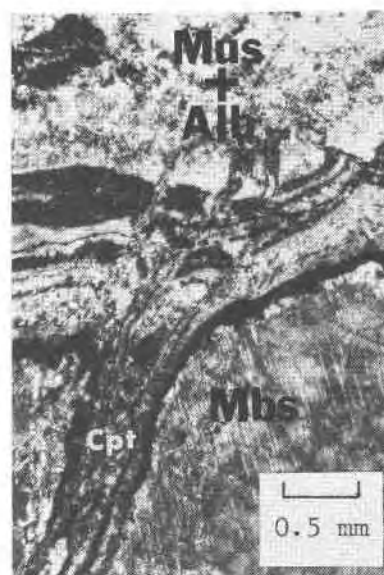


Fig. 9. Photomicrograph showing a rim of carbonate-apatite (Cpt) surrounding primary montebrasite (Mbs). The fine-grained assemblage above the apatite is an intergrowth of muscovite (Mus) + albite (Alb) after spodumene. As illustrated in this sample from the Midnight Owl pegmatite, wherever spodumene occurs with montebrasite (or near lithiophilite), the spodumene is invariably more extensively altered than the phosphate. Crossed polars.

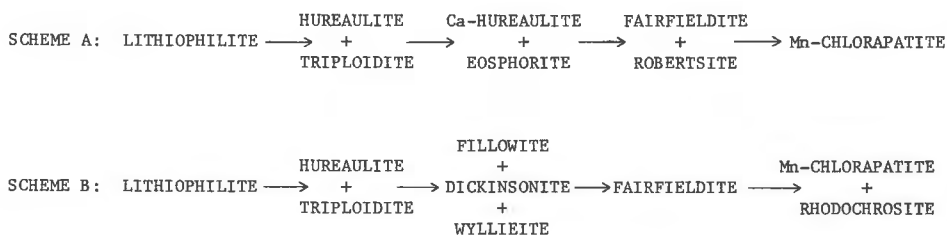


Fig. 10. General alteration sequence for lithiophilite. Scheme A pertains to lithiophilite embedded in massive quartz. Scheme B is for lithiophilite embedded in coarse-grained albite (cleavelandite).

appear to be the result of weathering rather than of postmagmatic pegmatitic alteration.

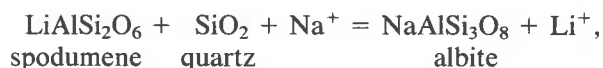
Jahns (1952) reported sicklerite as a common alteration product of lithiophilite in these pegmatites, but most such material probably was robertsite. Sicklerite does occur as the principal alteration product of lithiophilite at the White Ridge pegmatite (which was not exposed during Jahns' study). The White Ridge is the only lithium pegmatite in this district that did not undergo appreciable postmagmatic cation metasomatism. Spodumene and montebrasite from this pegmatite are relatively fresh and unreplaced.

### Discussion

#### Alteration of spodumene

The alteration sequence for spodumene from the White Picacho pegmatites and from other localities (London and Burt, 1980, 1981b) implies that initial replacement involved sodium-for-lithium ion exchange (as evidenced by the formation of albite), followed by potassium + hydrogen metasomatism

(resulting in the conversion of eucryptite, then spodumene and albite, to mica). Albitization of spodumene may be described by two reactions:



which explains the thin reaction rims of pure albite separating altered spodumene from quartz, and



which accounts for the formation of eucryptite + albite intergrowths within spodumene crystals (London and Burt, 1980, 1981b). Whether spodumene breaks down to albite or to eucryptite + albite depends primarily on the presence or absence of quartz, and thus on the activity of silica within and around large spodumene crystals (London and Burt, 1980, 1981b).

The conversion of eucryptite to muscovite is facilitated by the fact that the Al:Si ratios are the same in both minerals, and thus the formation of pseudomorphic mica in spodumene is enhanced by a local lowering of silica activity (London and Burt,

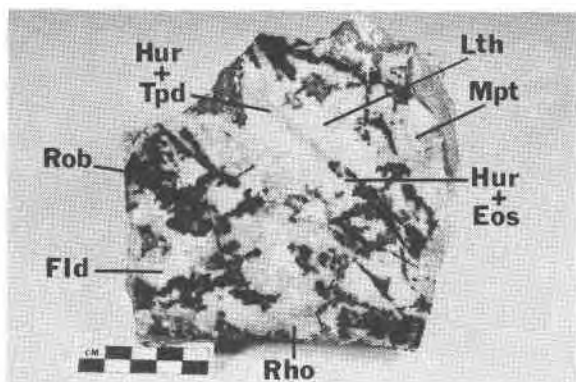


Fig. 11. Lithiophilite specimen from the Midnight Owl pegmatite, showing the alteration assemblages observed in specimens embedded in quartz (Scheme A, Fig. 10). The phases include lithiophilite (Lth), hureaulite (Hur), triploidite (Tpd), eosphorite (Eos), robertsite (Rob), fairfieldite (Fld), Mn-chlorapatite (Mpt), and rhodochrosite (Rho).

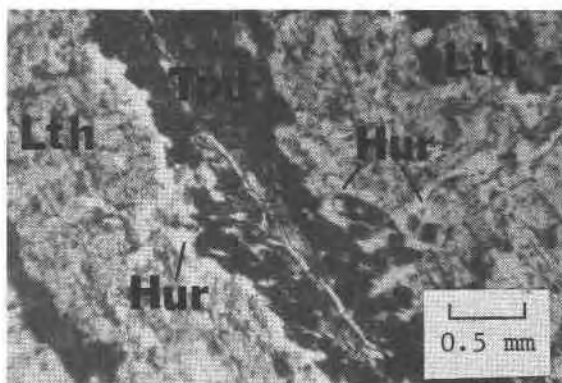


Fig. 12. Photomicrograph showing the incipient replacement of lithiophilite (Lth) by hureaulite (Hur) + triploidite (Tpd). Specimen is from the Midnight Owl pegmatite. Crossed polars.



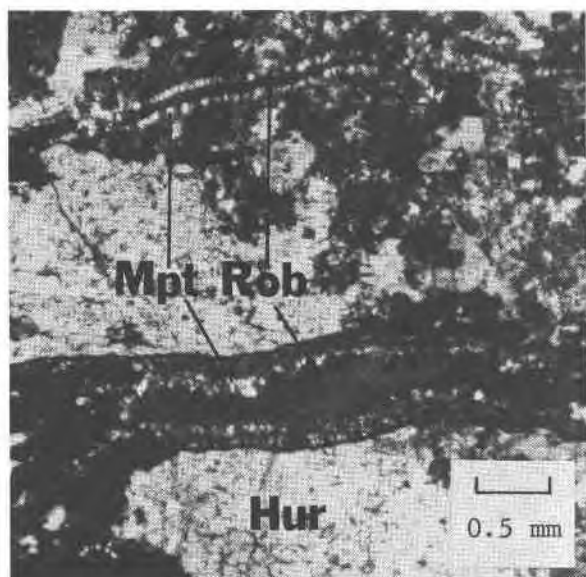
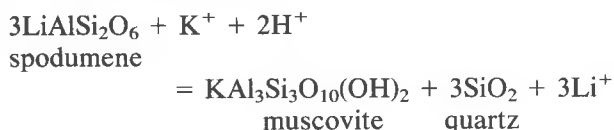


Fig. 13. Photomicrograph showing the late-stage replacement of robersite (Rob) by Mn-chlorapatite (Mpt). The veinlet cuts hureaulite (Hur). Sample is from the Midnight Owl pegmatite. Crossed polars.

1980, 1981b). The direct conversion of spodumene to muscovite liberates silica:



but quartz usually is not present in muscovite pseudomorphs after spodumene from the White Picacho district or from other localities (*e.g.*, Graham, 1975). Graham (1975) suggested that some, but not all, of the silica liberated by mica-forming reactions could be incorporated in secondary micas with high Si:Al ratios. Another possible explanation lies in the fact that mica pseudomorphs after spodumene in the White Picacho pegmatites (and at other localities) usually are embedded in nearly pure cleavelandite that in some cases appears to have replaced pre-existing pegmatite. The replacement of quartz-spodumene pegmatite by large masses of cleavelandite (with locally complete consumption of quartz) may facilitate the conversion of remnant spodumene to mica without producing additional quartz (see Figs. 7 and 8, London and Burt, 1981b).

The pseudomorphic replacements of spodumene in the White Picacho pegmatites are identical in mineralogy and texture to those observed in pegmatites at Branchville, Connecticut, and at Center

Strafford, New Hampshire (see London and Burt, 1981b). Various replacement assemblages in the alteration sequence described above (*i.e.*, albite, eucryptite + albite, mica + albite, and pure mica) have been documented from many pegmatites, some of which are listed in Table 2 of London and Burt (1981b). These reported occurrences indicate that the type of spodumene alteration observed in the White Picacho lithium pegmatites is common in zoned lithium pegmatites elsewhere, especially in those pegmatites that contain cleavelandite or cleavelandite-mica complexes near spodumene-bearing zones.

#### Alteration of montebrasite

The formation of secondary montebrasite by OH-for-F exchange in the primary phase presumably reflects an increase in the ratio  $a_{\text{H}_2\text{O}}/a_{\text{HF}}$  in the residual fluid. Increase in this activity ratio implies a depletion in fluorine (perhaps due to crystallization of apatite or of micas, or of the montebrasite itself) or a relative increase in  $a_{\text{H}_2\text{O}}$  with decreasing

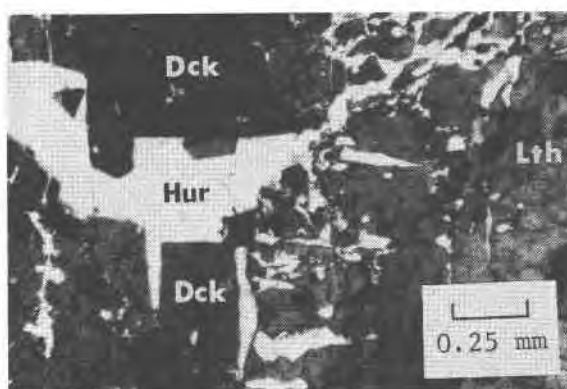


Fig. 14. Photomicrograph showing the replacement of hureaulite (Hur) + triploidite (Tpd) by dickinsonite (Dck) (top) and followite (Fil) (bottom). Homestead specimen, in crossed polars.

temperature (Korzhinskii, 1957; Munoz and Eugster, 1969).

The initial cation metasomatism of primary and secondary montebrasite involved Ca-for-Li exchange, producing hydroxyl-apatite and minor crandallite. Subsequent conversion of montebrasite to muscovite was far more extensive and reflects a high mobility of Li, K, Si, and P, but not Al.

In spite of their rarity in these pegmatites, the occurrences of scorzalite, kulanite, wyllieite, augelite, and brazilianite offer additional insight into the chemistry of the postmagmatic fluids. Except for early formed schorl near the pegmatite borders, scorzalite, kulanite, and wyllieite are the only Fe-rich phases in the White Picacho pegmatites. The rarity and volumetric insignificance of these three phosphates emphasizes the extreme depletion in Fe (and enrichment in Mn) found in these pegmatites. The composition of White Picacho wyllieite is notable in that the weight ratio MnO:FeO is nearly 3:1 (analyses 69–72, Appendix 1), implying that the M(1) and M(2a) sites are occupied predominantly by Mn (*cf.* Moore and Ito, 1979). Kulanite was identified in altered montebrasite from the Midnight Owl pegmatite by a comparison of properties reported by Mandarino and Sturman (1976) for kulanite and by Moore *et al.* (1973) for bjarebyite,  $(\text{Ba,Sr})(\text{Mn}^{2+},\text{Fe}^{2+},\text{Mg})_2\text{Al}_2(\text{PO}_4)_3(\text{OH})_3$ , from the Palermo #1 pegmatite, New Hampshire. As in its type occurrence, kulanite from the White Picacho pegmatites contains no Sr, and this fact may indicate that the White Picacho pegmatites were relatively depleted in Sr (as compared to the phosphorus-rich Palermo #1 pegmatite, which contains bjarebyite, goyazite, and other Sr-bearing phases: Kampf, 1981). The general absence of aluminum phosphates such as augelite, trolleite, *etc.*, in the White Picacho pegmatites may be explained by the fact that the postmagmatic fluids were relatively rich in K, Ca, and Si, thus favoring formation of apatite + muscovite over augelite. Of the five rare secondary phosphates noted above, brazilianite is the most abundant. Its occurrence late in the montebrasite alteration sequence suggests that its stability is analogous to that of lacroixite,  $\text{NaAlPO}_4(\text{F},\text{OH})$ . Lacroixite is incompatible with lithium aluminosilicates in the presence of quartz (Burt and London, 1978; London and Burt, 1981b). In the White Picacho pegmatites, the presence of spodumene with albite and quartz probably buffered the  $a_{\text{Na}^+}/a_{\text{Li}^+}$  ratio in the co-existing fluid at values sufficiently low that brazilianite, like lacroixite, was

unstable throughout most of pegmatite crystallization. Because montebrasite occurs near or with spodumene + quartz in these pegmatites, the alteration of montebrasite to brazilianite probably took place only after spodumene had been locally destroyed (*i.e.*, converted to albite and/or muscovite).

The alteration sequence of montebrasite from the White Picacho pegmatites has few known parallels in other districts. Extensive replacement of the primary phase by low-fluorine secondary montebrasite has been documented only from the Tanco pegmatite, Manitoba (Černá *et al.*, 1972), but this alteration probably is more common than is presently recognized. Products of Ca-for-Li ion exchange (*e.g.*, foggite, crandallite, and especially apatite) have been reported from numerous localities (*e.g.*, Ginzburg, 1950; Fisher and Runner, 1958; Gallagher, 1967; Moore *et al.*, 1975), but the extensive replacement of White Picacho montebrasite by apatite + muscovite and by pure muscovite appears to be unique. Late-stage rims of colloform gray carbonate-apatite surrounding amblygonite-montebrasite may be common in pegmatite districts other than the White Picacho (Moore, 1973), but they are not well documented.

#### *Alteration of lithiophilite*

The incipient alteration of lithiophilite coupled hydration with removal of lithium to form hureaulite and triploidite. These secondary phosphates are abundant in most of the pegmatites that contain lithiophilite, and most subsequent alteration of lithiophilite apparently involved replacement of these two phases. Following the formation of hureaulite and triploidite, alteration of lithiophilite nodules essentially involved progressive Ca-for-Mn cation exchange (Fig. 15). Dickinsonite, fillowite, and wyllieite occur only in lithiophilite nodules embedded in albite. Formation of these three phases reflects an increasing  $a_{\text{Ca}^{2+}}/a_{\text{Mn}^{2+}}$  in the aqueous fluid, as well as a locally high activity of  $\text{Na}^+$ . In the same way that brazilianite is chemically analogous to lacroixite, dickinsonite, fillowite, and wyllieite can be considered analogous to natrophilite,  $\text{NaMnPO}_4$  (*i.e.*, they are principally Na–Mn phosphates). Natrophilite, like lacroixite, is incompatible with spodumene in the presence of quartz (Burt and London, 1978; London and Burt, 1981) and is absent in the White Picacho pegmatites. In its only known occurrence at Branchville, Connecticut (Brush and Dana, 1890), natrophilite appears to be the direct product of Na-for-Li exchange in lithiophilite, and

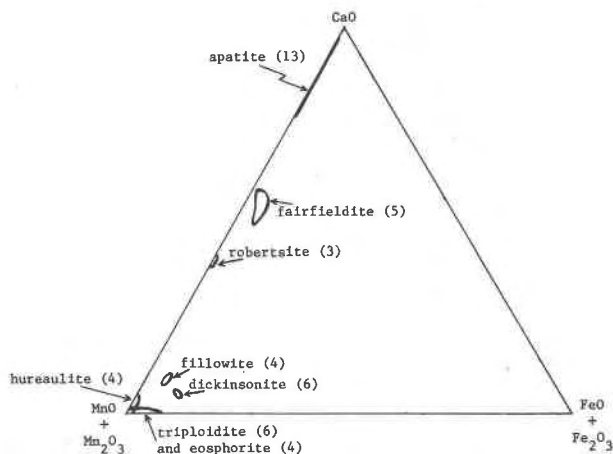


Fig. 15. Compositions of lithiophilite replacement minerals (in wt.%) on the ternary  $\text{CaO}-(\text{MnO} + \text{Mn}_2\text{O}_3)-(\text{FeO} + \text{Fe}_2\text{O}_3)$ . Numbers in parentheses indicate the number of specimens analyzed (by electron microprobe). Representative analyses are given in Appendix 1.

the structural similarities between these two minerals seems to confirm this (Moore, 1972). In the White Picacho pegmatites, it appears that the presence of spodumene with albite and quartz kept values of  $a_{\text{Na}^+}/a_{\text{Li}^+}$  in the fluid sufficiently low that lithiophilite was not converted to natrophilite. By the time the ratio  $a_{\text{Na}^+}/a_{\text{Li}^+}$  had increased sufficiently to promote the growth of Na-rich phosphates (*i.e.*, after spodumene had been destroyed by albitization), most lithiophilite probably had been converted to hureaulite + triploidite, and the activity of  $\text{Ca}^{2+}$  may have increased in the fluid. This circumstance apparently led to the formation of dickinsonite, fillowite, and wyllieite from hureaulite and triploidite.

Fillowite, dickinsonite and wyllieite are usually intimately intergrown, and this fact suggests that they formed contemporaneously. In the White Picacho material, these three phases possess sharp crystal boundaries and appear to be optically homogeneous; however in some respects, the distinction between phases is unclear. For example, some material that possesses the optical properties and composition (analyses 21–24, Appendix 1) of dickinsonite apparently has the unit cell (both symmetry and dimensions) of wyllieite. Fisher (1965) has demonstrated that a complex paragenetic relationship exists among these minerals that depends on temperature and  $a_{\text{H}_2\text{O}}$ . There is little doubt that the crystal-chemical relations among these three phases are very complex (Moore and Ito, 1979; Moore, 1981), and an understanding of their stability rela-

tions suffers from their extremely limited occurrences. The subsequent formation of fairfieldite, robertsite, and apatite implies that  $a_{\text{Ca}^{2+}}/a_{\text{Mn}^{2+}}$  increased throughout the alteration episode.

Chlorine-rich apatites produced at this stage of alteration further reflect that postmagmatic fluids in these pegmatites were F-deficient. Although primary apatite containing 5–7 wt.% MnO is common in these and other pegmatites, the secondary apatite in this association contains almost 14 wt.% MnO and is the most Mn-rich apatite known to us. The high Mn contents of these apatites can reasonably be attributed to the locally high activity of  $\text{Mn}^{2+}$  (liberated by the breakdown of hureaulite, triploidite, *etc.*). The highly oxidized phases, such as purpurite, stewartite, strengite, *etc.*, reported by Jahns (1952) appear to be weathering products. Sicklerite at the White Ridge pegmatite also may be the result of weathering or of near-surface reactions with meteoric water, inasmuch as spodumene and montebrasite from this pegmatite do not exhibit the metasomatic alteration observed in the other pegmatites.

The metasomatic replacement assemblages identified in the White Picacho lithiophilite are most similar to those described by Brush and Dana (1878, 1879a, 1879b, 1890) from the Branchville pegmatite, Connecticut; however, the sequence of replacements in Branchville lithiophilite has not been clearly established, largely because the replacement products are relatively coarse grained and occur as irregularly distributed patches in nodules rather than in the discrete veinlets often observed in the White Picacho material. These suites of Mn-rich secondary phosphates reflect the high  $\text{MnO}/(\text{MnO} + \text{FeO})$  ratios of the primary lithiophilite at these localities. They are similar to the products of metasomatically altered lithiophilite from other localities (*e.g.*, Matsubara and Kato, 1980), except that the higher Fe content of primary lithiophilite in most other pegmatites leads to a somewhat different suite of alteration minerals that contain essential  $\text{Fe}^{3+}$  (see Moore, 1973, for a list of secondary phosphates containing  $\text{Fe}^{3+}$ ).

Na- and Ca-rich phosphates similar to those identified in the White Picacho district are common products of metasomatic alteration of lithiophilite-triptylite. Moore (1971) has identified large masses of alluaudite that replace triptylite in several pegmatites of the Black Hills district, South Dakota. In an occurrence similar to that described from the White Picacho district, Moore (1973) also reported

an occurrence of large, partially replaced crystals of triphylite from the Pleasant Valley pegmatite, South Dakota, in which relict cores of triphylite were surrounded by a thick mass of secondary alluaudite, which is finally rimmed by secondary apatite.

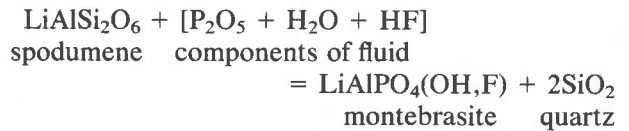
Sicklerite is a common product of oxidation and alkali leaching in Fe-rich lithiophilite and triphylite, as at the Stewart pegmatite, California (Shigley and Brown, 1980), and the Varuträsk pegmatite, Sweden (Quensel, 1957). Sicklerite occurs sparingly at the White Ridge pegmatite in the White Picacho district; lithiophilite from the White Ridge also is much more Fe-rich than at the other localities in the district (analysis 3, Appendix 1), a factor that undoubtedly facilitated its oxidation and conversion to sicklerite. As at most other lithiophilite-triphylite localities, highly oxidized and alkali-leached phases such as purpurite, stewartite, and strengite are common in White Picacho lithiophilite (Jahns, 1952); however, as noted above, these phosphates and sicklerite appear to have been formed by weathering.

### Geochemical trends

#### *Crystallization of the primary lithium minerals*

The primary textural and zonal features observed in the White Picacho pegmatites are typical of steeply dipping, zoned lithium pegmatites elsewhere. Nevertheless, a few details are worthy of emphasis. Primary montebrasite (or amblygonite) and lithiophilite (or triphylite) are commonly embedded in massive quartz in the White Picacho pegmatites, as at other well-known, P-rich pegmatites such as the Palermo #1 pegmatite, New Hampshire, and the Newry pegmatite, Maine (Cameron *et al.*, 1954). In the White Picacho pegmatites, the primary lithium phosphates appear to have crystallized after spodumene and primary feldspars, but this relationship has not been demonstrated in pegmatites from most other districts (*cf.* zonal assemblages 6 through 11 in the generalized crystallization sequence proposed by Cameron *et al.*, 1949). These observations imply that successive, fluid-saturated magmas in the White Picacho lithium pegmatites became increasingly rich in phosphorus, and phosphates, rather than silicates, were the last primary minerals to crystallize with quartz. Thus montebrasite and lithiophilite apparently succeeded spodumene as the stable primary lithium phases in the White Picacho pegmatites. This sequence implies that the activities of the acidic

volatiles P and to a lesser extent F increased as crystallization proceeded, and that spodumene eventually became unstable with respect to montebrasite + quartz:



The composition of primary montebrasite indicates that the White Picacho pegmatites were not F-rich (*cf.* Loh and Wise, 1976). Although Jahns (1952) reported F-rich minerals such as lepidolite, triplite, and fluorite from the White Picacho district, lepidolite is not abundant, and triplite and fluorite must be very rare (the latter two phases were sought but not found during this study). Topaz was not observed by Jahns or by us.

The abundance of minerals containing Li, Be, Mn, Nb, Ta, and Bi in these pegmatites implies that they originated from a highly differentiated source magma. The very high MnO/(MnO + FeO) ratio in lithiophilite and other Fe-Mn minerals (columbite and tourmaline) with which it occurs indicates that the White Picacho pegmatites were highly differentiated with respect to Mn *vs.* Fe when they were emplaced. Foord (1976) similarly observed that garnets and tourmalines from the Mesa Grande district, California, show increasing enrichment in Mn *vs.* Fe at successively later stages of pegmatite development. The sudden and late appearance of Mn-rich minerals in the White Picacho pegmatites remains unexplained.

Relatively coarse-grained cleavelandite units containing lithiophilite, columbite, beryl, apatite, zircon, tourmaline, and some mica are present in most of the White Picacho lithium pegmatites. Cleavelandite units with similar mineralogy and texture have been described from at least fifty pegmatites in the United States alone (*e.g.*, by Page *et al.*, 1953; Cameron *et al.*, 1954; Norton *et al.*, 1962; Jahns and Ewing, 1976), and summaries of pegmatite occurrences elsewhere (*e.g.*, Vlasov, 1961; Beus, 1960) indicate that these units are present in highly differentiated lithium pegmatites throughout the world. The origin of cleavelandite bodies has been a subject of considerable speculation. For example, their formation may be explained by the separation of a volatile- and silica-rich fluid from primary magma, in a model of differentiation similar to that proposed by Jahns and Tuttle (1963) and by Osieki and Jahns (1980) for the

segregation of large K-feldspar masses from finer-grained albite. In this context, cleavelandite units may be analogous to sodic aplite from which a K-, Li-, and Si-rich fluid separated but did not escape the closed pegmatite system. These cleavelandite units may have crystallized from essentially albitic melts that also might be enriched in less volatile, residual elements such as Ca and Mn; such melts also would be enriched in the elements F, P, Zr, Nb, and LREE that form especially stable complexes with alkalis and alkaline earths (*e.g.*, see Kogarko *et al.*, 1968; Fleischer and Altschuler, 1969; Watson, 1979). Alternatively, cleavelandite complexes may be produced by reaction of solid phases (especially spodumene + quartz) with residual magma (magmatic replacement) or with residual fluids (postmagmatic replacement). Although albite complexes clearly replaced pre-existing pegmatite at a few localities (*e.g.*, Norton *et al.*, 1962; Jahns and

Ewing, 1976), textural evidence usually does not provide sufficient proof of an origin by replacement. In the White Picacho pegmatites, however, textural features (described above) indicate that at least some parts of cleavelandite or cleavelandite-mica complexes replaced quartz-spodumene pegmatite. It is not clear if spodumene reacted with residual magma or aqueous fluids, but the formation of these complexes seems to represent the last stage of coarse-grained crystallization that preceded the fine-grained, postmagmatic pseudomorphism of the primary lithium minerals.

#### Postmagmatic fluids

The initial subsolidus metasomatism of lithium minerals in these pegmatites took place in an alkaline environment (Fig. 16), as evidenced by Na-for-Li exchange (albitization) in spodumene and Ca-for-Li and Ca-for-Mn exchange in the phosphates. This

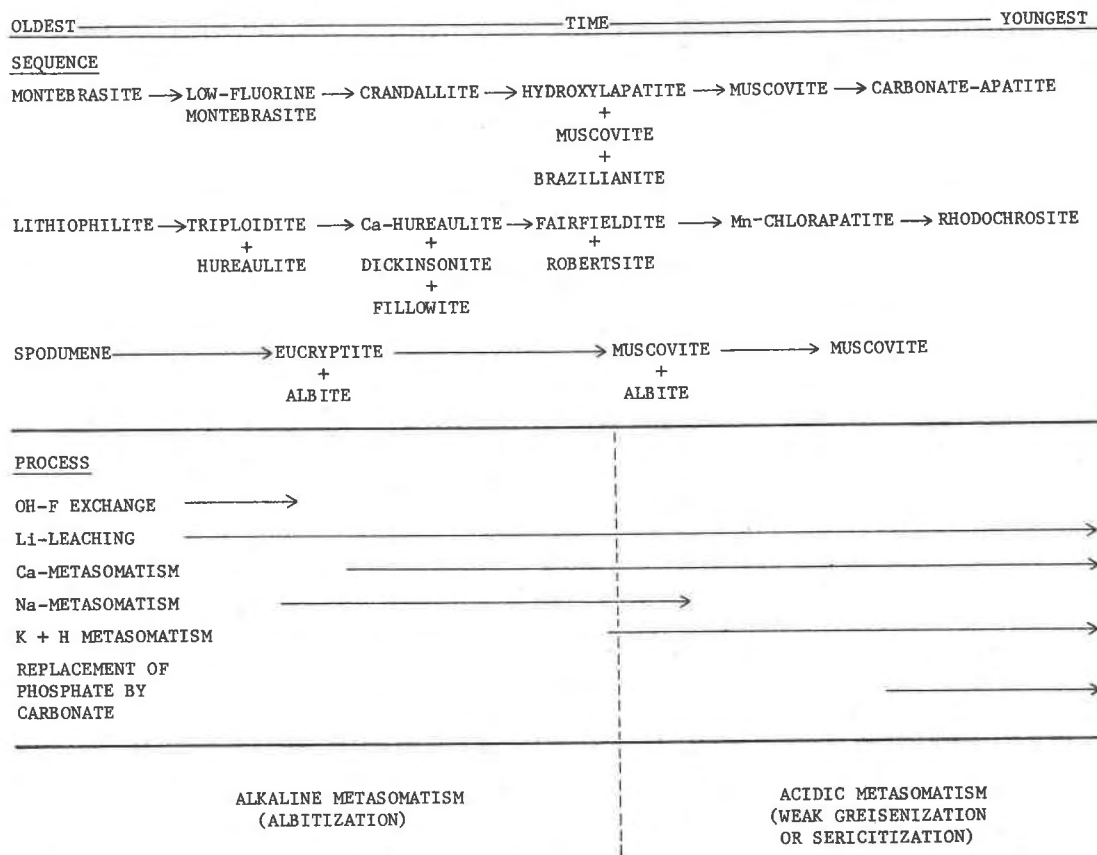


Fig. 16. Generalized replacement sequences for spodumene, montebbrasite, and lithiophilite, and the inferred chemical processes that give rise to the observed alteration assemblages. The replacement sequences for montebbrasite and lithiophilite have been abbreviated to show the essential mineralogy. The assemblages are laid out along the time axis in the order and relative timing in which they seem to occur. The beginning of acidic metasomatism is marked by the appearance of muscovite in spodumene and montebbrasite.

observation implies that the fluid chemistry changed significantly from the later primary stage, when acidic P- and F-rich fluids promoted the formation of montebrasite + quartz, to subsolidus conditions sufficiently alkaline to stabilize eucryptite + albite (*cf.* the stabilities of eucryptite, spodumene, and amblygonite in Fig. 14 of London and Burt, 1981b). The sodium phosphates brazilianite, filloelite, wyllieite, and dickinsonite occur late in the alkaline stage of metasomatic alteration, and these phases probably formed only after spodumene had been converted to albite and/or micas.

The widespread formation of secondary mica in spodumene, montebrasite, tourmaline, and much of the feldspar (especially in oligoclase of the granitic zones) signifies a gradual change from alkaline to relatively acidic postmagmatic fluids, as (K+H)-metasomatism produced alteration characteristic of sericitization or weak greisenization. Late-stage fluids were not F-rich, however, as evidenced by the low F contents of secondary montebrasite, by the formation of OH- and Cl-apatites, and by the absence of F-rich phases.

Fluid composition probably varied with location (as well as time) in these pegmatites. The large, sharply bounded pegmatitic zones are essentially mono- or bi-mineralic, and with respect to the fluid phase, each zone may have constituted its own chemical system. As a result of this isolation, much of the observed pseudomorphic alteration may have been produced as (upwardly) migrating fluids attempted to re-equilibrate with different solid-phase assemblages from zone to zone. The movement of fluids through the crystallized pegmatite appears to have been controlled by fracturing, with the result that fluids almost certainly moved across zonal boundaries as channelways opened up. As an example, the albitization of spodumene observed in these and other pegmatites may have been produced as Na-rich fluids escaped along fractures from cleavelandite complexes into (overlying) quartz-spodumene pegmatite. The sporadic distribution and the variations in observed alteration assemblages are further confirmation that the fluid composition was non-uniform with location (and with time).

Lithium was removed from the pegmatites during the alteration episode. Although some Li was incorporated in the fine-grained secondary micas, spectroscopic evidence indicates that much Li (perhaps liberated by the pseudomorphic replacement of the primary lithium minerals) was trapped in large masses of metasomatic micas and tourmalines at

the exocontacts of these pegmatites. The lithium amphibole holmquistite, common in some districts (reviewed by Heinrich, 1965), appears to be absent in the White Picacho district.

### Summary and conclusions

As in most other pegmatite districts, the vast majority of pegmatites exposed in the White Picacho district are granitic in composition, poorly zoned, and do not contain lithium minerals. The nine lithium pegmatites that have been recognized in the district are complexly zoned and contain minerals of the elements Li, Be, P, Nb, Ta, Bi, and probably other rare elements. Spodumene, montebrasite, lithiophilite, lithian muscovite, and lithian tourmaline are the primary lithium minerals found in these pegmatites; however, only spodumene and montebrasite occur in abundance (Table 2). In general, the lithium minerals are restricted to the inner zones and cores of essentially granitic pegmatite.

If crystallization proceeded sequentially from borders to core, then the primary crystallization sequence in these pegmatites reflects the usual increase in activities of Li species (spodumene follows perthitic microcline as the stable alkali aluminosilicate), as well as an increase in the activities of the acidic volatiles P and F (montebrasite succeeds spodumene as the stable primary lithium phase). Coarse-grained cleavelandite units, commonly containing major or accessory lithiophilite, apatite, columbite, beryl, and zircon, occur in all of the lithium pegmatites and are located near the margins of quartz-spodumene zones. These appear to be the latest-crystallizing coarse-grained units, and they formed at least in part by replacement of quartz-spodumene pegmatite.

Subsolidus metasomatic alteration of spodumene, montebrasite, and lithiophilite was pseudomorphic in nature and produced a large number of fine-grained secondary phases and replacement assemblages. As summarized in Figure 16, the subsolidus replacement of the primary lithium minerals in these pegmatites can be divided into two stages: an alkaline stage (principally involving albitization), followed by an acidic stage (with alteration characteristic of greisenization or sericitization). The incipient alteration of these primary lithium minerals involved cation exchange with a fluid rich in Na and Ca relative to Li. This initial stage of alteration seems to indicate that in some interval between late primary crystallization and the onset of postmag-



matic alteration, the pegmatitic fluid possibly evolved from a relatively acidic phase (rich in volatile P- and F-species) to an F-deficient but presumably saline fluid dominated (chemically) by alkalis and alkaline earths. Albitization of spodumene may have been contemporaneous with Cametasomatism of the phosphates, but the formation of the Na-rich phosphates brazilianite, fillowite, dickinsonite, and wylieite probably occurred only after nearby spodumene had been converted to albite or micas. The subsequent replacement of eucryptite, spodumene, and montebbrasite by muscovite records the development of a weakly acidic K- and H-rich fluid. This sericitic or greisen-like alteration also is widespread in tourmaline and in much feldspar (mostly in plagioclase of the outer, granitic zones). Finally a more CO<sub>2</sub>-rich fluid deposited carbonates (mostly rhodochrosite in lithiophilite) and carbonate-rich apatite as rims on montebbrasite nodules. Similar rims of apatite surrounding altered lithiophilite are very manganese- and chlorine-rich.

The extremely high MnO/(MnO + FeO) ratios observed in White Picacho lithiophilite, columbite, *etc.* suggest that these pegmatites originated from a highly differentiated granitic source. The pegmatites introduced Li, K, and B to the metamorphic rocks, producing masses and veins of metasomatic micas and tourmaline at the pegmatite exocontacts.

All of the minerals and most of the assemblages identified in the White Picacho pegmatites occur in complex lithium pegmatites elsewhere. In fact, many of the textures and assemblages in these pegmatites are characteristic of lithium pegmatites. However, we know of no other pegmatite or group of pegmatites where the history of subsolidus metasomatism involving cation exchange between crystals and fluid is so complex, yet decipherable. To encourage further studies of these and other pegmatites, we have made representative samples from the White Picacho pegmatites available for study from the museums listed below:

Department of Geology, Arizona State University, Tempe, Arizona 85281; collection numbers 3288-3303.

U.S. National Museum, Division of Mineralogy, Smithsonian Institution, Washington, District of Columbia 20560; collection numbers 145123-145130.

Mineralogical Museum, Harvard University, 24 Oxford Street, Cambridge, Massachusetts 02138; collection numbers 117233-117244.

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### References

- Albee, A. L. and Ray, L. (1970) Correction factors for electron probe microanalysis of silicates, oxides, carbonates, phosphates, and sulfates. *Analytical Chemistry*, 42 (12), 1408-1414.
- Anderson, C. A., Blacet, P. M., Silver, L. T., and Stern, T. W. (1971) Revision of the Precambrian stratigraphy in the Prescott-Jerome area, Yavapai County, Arizona. U.S. Geological Survey Bulletin 1324-C, C1-C16.
- Appleman, D. E. and Evans, H. T., Jr. (1973) Indexing and least-squares refinement of powder diffraction data. U.S. Geological Survey Computer Contribution 20 (Available through National Technical Information Service, file no. USGS-GD-73-003).
- Beus, A. A. (1960) Geochemistry of Beryllium and Genetic Types of Beryllium Deposits. Akademii Nauk SSSR, Moscow (transl. W. H. Freeman, San Francisco, 1967).
- Brush, G. J. and Dana, E. S. (1878) On a new and remarkable mineral locality in Fairfield County, Connecticut; with a description of several new species occurring there. *American Journal of Science*, 116, 33-46 and 114-123.
- Brush, G. J. and Dana, E. S. (1879a) On the mineral locality in Fairfield County, Connecticut. Second paper. *American Journal of Science*, 117, 359-368.
- Brush, G. J. and Dana, E. S. (1879b) On the mineral locality in Fairfield County, Connecticut. Third paper. *American Journal of Science*, 118, 45-50.
- Brush, G. J. and Dana, E. S. (1880) On the mineral locality at Branchville, Connecticut. Fourth paper. Spodumene and the results of its alteration. *American Journal of Science*, 118, 257-285.
- Brush, G. J. and Dana, E. S. (1890) On the mineral locality at Branchville, Connecticut. Fifth paper. Analyses of several manganese phosphates. *American Journal of Science*, 139, 201-216.
- Burt, D. M., London, D., and Smith, M. R. (1977) Eucryptite from Arizona, and the lithium aluminosilicate phase diagram. (abstr.) *Geological Society of America, Abstracts with Programs*, 9 (7), 917.
- Cameron, E. N., Jahns, R. H., McNair, A. H., and Page, L. R., (1949) Internal structure of granitic pegmatites. *Economic Geology Monograph* 2, 115 p.

- Cameron, E. N., and others (1954) Pegmatite investigations, 1942-45, New England. U.S. Geological Survey Professional Paper 255.
- Černá, I., Černý, P., and Ferguson, R. B. (1972) The Tanco pegmatite at Bernic Lake, Manitoba. III. Amblygonite-montebbrasite. *Canadian Mineralogist*, 11 (3), 643-659.
- Černá, I., Černý, P., and Ferguson, R. B. (1973) The fluorine content and some physical properties of the amblygonite-montebbrasite minerals. *American Mineralogist*, 58, 291-301.
- Fisher, D. J. (1965) Dickinsonites, fillowite, and alluaudites. *American Mineralogist*, 50, 1647-1669.
- Fisher, D. J. and Runner, J. J. (1958) Morinite from the Black Hills. *American Mineralogist*, 54, 585-594.
- Fleischer, M. (1980) 1980 Glossary of Mineral Species. Mineralogical Record, Inc., P.O. Box 35565, Tucson, Arizona.
- Fleischer, M. and Altschuler, Z. S. (1969) The relationship of rare-earth composition of minerals to geologic environment. *Geochimica et Cosmochimica Acta*, 33 (6), 725-732.
- Foord, E. E. (1976) Mineralogy and petrogenesis of layered pegmatite-aplite dikes in the Mesa Grande district, San Diego County, California. Ph.D. thesis, Stanford University, Stanford, California.
- Gallagher, M. J. (1967) Phosphates and other minerals in pegmatites of Rhodesia and Uganda. *Mineralogical Magazine*, 36, 50-59.
- Ginzburg, A. I. (1950) Montebbrasite and its replacement reactions [in Russian]. *Trudy Mineralogicheskogo Muzeya, Akademii Nauk SSSR*, 2, 72-85 (not seen; extracted from *Chemical Abstracts*, 49, #12207, 1955).
- Graham, J. (1975) Some notes on  $\alpha$ -spodumene,  $\text{LiAlSi}_2\text{O}_6$ . *American Mineralogist*, 60, 919-923.
- Heinrich, E. W. (1965) Holmquistite and pegmatitic lithium exomorphism. *Indian Mineralogist*, 6, 1-13.
- Heinrich, K. F. J., Yakowitz, H., and Vieth, D. L. (1972) The correction for absorption of primary X-rays. *Proceedings of the 7th Annual Meeting of the Electron Microprobe Analysts Society of America*, San Francisco, 3A-3F.
- Jagger, T. A. and Palache, C. (1905) Description of the Bradshaw Mountains quadrangle, Arizona. U.S. Geological Survey Geologic Atlas, Folio 126.
- Jahns, R. H. (1952) Pegmatite deposits of the White Picacho district, Maricopa and Yavapai Counties, Arizona. *Arizona Bureau of Mines Bulletin* 162.
- Jahns, R. H. and Ewing, R. C. (1976) The Harding Mine, Taos County, New Mexico. *New Mexico Geological Society Guidebook*, 27th Field Conference, Vermejo Park, 263-276.
- Jahns, R. H. and Tuttle, O. F. (1963) Layered pegmatite-aplite intrusives. *Mineralogical Society of America Special Paper* 1, 78-92.
- Julien, A. A. (1879) On spodumene and its alterations from granite-veins of Hampshire County, Massachusetts. *Annals of the New York Academy of Science*, 1, 318-359.
- Kampf, A. R. (1981) The phosphate mineralogy of the Palermo pegmatite. (abstr.) *Fourth Annual Meeting of the Mineralogical Society of America—Friends of Mineralogy Symposium on the Mineralogy of Pegmatites*, February 15-16, 1981, Tucson, Arizona, 19-20.
- Kogarko, L. N., Krigman, L. D., and Sharudilo, N. S. (1968) Experimental investigations of the affect of alkalinity of silicate melts on the separation of fluorine into the gas phase. *Geokhimiya*, (8), 948-956 (transl. *Geochemistry International*, 5, 782-790, 1968).
- Korzhinskii, D. S. (1957) Physicochemical Basis of the Analysis of the Paragenesis of Minerals. *Izvestiya Akademii Nauk SSSR*, Moscow (transl. Consultants Bureau, New York, 1959).
- Laughlin, A. W. (1969) Excess Radiogenic Argon in Pegmatite Minerals. Ph.D. thesis, University of Arizona, Tucson, Arizona.
- Loh, S. E., and Wise, W. S. (1976) Synthesis and fluorine-hydroxyl exchange in the amblygonite series. *Canadian Mineralogist*, 14, 357-363.
- London, D. (1979) Occurrence and Alteration of Lithium Minerals, White Picacho Pegmatites, Arizona. Masters thesis, Arizona State University, Tempe, Arizona.
- London, D., Bandy, G. L., and Kealy, S. L. (1978) Metasomatic alteration of primary lithium phosphates from the White Picacho pegmatite district, Maricopa and Yavapai Counties, Arizona. (abstr.) *Geological Society of America, Abstracts with Programs*, 10 (7), 446.
- London, D. and Burt, D. M. (1978) Lithium pegmatites of the White Picacho district, Maricopa and Yavapai Counties, Arizona. In Burt, D. M. and Péwé, T. L., Eds., *Guidebook to the Geology of Central Arizona*. Arizona Bureau of Geology and Mineral Technology, Special Paper 2, 61-72.
- London, D. and Burt, D. M. (1979) Processes of formation and destruction of eucryptite in lithium pegmatites. (abstr.) *Transactions of the American Geophysical Union*, 60 (18), 417.
- London, D. and Burt, D. M. (1980) Local lowering of silica activity during albitization of spodumene—its relation to the formation of micas and eucryptite. (abstr.) *Transactions of the American Geophysical Union*, 61 (17), 404.
- London, D. and Burt, D. M. (1981a) Lithium-aluminosilicate occurrences in pegmatites, and the lithium aluminosilicate phase diagram. *American Mineralogist*, in press.
- London, D. and Burt, D. M. (1981b) Chemical models for lithium aluminosilicate stabilities in pegmatites and granites. *American Mineralogist*, in press.
- Mandarino, J. A. and Sturman, B. D. (1976) Kulanite, a new barium iron aluminum phosphate from the Yukon Territory, Canada. *Canadian Mineralogist*, 14, 127-131.
- Matsubara, S. and Kato, A. (1980) Pegmatite phosphates from Yukiiri, Ibaraki Prefecture, Japan [in Japanese]. *Kobutsugaku Zasshi*, 14 (4), 269-286 (not seen; extracted from *Chemical Abstracts*, 94, #33833t, 1981).
- Moore, P. B. (1971) Crystal chemistry of the alluaudite structure type; contribution to the paragenesis of pegmatite phosphate giant crystals. *American Mineralogist*, 56, 1955-1975.
- Moore, P. B. (1972) Natrophilite,  $\text{NaMnPO}_4$ , has ordered cations. *American Mineralogist*, 57, 1333-1344.
- Moore, P. B. (1973) Pegmatite phosphates: descriptive mineralogy and crystal chemistry. *Mineralogical Record*, 4, 103-130.
- Moore, P. B. (1974) I. Jahnsite, segelerite, and robertsite, three new transition metal phosphate species. II. Redefinition of overite, an isotope of segelerite. III. Isotopy of robertsite, mitridatite, and arseniosiderite. *American Mineralogist*, 59, 48-59 and 640.
- Moore, P. B. (1981) The primary pegmatite phosphate minerals. (abstr.) *Fourth Annual Meeting of the Mineralogical Society of America—Friends of Mineralogy Symposium on the Mineralogy of Pegmatites*, February 15-16, 1981, Tucson, Arizona, 17-18.
- Moore, P. B., Irving, A. J., and Kampf, A. R. (1975) Foggite,  $\text{CaAl}(\text{OH})_2(\text{H}_2\text{O})[\text{PO}_4]$ ; goedenite  $(\text{Sr}, \text{Ca})_2\text{Al}(\text{OH})[\text{PO}_4]_2$ ;

- and samuelsonite,  $(\text{Ca,Ba})\text{Fe}_2^{2+}\text{Mn}_2^{2+}\text{Ca}_8\text{Al}_2(\text{OH})_2[\text{PO}_4]_{10}$ : three new species from the Palermo No.1 pegmatite, North Groton, New Hampshire. *American Mineralogist*, 60, 957-964.
- Moore, P. B. and Ito, J. (1979) Alluaudites, wyllieites, and arrojadites: crystal chemistry and nomenclature. *Mineralogical Magazine*, 43, 227-235.
- Moore, P. B., Lund, D. H., and Keester, K. L. (1973) Bjarebyite,  $(\text{Ba,Sr})(\text{Mn,Fe,Mg})_2\text{Al}_2(\text{OH})_3(\text{PO}_4)_3$ , a new species. *Mineralogical Record*, November-December, 282-285.
- Munoz, J. L. and Eugster, H. P. (1969) Experimental control of fluorine reactions in hydrothermal systems. *American Mineralogist*, 54, 943-959.
- Osieki, R. A. and Jahns, R. H. (1980) Feldspar zonation within pegmatite masses of the Milford-Mason, New Hampshire granite. (abstr.) *Geological Society of America, Abstracts with Programs*, 12 (2), 76.
- Page, L. R. and others (1953) Pegmatite investigations, 1942-45, New England. U.S. Geological Survey Professional Paper 247.
- Palache, C., Berman, H., and Frondel, C. (1951) *The System of Mineralogy*, Volume 2, 7th Edition. Wiley, New York.
- Quensel, P. (1937) Minerals of the Varuträsk pegmatite. VIII. The amblygonite group. *Geologiska Föreningen i Stockholm Förhandlingar*, 59, 455-468.
- Quensel, P. (1956) The paragenesis of the Varuträsk pegmatite including a review of its mineral assemblages. *Arkiv för Mineralogi och Geologi*, 2, 9-125.
- Shigley, J. E. and Brown, G. E., Jr. (1980) Phosphate mineralogy of the Stewart pegmatite, Pala district, San Diego County, California. (abstr.) *Geological Society of America, Abstracts with Programs*, 12 (7), 521.
- Thomssen, R. W. and Anthony, J. W. (1977) Lithiophilite crystals from the Foote mine. *Mineralogical Record*, 8 (2), 95-97.
- Vlasov, K. A. (1961) Principles of classifying granite pegmatites and their textural-paragenetic types. *Izvestiya Akademii Nauk SSSR, Seriya Geologicheskaya*, 1, 5-20 (transl. *Izvestiya of the Academy of Sciences, USSR, Geologic Series*, 1, 5-20, 1961).
- von Knorring, O. (1963) VI(c) Report on mineralogical research. 7th Annual Report (1961-1962) Research Institute of African Geology, University of Leeds, 33-37.
- Mineralogische und Petrographische Mitteilungen, 55, 9-18.
- von Knorring, O. and Fransolet, A. M. (1975) An occurrence of bjarebyite in the Buranga pegmatite, Rwanda. *Schweizerische mineralogische und petrographische Mitteilungen*, 55, 9-18.
- Watson, E. B. (1979) Zircon saturation in felsic liquids: experimental results and applications to trace element geochemistry. *Contributions to Mineralogy and Petrology*, 70 (4), 407-420.

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