

Occurrence and alteration of phosphate minerals at the Stewart Pegmatite, Pala District, San Diego County, California

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Abstract

Paragenetic relationships among lithiophilite $\text{Li}(\text{Mn, Fe})^{2+}\text{PO}_4$ and its alteration products are described for one of the complex granitic pegmatites in the Pala pegmatite district, San Diego County, California. At the Stewart pegmatite, lithiophilite occurs in the upper-intermediate, microcline-quartz zone while spodumene and amblygonite are found in the quartz core. The sequence of primary mineral formation within the pegmatite reflects an increase in the activities of both lithium species and volatile components (phosphorus and fluorine). Extensive alteration of lithiophilite involved oxidation, hydration, and cation leaching, but surprisingly little metasomatism. Secondary minerals present include sicklerite, hureaulite, purpurite, stewartite, phosphosiderite, several incompletely identified phases, and various manganese oxides. Secondary phosphates formed during the initial stages of alteration pseudomorphously replaced lithiophilite as a result of its limited hydrothermal interaction with late-stage pegmatitic fluids. Later members of the alteration sequence represent supergene weathering products. The Stewart pegmatite crystallized from a highly-differentiated granitic magma at shallow crustal depths (about 3–5 km). The lack of extensive metasomatic replacement, which is so evident among the phosphate mineral assemblages of other granitic pegmatites, is thought to primarily be a result of the relatively rapid cooling and volatile fluid loss at the shallow depths of formation of the Stewart pegmatite. Under these conditions, there was little opportunity for metasomatic reaction to take place between lithiophilite and residual pegmatitic fluids.

Introduction

For almost a century the granitic pegmatites of southern California have been a well-known source of gemstones and other minerals (Kunz, 1905; Merrill, 1914; Donnelly, 1936; Jahns and Wright, 1951; Sinkankas, 1957; Foord, 1976). In addition to gem material, some of these pegmatites contain interesting accessory minerals. The present study of the primary phosphate mineral lithiophilite and its secondary alteration products from the famous Stewart pegmatite near Pala was undertaken to better understand the occurrence and paragenesis of phosphate minerals in granitic pegmatites.

Phosphate minerals such as apatite, amblygonite, lithiophilite and others are common minor constituents of numerous granitic pegmatites (Moore, 1973, 1982). These pegmatitic phosphates are generally found to be altered by oxidation, hydration, cation leaching, and metasomatic replacement reactions. Such alteration is responsible for most of the nearly 150 secondary phosphate species now recognized from pegmatites. The extent of this phosphate alteration appears to be somewhat greater than is the case for many of the associated pegmatitic silicates. Because of this

general susceptibility to alteration, the potential usefulness of the phosphate minerals as indicators of changing conditions during the post-crystallization history of a pegmatite has long been recognized (Mason, 1941; Fisher, 1958; Černý, 1970; van Wambeke, 1971; Moore, 1982). Moreover, the widespread occurrence and diversity of the pegmatitic phosphates also provide a rationale for using these minerals to better understand the details of pegmatite crystallization. However, the complex parageneses of these phases have only recently begun to be elucidated (Moore, 1970, 1971, 1972a, 1981, 1982; Moore and Molin-Case, 1974; Fontan et al., 1976; Fransolet, 1976; Shigley and Brown, 1980; Mücke, 1981; Segeler et al., 1981; London and Burt, 1982a). While the broad outlines of phosphate crystal chemistry and the crystal structures of a number of phosphate minerals have been established as a result of these recent studies, details of the thermodynamic relationships among phosphate minerals have yet to be addressed in a comprehensive manner.

Schaller (1912) first described the phosphate minerals from Pala, but unfortunately his complete study of pegmatite mineralogy of this area was never published. Beyond some additional information reported by Murdoch (1943) and Jahns and Wright (1951), there has been little subsequent investigation of the Pala phosphates. This is in marked contrast with the extensive recent studies of phos-

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Table 1. Primary and secondary phosphate minerals from the Stewart pegmatite.

| Mineral* | Chemical formula** |
|----------------------------|---|
| Lithiophilite [†] | Li(Mn,Fe) ²⁺ PO ₄ |
| Sicklerite | Li _{1-x} (Mn _{1-x} Fe _x ³⁺)PO ₄ |
| Hureaulite | (Mn,Fe) ₅ ²⁺ (H ₂ O) ₄ (PO ₄) ₂ (PO ₃ OH) ₂ |
| Purpurite | (Mn,Fe) ³⁺ PO ₄ |
| Heterosite | (Fe,Mn) ³⁺ PO ₄ |
| Phosphosiderite | Fe ³⁺ (H ₂ O) ₂ PO ₄ |
| Stewartite | Mn ²⁺ (H ₂ O) ₄ (Fe ₂ ³⁺ (OH) ₂ (H ₂ O) ₂ (PO ₄) ₂) ₂ ·2H ₂ O |
| Amblygonite [‡] | (Li,Na)Al(PO ₄)(F,OH) |
| Triplite [§] | (Mn,Fe) ²⁺ F(PO ₄) |
| Triphylite [§] | Li(Fe,Mn) ²⁺ PO ₄ |

* List does not include several incompletely identified phosphate phases noted during this study.
 ** Taken from Moore (1982) and Fleischer (1983).
 † Primary phosphate minerals.
 ‡ Reported to occur by Jahns and Wright (1951), but not examined during this study.

phate minerals from other granitic pegmatites (see Mücke, 1981; Segeler et al., 1981; London and Burt, 1982a). Thus, the purposes of the present investigation were (1) to carefully reexamine the phosphate mineralogy of one of the Pala pegmatites to extend Schaller's earlier work in light of more recent ideas; (2) to use this information to evaluate the geologic history of the pegmatite; and (3) to compare these minerals with the phosphates reported from other granitic pegmatites. The Stewart pegmatite was chosen for study because it contains abundant lithiophilite crystals, and its interior portions are partly accessible through the existing underground workings of the Stewart Lithia mine. Table 1 lists the phosphate minerals reported from the pegmatite. Data gathered on the phosphate mineralogy and alteration sequence are used to interpret aspects of the overall geologic history of the Stewart pegmatite in the context of the Jahns-Burnham model of granitic pegmatite formation (Jahns and Burnham, 1969; Jahns, 1982).

Geologic setting

Pala is located in the northwest corner of San Diego County (Fig. 1). Several hundred granitic pegmatites, chiefly dikes, are exposed on the hillsides immediately surrounding the town. The geology of the area has been described by Larsen (1948, 1951) and Jahns (1954a, 1954b, 1979).

Much of the Pala pegmatite district is underlain by igneous intrusive rocks of the Cretaceous-age Peninsular Ranges (or Southern California) batholith. U-Pb and K-Ar radiometric age dates for batholithic rocks fall within the 130-90 m.y. time span (Banks and Silver, 1969; Krummenacher et al., 1975; Dalrymple, 1976). This orogenic-type batholith is a large, composite intrusive body

consisting of hundreds of individual plutons ranging up to several kilometers or larger in diameter. These plutons intrude into prebatholithic metasedimentary and metavolcanic rocks. They are composed of older gabbro grading to tonalite, granodiorite, quartz monzonite, and younger granite; with the first two rock types being the most voluminous constituents.

The pegmatite dikes at Pala are generally confined to the gabbroic plutons of the batholith, and are believed to represent products of the final stages of its magmatic differentiation and crystallization (Jahns, 1947; Jahns and Wright, 1951). The observed uniformity in the attitude and tabular form of these pegmatites has been taken as evidence for their formation by the crystallization of late-stage residual magmas as vein fillings along sheet-like fractures in the older and more competent gabbro. The pegmatites range from centimeters to meters in thickness and up to a kilometer in exposed length. They are composed primarily of feldspars, quartz, and micas, and most can be considered "simple" pegmatites on the basis of their homogeneous internal structure. However, several of the larger dikes such as the Stewart have a more complex internal structure and diverse mineralogy. Lithium minerals and gem materials, as well as the more unusual accessory minerals such as the phosphates, are virtually restricted to these "complex" pegmatites.

The Stewart pegmatite

The Stewart pegmatite occurs as an elongate outcrop of light-colored rock on the south-facing slope of Tourmaline Queen mountain two kilometers north of Pala. It extends over a distance of a kilometer with a northerly strike and a moderate westerly dip, and attains a maximum thickness of 25 meters. The Stewart Lithia mine, near the southern end of the dike, is a major gem producer (Jahns et al., 1974).

While an accurate modal composition is unavailable, Jahns (1953) published the following bulk composition for

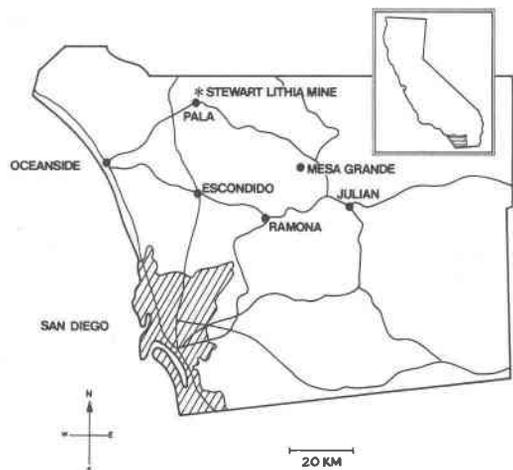


Fig. 1. Map of San Diego County showing the location of the Stewart Lithia mine near Pala.

the southern portion of the pegmatite (in wt.% oxides): SiO₂ 74.9, Al₂O₃ 14.9, CaO 0.1, Na₂O 3.6, K₂O 5.2, Li₂O 0.7, F 0.4, H₂O 0.4, total 100.2. Major constituents include microcline-perthite, albite, quartz, muscovite, lepidolite, spodumene, amblygonite, and tourmaline, while additional accessory minerals are rich in Li, P, Be, B, and Mn (for details, see Jahns and Wright, 1951). Within the pegmatite, mineral assemblages are arranged in subparallel, layered zones both above and below a discontinuous quartz-spodumene core (Fig. 2). Zones above the core are generally coarser-grained and rich in microcline, whereas those below contain both coarse- and fine-grained material and have more albite. Gem-bearing pockets and massive lepidolite orebodies are located directly underneath the quartz core. This zonal arrangement corresponds to the generalized internal zonal sequence of Cameron et al. (1949) and Norton (1983).

Occurrence of phosphate minerals

Phosphate minerals can be recognized as dark-stained masses or nodules on the tunnel walls in the Stewart Lithia mine (Fig. 3). These masses are as much as 40 cm across, are somewhat equidimensional in shape, and occur in the upper quartz-microcline intermediate zone (Fig. 2). Although quite altered, they represent large, subhedral to euhedral crystals of lithiophilite whose exterior surfaces are covered by either a few simple crystal faces (Fig. 4) or irregular growth surfaces. We infer lithiophilite to be a primary pegmatite constituent on the basis of its crystal morphology, coarse grain size, textural relationships with adjoining silicates, restricted zonal occurrence, and finally a lack of evidence that it has replaced any earlier-formed mineral. Some 130 crystals or crystal fragments from the mine were examined during the course of this study and are now housed in the Stanford University mineral collection.

Amblygonite occurs as coarse-grained crystalline aggregates with lepidolite in portions of the quartz-spodumene core (Jahns and Wright, 1951). It is now virtually impossible to collect in the mine because it was largely removed

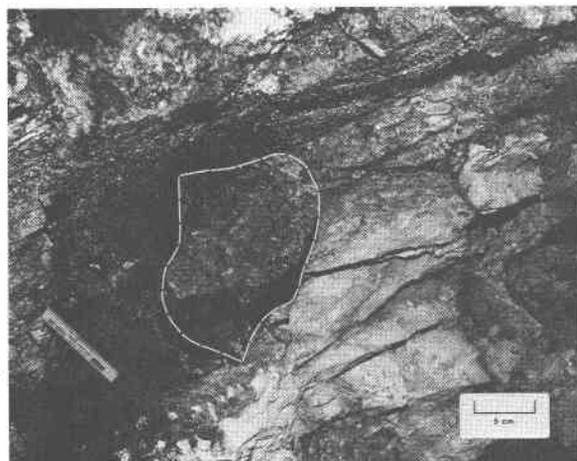


Fig. 3. Photograph of a lithiophilite crystal embedded in pegmatite host rock in the old underground workings of the Stewart Lithia mine. The outline of the crystal has been highlighted with a dashed white line.

during early mining operations. Thus, neither it nor its possible alteration products were characterized in this study (see, however, information in Murdoch and Webb, 1966, p. 78 and 234).

Schaller (1912) and Jahns and Wright (1951) reported small amounts of primary triphylite and triplite from the mine, but samples of neither phase could be collected to establish their parageneses.

Mineral characterization

Lithiophilite crystals from the pegmatite are extensively altered. While a few contain small areas of remnant lithiophilite, most are entirely composed of secondary phosphate minerals and manganese oxides present as impure massive areas, irregular grains, small veinlets, and rarely as tiny crystals. Optical properties were measured from fragments immersed in refractive index liquids. X-ray data, obtained with a Philips-Norelco diffractometer, were refined using the PODEX2 computer program of A. Sleight (Dupont Central Research Laboratories). Compositional data (summarized in Table 2) were primarily obtained using an ARL EMX-SM electron microprobe for all constituent elements initially identified by wavelength scans. Reduction of background- and drift-corrected data was carried out using the MAGIC IV computer program of Colby (1968). Selected samples were analyzed for lithium by atomic absorption and water by a micro-coulometric technique (Table 3), and for their trace elements by emission spectroscopy (Table 4).

To date only a small number of secondary phosphates have been identified from the Stewart Lithia mine. In general these phases are intergrown on a fine scale, and as such could not be separated as homogeneous grains. Thus, their complete characterization was impossible in some instances. Phases that could not be fully identified are designated by a letter (e.g., phase 'K') in the following dis-

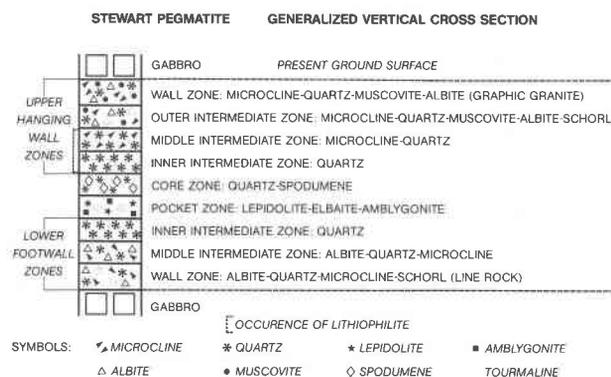


Fig. 2. Generalized vertical cross section through the southern portion of the Stewart pegmatite illustrating the mineral assemblages that comprise the internal zoning structure.

Table 2. Representative microprobe analyses of selected primary and secondary phosphates from the Stewart pegmatite.

| Microprobe analyses (weight percent oxides)* | | | | | | | | |
|--|----------------|-----------|---------------|------------|--------------|-----------|-----------------|------------|
| Mineral Sample # # of analyses | Lithiophilite | | Sicklerite | | Hureaulite I | | Hureaulite II | |
| | 7621 | P54 | P25 | P54 | P25 | P54 | P25 | 7621 |
| | 8 | 2 | 12 | 2 | 6 | 3 | 13 | 8 |
| P ₂ O ₅ | 45.87(61)† | 46.57(99) | 46.68(75) | 47.04(46) | 39.36(61) | 39.49(37) | 37.36(279) | 38.03(163) |
| FeO | 8.01(85) | 8.02(1) | - | - | 5.94(166) | 7.89(18) | 9.37(148) | 3.77(289) |
| Fe ₂ O ₃ | - | - | 8.06(36) | 9.07(7) | - | - | - | - |
| MnO | 36.46(52) | 37.81(44) | 37.12(32) | 38.53(22) | 39.26(115) | 39.62(35) | 31.98(482) | 38.73(328) |
| Mn ₂ O ₃ | - | - | - | - | - | - | - | - |
| CaO | 0.05(2) | 0.06(1) | 0.12(8) | 0.08(3) | 0.80(15) | 0.32(4) | 1.85(76) | 1.52(105) |
| MgO | n.d.‡ | n.d. | n.d. | n.d. | 0.08(7) | 0.07(3) | 0.10(9) | 0.10(3) |
| K ₂ O | 0.03(2) | n.d. | 0.04(3) | n.d. | n.d. | n.d. | 0.18(23) | 0.04(3) |
| Na ₂ O | 0.03(3) | 0.04(1) | 0.13(7) | 0.04(1) | 0.08(4) | n.d. | 0.35(20) | 0.27(25) |
| Σ | 90.45 | 92.50 | 92.15 | 94.76 | 85.52 | 87.39 | 81.19 | 82.46 |
| (Li ₂ O+H ₂ O)** | 9.55 | 7.50 | 7.85 | 5.24 | 14.48 | 12.61 | 18.81 | 17.54 |
| Cell contents (number of atoms)†† | | | | | | | | |
| Anion basis | 4 | 4 | 4 | 4 | 20 | 20 | 20 | 20 |
| P | 1.008 | 1.034 | 1.001 | 1.023 | 3.981 | 4.039 | 3.546 | 3.662 |
| Fe | 0.173 | 0.176 | 0.153 | 0.174 | 0.595 | 0.799 | 0.876 | 0.355 |
| Mn | 0.802 | 0.840 | 0.796 | 0.838 | 3.967 | 4.054 | 3.040 | 3.730 |
| Ca | 0.001 | 0.001 | 0.003 | 0.002 | 0.100 | 0.043 | 0.222 | 0.184 |
| Mg | - | - | - | - | 0.014 | 0.014 | 0.013 | 0.014 |
| K | 0.001 | - | 0.001 | - | - | - | 0.027 | 0.005 |
| Na | 0.001 | 0.002 | 0.006 | 0.002 | 0.014 | - | 0.067 | 0.055 |
| (Li+H) | 0.999 | 0.791 | 0.943 | 0.676 | 10.746 | 9.822 | 13.859 | 13.077 |
| Σ cations | 2.985 | 2.844 | 2.903 | 2.715 | 19.417 | 18.771 | 21.650 | 21.082 |
| Microprobe analyses (weight percent oxides)* | | | | | | | | |
| Mineral Sample # # of analyses | Hureaulite III | | Hureaulite IV | Phase 'F' | Purpurite I | Phase 'E' | Phosphosiderite | Phase 'K' |
| | P25 | P30 | 8122 | P30 | P30 | P25 | P30 | P30 |
| | 8 | 4 | 2 | 8 | 2 | 1 | 2 | 11 |
| P ₂ O ₅ | 38.52(93) | 39.51(49) | 40.13(6) | 39.71(521) | 48.08(66) | 36.61 | 37.82(95) | 40.84(116) |
| FeO | 0.48(66) | 0.27(23) | 0.22(1) | - | - | - | - | - |
| Fe ₂ O ₃ | - | - | - | 8.94(329) | 8.22(27) | 30.29 | 39.72(153) | 7.82(176) |
| MnO | 46.14(55) | 46.22(18) | 46.05(38) | - | - | - | - | - |
| Mn ₂ O ₃ | - | - | - | 31.37(370) | 43.18(38) | 23.05 | 3.15(30) | 39.09(340) |
| CaO | 0.21(16) | 0.27(33) | 0.10(1) | 16.77(519) | 0.15(5) | 0.74 | 0.08(5) | 0.29(24) |
| MgO | 0.03(1) | 0.04(2) | 0.04(1) | n.d. | n.d. | 0.03 | 0.04(2) | n.d. |
| K ₂ O | n.d. | 0.03(1) | 0.04(1) | 0.06(2) | 0.05(1) | 6.25 | 0.11(14) | 0.06(6) |
| Na ₂ O | n.d. | n.d. | n.d. | 0.46(26) | 0.27(2) | 0.59 | 0.18(17) | 0.10(13) |
| Σ | 85.38 | 86.34 | 86.58 | 97.31 | 99.95 | 97.56 | 81.10 | 88.20 |
| (Li ₂ O+H ₂ O) | 14.62 | 13.66 | 13.42 | 2.69 | 0.05 | 2.44 | 18.90 | 11.80 |
| Cell contents (number of atoms) | | | | | | | | |
| Anion basis | 20 | 20 | 20 | - | 4 | - | 6 | - |
| P | 3.836 | 3.961 | 4.016 | - | 1.012 | - | 1.001 | - |
| Fe | 0.049 | 0.028 | 0.021 | - | 0.154 | - | 0.934 | - |
| Mn | 4.592 | 4.636 | 4.614 | - | 0.818 | - | 0.075 | - |
| Ca | 0.028 | 0.036 | 0.014 | - | 0.004 | - | 0.002 | - |
| Mg | 0.005 | 0.007 | 0.007 | - | - | - | 0.002 | - |
| K | - | 0.004 | 0.005 | - | 0.001 | - | 0.004 | - |
| Na | - | - | - | - | 0.012 | - | 0.011 | - |
| (Li+H) | 11.389 | 10.788 | 10.592 | - | 0.008 | - | 3.942 | - |
| Σ cations | 19.899 | 19.460 | 19.296 | - | 2.009 | - | 5.896 | - |

* ARL EMX-SM electron microprobe, operating at 15 kV and 0.1 μA (sample current 0.02 μA), spot diameter < 10 μm. Mineral standards - spessartine (Mn), apatite (P), willemite (Mg), olivine (Fe), albite (Na,K,Ca), orthoclase (Na,K). Weight percentages of Fe and Mn oxides refined on the basis of assumed ideal stoichiometry.

† Number in parentheses represents the estimated standard deviation (esd) in terms of least units cited.

‡ n.d. = not detected; values less than 0.03 wt.%.

** Volatile content calculated by difference.

†† Calculated on the basis of assumed volatile content (H₂O:Li₂O in wt.%) derived from atomic absorption results - lithiophilite (0:total), sicklerite (2:total-2), hureaulite I (12:total-12), all other phases (total:0).

Table 3. Data on water and lithium content for selected minerals from the Stewart pegmatite.

| Mineral | H ₂ O(wt.%) [*] | No.** | Li ₂ O(wt.%) [†] | | No.** |
|--------------------|-------------------------------------|-------|--------------------------------------|-----------|-------|
| | | | Average | Range | |
| Lithiophilite | n.d. ^{††} | 0 | 6.47 | 4.36-9.61 | 5 |
| Sicklerite | 2.0 | 1 | 3.71 | 2.27-5.52 | 11 |
| Hureaulite I | 12.0 | 1 | 0.83 | 0.32-3.10 | 9 |
| Hureaulite II | 14.9 | 1 | 0.38 | 0.37-0.78 | 3 |
| Hureaulite III | 12.0 | 1 | 0.0 | 0.0 | 1 |
| Phosphosiderite | 18.0 | 1 | n.d. | n.d. | 0 |
| Phase 'F' | 3.7 | 1 | 0.18 | 0.00-0.37 | 2 |
| Manganese Oxide(s) | 35.0 | 1 | 0.0 | 0.0 | 8 |

* Water contents measured on representative, one-milligram samples of the indicated minerals by a microcoulometric technique using a Dupont Moisture Analyzer. Performed by M. Cremer, Analytical Branch, U.S. Geological Survey, Menlo Park (Job #KS42).

** Number of samples analyzed for each mineral.

† Lithium contents measured on representative samples of the indicated minerals by the atomic absorption method. Using a Perkin-Elmer Model 303 Spectrophotometer, standard solutions covering the range of 1-20 ppm Li were run against unknown solutions containing the dissolved minerals. Values listed represent calculated Li₂O contents for each mineral.

†† n.d. = not measured. Sufficient unaltered lithiophilite could not be obtained for a water content determination.

discussion. Table 5 summarizes mineralogical data on the various secondary phosphates examined during this study.

Descriptions of individual minerals

Lithiophilite $Li(Mn, Fe)^{2+}PO_4$

The large crystals of lithiophilite from the mine are equant to tabular in shape and have a simple morphology (similar to that noted by Goldschmidt (1923) and Chapman (1943)). From measurements with a contact goniometer on 68 crystals, the more important crystal faces in terms of both development and frequency of occurrence are: d {011}, l {021}, b {010}—present on all crystals; ε {120}, t {110}, e {101}—present on some crystals; and a {100}, v {203}—rarely present. Most specimens represent single crystals, but a few consist of two or more intergrown crystals (Fig. 4). No twinning relationships were noted in such instances. Frequently, crystal faces are slightly curved or otherwise deformed due perhaps to uneven initial growth or to secondary alteration of the parent lithiophilite.

In hand specimen, remnant lithiophilite has a pale pinkish-brown color, while under the microscope it is seen as colorless, blocky areas replaced by either reddish-orange hureaulite (Fig. 5) or pale yellow sicklerite. Microprobe analyses (Table 2) show Stewart lithiophilite to have an Mn/(Mn + Fe) ratio of about 0.8; it displays optical and physical properties and unit-cell parameters consistent with values expected on the basis of this composition (Penfield and Pratt, 1895; Blanchard, 1981; Franolet et al., 1982). All lithiophilite crystals examined have a similar Mn-Fe content. There is no evidence for more than one generation

of lithiophilite from the pegmatite, nor for any compositional zonation within a given crystal. Compared to specimens from other pegmatites, Stewart lithiophilite is most similar to material from Branchville (Brush and Dana, 1878), Varuträsk (Quensel, 1940), Wodgina (Mason, 1941), Viitaniemi (Volborth, 1954), and the White Picacho area (London and Burt, 1982a). At these occurrences, lithiophilite is somewhat more abundant than triphylite, thus reflecting their overall "manganese-rich" pegmatite chemistry. In contrast, triphylite and its secondary alteration products dominate the phosphate parageneses at more "iron-rich" granitic pegmatites such as those in the Black Hills (Moore, 1973, 1982), in the New England area (Moore, 1973; Segeler et al., 1981), and at Hagendorf (Strunz, 1952; Mücke, 1981).

Sicklerite $Li_{1-x}(Mn^{2+}_x Fe^{3+}_x)PO_4$

Based on textural relationships, sicklerite appears to be the initial replacement product of Stewart lithiophilite. Sicklerite is typically referred to as a species with the above simplified formula where the iron is supposedly all trivalent, the manganese all divalent, and with a proportionate amount of lithium removed by leaching (Mason, 1941; Fleischer, 1983). However, analyses of sicklerite frequently show appreciable Mn³⁺ (e.g., Schaller, 1912; Mason, 1941; Fontan et al., 1976), and considering the potential difficulties of analyzing impure materials such as some secondary phosphates for several valence states of iron and/or manganese, this formulation for sicklerite may not be entirely correct. Sicklerite is structurally and chemically very similar to lithiophilite, and may not represent a distinct species but rather only a less well defined intermediate stage between lithiophilite and purpurite (see Moore, 1982). Thus, further work on pure material, if such becomes available, appears necessary to establish a suitable formula for sicklerite.

Table 4. Data on trace elements in a sample of lithiophilite from the Stewart pegmatite.

| Concentration | Elements* |
|---------------|---|
| major | P, Mn, Fe, Li |
| >0.1% | Al, Ca, Na, K |
| <0.1% | Ge, Hf, U, La |
| <0.01% | Sb, As, Bi, B, Cd, Cs, Cr, Co, Cu, Au, In, Ir, Pb, Mg, Hg, Mo, Ni, Os, Pd, Pt, Si, Sn, V, Y, Zn, Zr, Th |
| <0.001% | Ba, Be, Ga, Ag, Sr, Ce |
| not detected | Re, Rb, Rh, Ru, Sc, Ta, Te, Tl, Ti, W |

* Semiquantitative spectrographic analysis of a representative sample of lithiophilite from the Stewart pegmatite. Sample prepared and analyzed by M. Pyzyra (Center for Materials Research, Stanford University) using a Jarrell-Ash 3.4-meter emission spectrograph. Analyses of several secondary phosphates from the pegmatite gave similar results.

Table 5. Mineralogical data for selected primary and secondary phosphate minerals from the Stewart pegmatite.

| Mineral Sample # | Lithiophilite 7621 | Sicklerite 7621 | Hureaulite I P25 | Hureaulite II P25 | Hureaulite III P25 | Hureaulite IV 8621 | Phosphosiderite 8669 |
|-----------------------------------|-----------------------|----------------------|---------------------------|--------------------------|-----------------------|-----------------------|--------------------------|
| (Mn/Mn+Fe) ratio | 0.82 | 0.80-0.82 | 0.83-0.92 | 0.71-0.91 | 0.99 | 0.99 | 0.07-0.08 |
| D | 3.42(19) [†] | 3.37(25) | 3.04(26) | 2.76(25) | 3.28(65) | n.d. ^{††} | 2.65(10) |
| Unit-cell parameters [§] | | | | | | | |
| a(Å) | 6.074(2) | 6.030(15) | 17.589(3) | 17.547(13) | 17.623(3) | 17.598 | 5.331(6) |
| b(Å) | 10.451(2) | 10.082(9) | 9.097(2) | 9.077(21) | 9.127(3) | 9.066 | 9.795(7) |
| c(Å) | 4.727(1) | 4.750(5) | 9.433(3) | 9.437(14) | 9.490(4) | 9.398 | 8.710(8) |
| β(°) | — | — | 96.78(4) | 96.57(13) | 96.57(33) | 96.58 | 90.91(19) |
| V(Å ³) | 300.11(8) | 288.76(52) | 1498.79(54) | 1493.21(231) | 1516.62(64) | 1489.50 | 454.81(56) |
| # of reflections | 19 | 17 | 33 | 25 | 37 | — | 16 |
| Optical parameters | | | | | | | |
| α | 1.669(1) | 1.710-1.720 | 1.648(1) | n.d. | 1.652-1.654 | 1.640(2) | >1.69 |
| β | 1.673(1) | 1.730-1.738 | 1.659(1) | n.d. | 1.656-1.657 | 1.649(2) | >1.69 |
| γ | 1.680(1) | >1.738 | 1.662(1) | n.d. | >1.660 | 1.655(2) | >1.69 |
| 2V | 70° | >60° | 70-80° | >60° | >70° | 77° | moderate |
| optic sign | (+) | (-) | (-) | (-) | (-) | (-) | n.d. |
| dispersion | r<<v | r>>v | r<<v | r<<v | n.d. | r<v | n.d. |
| relief | moderate | moderate | moderate | moderate | moderate | moderate | moderate |
| birefringence | low | moderate | moderate | moderate | moderate | moderate | moderate |
| color | | | | | | | |
| hand specimen | pink-brown | yellow- to red brown | yellow- to red brown | brown- to gray-yellow | pink- to red-brown | pink-red | violet to blue-violet |
| thin section | colorless | brown-yellow | colorless to yellow-green | yellow-green | colorless | colorless | pale blue to pale violet |
| pleochroism | none | pale to deep yellow | colorless to red-orange | pale green to red-orange | none | none | pale blue to pale violet |

[†] Numbers in parentheses represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left.

^{††} n.d. = not determined due to a lack of suitable material.

[§] Refined unit-cell parameters derived from X-ray powder diffraction patterns for all minerals shown except Hureaulite IV, whose parameters were measured from precession photographs. A silicon metal internal standard (Hubbard *et al.*, 1975) was used in the preparation of the diffractometer patterns.

In hand specimen sicklerite is present as dark brown masses. Under the microscope it is usually seen as being intergrown with other secondary phosphates (Fig. 6). The brownish-yellow sicklerite has an optical orientation and faint relict cleavage inherited from the parent lithiophilite.

Sicklerite compositional data (Table 2) agree with earlier published information of Schaller (1915). The consistent Mn/(Mn+Fe) ratio (0.80-0.82) in this material confirms

that these two cations are relatively immobile during the lithiophilite alteration sequence when little metasomatism is involved (Mason, 1941; Moore, 1973, 1982). Stewart sicklerite resembles material from the pegmatites at Viita-

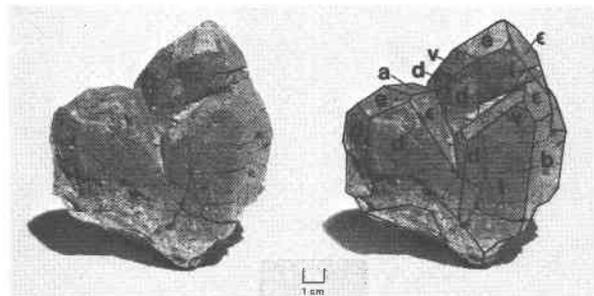


Fig. 4. Photograph and superimposed drawing of a lithiophilite crystal group from the Stewart Lithia mine. The group consists of several intergrown crystals oriented in a parallel fashion. Crystal faces are outlined and are identified by conventional letter designations (see text).

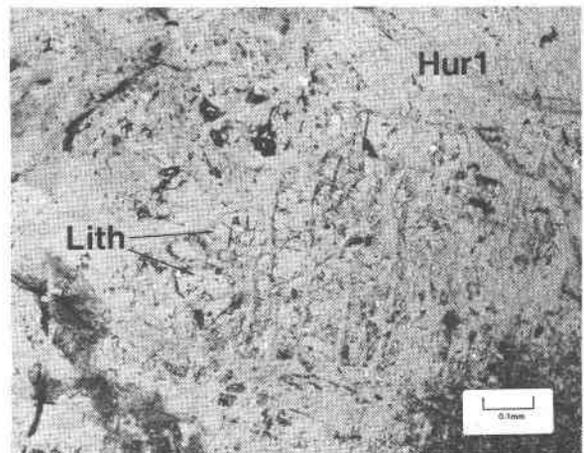


Fig. 5. Photomicrograph showing the alteration of lithiophilite (lith) to hureaulite I (hur1). The lithiophilite appears as colorless, high-relief grains surrounded by colorless hureaulite and other minor secondary phosphates. Plain light.

niemi (Mason, 1941; Volborth, 1954), Wodgina (Mason, 1941), the White Picacho district (London and Burt, 1982a), and a locality in Siberia (Kosals, 1968), and represents one of the more Mn-rich members of the sicklerite-ferisicklerite series yet described (see Fontan et al., 1976).

Hureaulite $(Mn,Fe)_5^{2+}(H_2O)_4(PO_4)_2(PO_3OH)_2$

Hureaulite has previously been reported from Pala (Schaller, 1912, 1915; Mason, 1941; Jahns and Wright, 1951). However, from data gathered during this study, four types of hureaulite (labeled I–IV) can be distinguished on the basis of their chemistry and appearance. We suggest that these are only compositional varieties of the same mineral (or an impure mixture of it and some unknown phase(s) in the case of hureaulite II) that may or may not be represented in phosphate material from other pegmatites. We do not propose that these type designations be formally adopted unless it could be shown that their Stewart occurrence is not unique. With the exception of hureaulite II, powder diffraction data for the other varieties of hureaulite are consistent with the calculated and observed X-ray patterns for this mineral (Fisher, 1964; Moore and Ito, 1978) with no indication of other admixed phases.

Hureaulite I is a pinkish-, reddish-, or yellowish-brown massive phase associated with lithiophilite and sicklerite. Although normally colorless in thin section, it sometimes displays vivid orange-red pleochroism. The cause of this color variation is probably due to differences in the Mn/Fe content or to the incipient oxidation of these cations. Compositional data (Table 2) indicate this material is an Fe-bearing hureaulite, $Mn/(Mn+Fe) = 0.83\text{--}0.92$. This range of Fe content is consistent with both the Mn–Fe variability noted in lithiophilite and sicklerite, and what has been reported for hureaulite from other localities (Moore and Araki, 1973; Fransolet, 1976).

Hureaulite II is more difficult to clearly identify because of its intergrown association with other secondary phosphates. In hand specimen it appears brownish- or yellowish-gray, while under the microscope it is pale green with occasional orange-red pleochroism (Figs. 6 and 7). With crossed nicols, a random, mosaic arrangement of irregular-shaped grains or “domains” exhibiting anomalous birefringence and extinction is visible. Like hureaulite I, hureaulite II contains some Fe, $Mn/(Mn+Fe) = 0.71\text{--}0.91$, but it exhibits greater variability in other constituent oxides. Both types may represent the same generation of this mineral, but the lack of uniform extinction, greater variation in composition, and apparent inhomogeneity of the type II material suggest that they are not the same. Hureaulite II may possibly be a mixture of hureaulite and some other unknown phase, although the identity of this other phase(s) could not be clearly established from X-ray data.

Hureaulite II seems to be related to the enigmatic mineral “salmonsite” reported by Schaller (1912). While his description matches the observed appearance of our hureaulite II, X-ray diffraction peaks attributed to “salmonsite” by Fisher and Atlas (JCPDS File 13-337) could not be

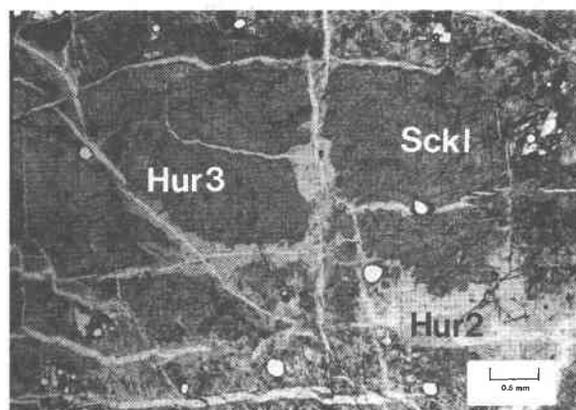


Fig. 6. Photomicrograph of massive, yellow sicklerite (sck1) being replaced by pale green hureaulite II (hur2). Both minerals are cut by narrow veinlets of colorless hureaulite III (hur3). Plain light.

identified in hureaulite II powder patterns. From a reexamination of Stewart material studied earlier by Fisher (1958), Moore and Ito (1978) showed “salmonsite” to be a mixture of hureaulite and jahnsite. Our hureaulite II may be the same as the material they described, but jahnsite could not be recognized in thin section or X-ray diffraction patterns. A lack of suitable samples of hureaulite II prevented its full characterization. We suggest it is the same phase as Schaller’s “salmonsite” and, at least in part, the same as the material examined by Moore and Ito (1978).

The third type of Stewart hureaulite, which occurs as pinkish veinlets, is equivalent to the phase “palaite” of Schaller (1912; also Mason, 1941; Moore and Araki, 1973). Under the microscope, these veinlets are colorless and have a fibrous appearance (Figs. 6, 7, and 8). In contrast to the two previous types, hureaulite III has almost no Fe, $Mn/(Mn+Fe) = 0.99$, or other minor constituents (Table

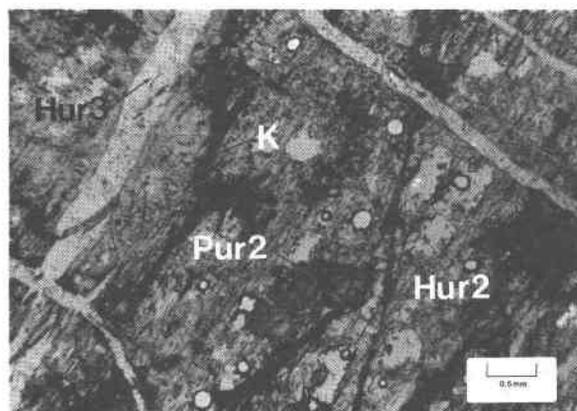


Fig. 7. Photomicrograph of massive, pale green hureaulite II (hur2) containing small areas of violet-red purpurite II (pur2), greenish-yellow veinlets of phase ‘K’ (K), and transected by later veinlets of colorless hureaulite III (hur3). Plain light.

2). Textural evidence suggests that material on either side of hureaulite III veinlets was either spread apart or somewhat replaced during veinlet formation.

Hureaulite IV occurs as small, rose-red euhedral crystals as much as 1 mm across. It is found in exterior cavities in the altered lithiophilite along with phosphosiderite and stewartite (see Murdoch, 1943). It is the least abundant of the four varieties, and like type III, it contains little Fe ($Mn/(Mn+Fe) = 0.99$; see Table 2).

These four types of Stewart hureaulite correspond to material from the pegmatites at Hagendorf (Strunz, 1954), Mangualde (Mário de Jesus, 1933), La Vilate (Des Cloizeaux, 1858), Viitaniemi (Volborth, 1954), and Branchville (Brush and Dana, 1890). From a study of lithiophilite alteration at several localities, Fransolet (1976) distinguished two genetic types of hureaulite: (1) an early iron-bearing colorless variety similar to our types I and II, and (2) a later, iron-poor reddish variety that corresponds to our types III and IV.

Purpurite $(Mn,Fe)^{3+}PO_4$

Purpurite, first described from Pala by Graton and Schaller (1905), is found in two forms in the altered lithiophilite. Purpurite I occurs as bright red rims on some yellow sicklerite—these rims are optically continuous with the sicklerite and display a vivid red-green pleochroism. Purpurite II is present as red- to brownish-violet areas with a fibrous, radiating habit (Fig. 7). Neither type was found in sufficient, homogeneous amounts for complete characterization, but compositional data (Table 2) indicate both have similar chemistry, $Mn/(Mn+Fe) = 0.80$. We believe that both types represent the same generation of purpurite.

Phosphosiderite $Fe^{3+}(H_2O)_2PO_4$

Phosphosiderite is occasionally found as conspicuous, bright, blue-violet microcrystalline aggregates along with stewartite in exterior cavities in the altered lithiophilite. Schaller (1912) referred to this material as "strengite." Phosphosiderite can sometimes be confused with purpurite II because of their similar appearance, but it is more bluish-violet in color whereas the latter is reddish-violet. Phosphosiderite is the most Fe-rich secondary phosphate from the pegmatite (Table 2; also Schaller, 1915), which serves to further differentiate it from purpurite. In comparison to material from the pegmatites at Boqueirão (Murdoch, 1958) and Pleystein (Wilk, 1960), Stewart phosphosiderite is remarkably Mn-rich (about 3 wt.% MnO). In spite of this, X-ray data are consistent with the Pleystein material (McConnell, 1939; Wilk, 1960).

Stewartite $Mn^{2+}(H_2O)_4(Fe_2^{3+}(OH)_2(H_2O)_2(PO_4)_2) \cdot 2H_2O$

Stewartite is perhaps the most noticeable but at the same time one of the rarest of the Pala phosphates described by Schaller (1912). It was found as small, bright yellow crystals on only two altered lithiophilite crystals, and was identified primarily by its described association with phosphosiderite.

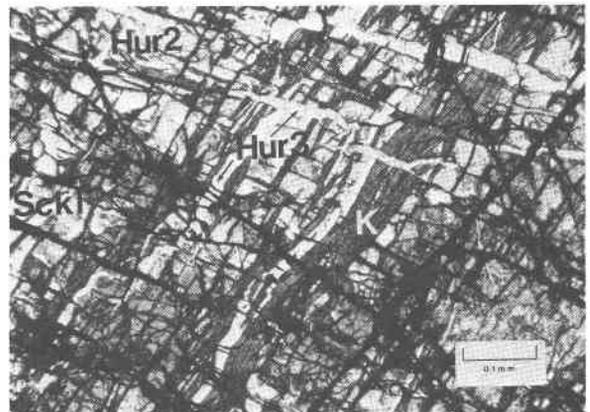


Fig. 8. Photomicrograph of massive, yellow sicklerite (sck1) and minor pale green hureaulite II (hur2) cut by veinlets of yellowish-green phase 'K' (K) and then by veinlets of colorless hureaulite III (hur3). Plain light.

Insufficient material could be found for complete characterization, thus making it one of the least well documented of the Stewart phosphates.

Minor phases

Several additional secondary phosphates were noted in the altered lithiophilite but could not be fully identified because of their limited abundance and impure condition. Phase 'K' (Fig. 7, 8) occurs as thin, greenish-yellow veinlets, and may be related to a second type of stewartite according to Schaller (1912). Phase 'F' (Fig. 9), found as reddish-brown areas in sicklerite, appears to be a calcic-sicklerite similar to the material described by Jahns (1952). Several violet grains, referred to as phase 'E', have a relatively high potassium content, and may be leucophosphite (Moore, 1972b), but this could not be further substantiated. The abundant manganese oxides that coat the altered lithiophilite crystals were examined in a preliminary manner by infrared spectroscopy, which indicated this material to be a

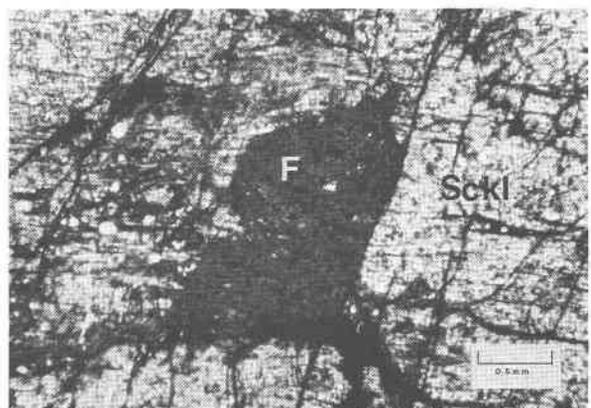


Fig. 9. Photomicrograph of reddish-brown phase 'F' (F) in massive, yellow sicklerite (sck1). Plain light.

mixture of several phases (G. Rossman, oral comm., 1980). Characterization of these minor phases awaits their discovery in quantities suitable for complete study.

Several silicate minerals were discovered in small amounts within the altered lithiophilite crystals. Thin quartz veinlets with minor pale green muscovite and blue tourmaline fill fractures in several altered crystals. In addition, small euhedral crystals of blue tourmaline within the massive lithiophilite is evidence for the contemporaneous crystallization of both minerals.

Secondary alteration of lithiophilite

General observations

The overall extent of lithiophilite alteration seems to have been independent of the size of the original crystals. There is no apparent difference in the nature or extent of this alteration with respect to either the kinds of surrounding silicates or the relative position of a particular crystal within the intermediate zone of the pegmatite. Due to limited accessibility of the older mine workings, the degree of alteration relative to the proximity of either the present-day topography or the ground-water level could not be fully evaluated, but no such differences were noted.

A similar suite of secondary phosphates was found in each of the altered crystals, suggesting that they were all originally lithiophilite and not some other primary phosphate. The temporal and spatial succession of secondary phosphate formation was established on the basis of textural relationships. While there are different degrees of alteration evident among various crystals, the same relative paragenetic sequence among the secondary phosphates was always observed. We conclude that the Stewart lithiophilite crystals were all subjected to similar alteration conditions.

Replacement reactions proceeded from the outside of the original crystals inward at rates that varied with direction. This variation is apparent in the non-uniform width of the concentric bands of secondary phosphates that rim the central, remnant areas of lithiophilite. No preferential crystallographic or compositional control of alteration was evident. Initial lithiophilite alteration involved gradual but pervasive replacement by sicklerite, followed at some later time by the formation of more hydrated and more oxidized phases such as hureaulite and purpurite. One important factor governing alteration was the location of fractures and cleavage planes in the original lithiophilite, since many of the secondary phosphates replaced one another along such features. Small-scale transport of components by solution also played a role as indicated by the extensive veinlet formation in the altered crystals. However, there is little evidence for the introduction of externally-derived constituents into the lithiophilite alteration products (except for several of the uncommon phases such as 'F'). Neither is there any indication for the transport and redistribution of lithiophilite-derived components to other nearby portions of the pegmatite, since secondary phosphates have so far only been found within the altered crystals. The staining of silicate minerals around phosphate nodules by secondary

phosphates noted at other pegmatites seems to be absent at the Stewart mine.

Secondary replacement of lithiophilite was not a constant volume process, since most of the altered crystals exhibit evidence for changes in size and shape (bulging surfaces, curved fractures, filled veinlets, etc.). However, there are few if any open cavities or boxwork structures from which material was leached out on a large scale.

Alteration sequence

Based on their own observations and those of Schaller (1912), Jahns and Wright (1951) suggested the following alteration sequence for Stewart lithiophilite: lithiophilite → hureaulite → sicklerite → "salmonsite" + purpurite + "palaite" + stewartite + phosphosiderite → manganese oxides. Our modified sequence is shown in Figure 10. The replacement of lithiophilite by sicklerite, purpurite, and manganese oxides, first proposed by Quensel (1937, 1940) and then Mason (1941), is commonly recognized at numerous localities (Palache et al., 1951; Moore, 1973). The initial Mn/(Mn+Fe) ratio of the Stewart lithiophilite is maintained in the secondary phosphates in the early stages of the sequence, but departs from this value in later phases (as noted by Mason, 1941; and since by others). Thus, Mn-rich lithiophilite is eventually replaced by both Mn-rich and Fe-rich secondary phosphates.

Alteration reactions affecting the Stewart lithiophilite involved oxidation of Fe and Mn, concomitant leaching of Li (and ultimately P), and hydration. With the exception of certain minor phases, none of the secondary phosphates seems to have resulted from the metasomatic introduction of externally-derived components. Thus, almost all of the constituents required for the formation of the observed secondary phosphates originated within the lithiophilite crystals themselves.

Discussion

While the alteration sequence in Figure 10 shows an overall temporal relationship among the various secondary phosphates, their intergrown nature indicates that they probably formed in part contemporaneously. Thus, there appears to be no strictly sequential development of alteration reactions, but rather a tendency for them to partly overlap one another in time.

It has been suggested that lithium-rich granitic pegmatites containing gem pockets, such as the Stewart, crystallized at shallow crustal depths of only several kilometers (Ginzburg, 1960; Jahns and Burnham, 1969; Černý, 1982; Jahns, 1982). If correct, this would indicate that lithiophilite alteration in the Stewart pegmatite occurred at the shallow depths of pegmatite formation, and then in a near-surface weathering environment when the pegmatite was exposed by uplift and erosion. All secondary phosphates were formed within the original lithiophilite crystals. We believe that lithiophilite replacement began during the final stages of pegmatite crystallization.

Although available data are limited, the neighboring silicates in the pegmatite appear to have undergone alteration

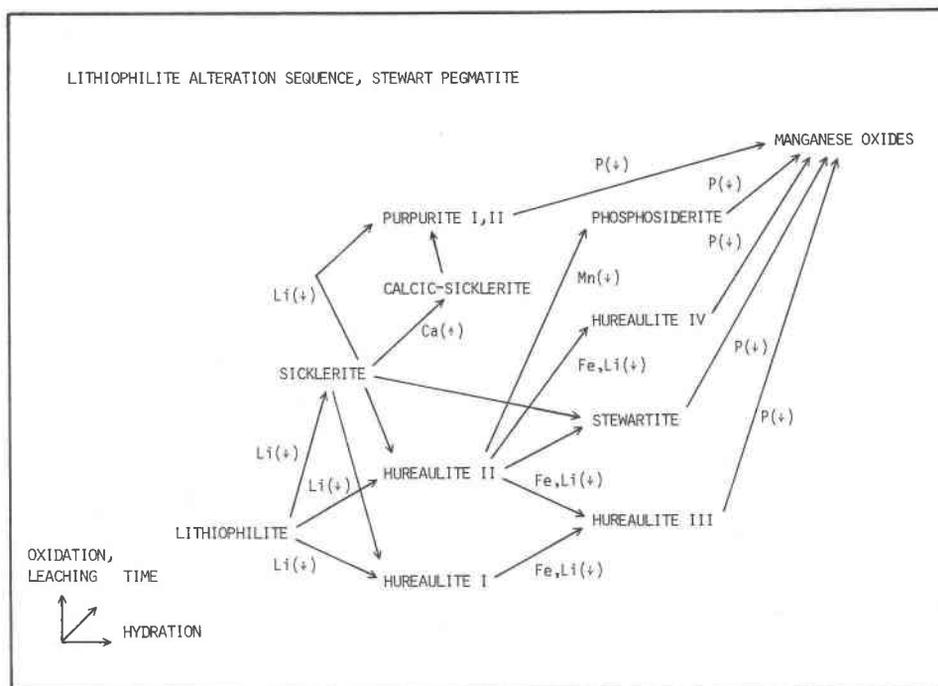


Fig. 10. A two-dimensional representation of the proposed alteration sequence for Stewart lithiophilite. Time succession proceeds from the lower left to upper right. In general, more hydrated phases (water and/or hydroxyl) are shown progressively to the right, while more oxidized and cation-leached phases are shown progressively upward. Symbols next to each element indicate its relative loss (\downarrow) or gain (\uparrow) during alteration reactions. Phase 'F' is shown as calcic-sicklerite.

similar to that of the lithiophilite. The intermediate zones of the pegmatite contains some clays of hydrothermal origin, but there are few indications of extensive metasomatic replacement since most primary silicates in this portion of the pegmatite are relatively fresh.

This lack of extensive metasomatism among the secondary phosphates was the most surprising result of this study, since most secondary phosphates seem to form by such processes (Moore, 1973, 1982). Thus, the extent of metasomatism is largely responsible for the diversity of secondary phosphate assemblages at various pegmatites (see Shigley, 1982). Since the types of secondary phosphates reflect the conditions and environment of pegmatite paragenesis, the phosphate assemblage of the Stewart pegmatite suggests a different set of alteration conditions as compared to many other localities. We believe these different conditions are primarily the result of rapid cooling and volatile loss from the pegmatite at the shallow depth of its formation.

Conditions of lithiophilite formation

The Stewart pegmatite is a typical example of a complex granitic pegmatite (Cameron et al., 1949; Jahns, 1955; Stewart, 1978; Norton, 1983), and its formation seems compatible with the Jahns-Burnham genetic model (1969; Jahns, 1982). The granitic pegmatites around Pala crystallized from residual, highly-differentiated magmas left over following the consolidation of the Peninsular Ranges

batholith. These magmas were injected into pre-existing, near-surface fractures in the batholithic host rocks, and there began to crystallize at temperatures around 800°C and pressures of 1-1.5 kbar (3-5 km; see Jahns and Wright, 1951; Foord, 1976; Taylor et al., 1979).

The primary nature of Stewart lithiophilite is clearly demonstrated by its textural relationships, and we infer a similar origin for amblygonite. Both minerals crystallized within the pegmatite magma system along with their respective associated primary silicates. Their restricted spatial distribution within the pegmatite suggests that they formed at specific and possibly limited periods of time. In both instances their occurrence is related to the internal zonal structure of the pegmatite, and not to the locations of later replacement mineralization.

The absence of primary phosphates among the first-formed mineral assemblages of the pegmatite wall and outer intermediate zones suggests the need for a period of magmatic differentiation to take place within the pegmatite magma before the phosphorus content reaches a sufficient level to permit the crystallization of lithiophilite and amblygonite. The exact level of phosphorus saturation in granitic pegmatitic magmas is unknown, but experimental results of Shigley and Brown (1982) demonstrate that lithiophilite can be crystallized from hydrous aluminosilicate melts containing about 2 wt.% P_2O_5 . For less siliceous felsic magmas, Watson and Capobianco (1981) suggest a saturation level of 1.4 wt.%.

Mutual textural relationships imply that lithiophilite crystallized along with the surrounding microcline and quartz. These features also indicate that the lithiophilite crystals did not grow outward into the magma from some point of attachment, as is thought to be the case for minerals in the later-formed gem pockets. Rather, field evidence suggests that both lithiophilite and the surrounding silicates formed contemporaneously in the presence of both pegmatite magma and exsolved volatile fluid during the intermediate stage of the Jahns–Burnham model (1969). We suggest that phosphorus and other components necessary for lithiophilite formation were selectively partitioned into and transported through this interconnected volatile fluid to the growing crystals. Similar mechanisms presumably contributed to the growth of the neighboring primary silicates. This magmatic behavior on the part of phosphorus is supported by the observation that lithiophilite and amblygonite are absent from the lower, albite-rich intermediate zones below the quartz core of the Stewart pegmatite that are believed to have formed at the same time but not in the presence of the volatile fluid (Jahns, 1982).

Moore (1973) concluded that formation of lithiophilite and amblygonite takes place over a temperature range of 500–700°C. Experimental results of Shigley and Brown (1982) suggest a lower interval of 400–500°C for the crystallization of lithiophilite. Deganello (1976) found triphylite to be unstable at temperature near 200°C in an oxidizing atmosphere. The presence of reduced phases such as lithiophilite may imply that relatively low oxygen fugacity conditions prevailed during the formation of the Stewart pegmatite, but this requires confirmation. Finally, the crystallization of only anhydrous phosphates such as lithiophilite from water-rich pegmatite magmas suggests that hydrated phosphates are not stable at temperatures of several hundred degrees Centigrade that are thought to exist during the formation of the intermediate zones of a pegmatite (Moore, 1973, 1982).

The scattered distribution of lithiophilite crystals within the intermediate zone of the pegmatite may be indicative of a rather slow rate of crystal nucleation with a more rapid growth once crystallization is initiated. Conversely, the components necessary for lithiophilite formation may have been limited in the pegmatite magma. The amount of P_2O_5 was apparently sufficient during lithiophilite formation since it was also plentiful during the later formation of amblygonite. The crystallization of lithiophilite could rather have been governed by the limited availability of iron or manganese. Small amounts of both elements could easily be taken up in garnet or tourmaline, whereas they would have been needed as major constituents in lithiophilite where $MnO + FeO = 45$ wt.%. This may account for the absence of lithiophilite as a mineral in the gem pockets, which formed during a later stage when the availability of iron and manganese was somewhat reduced. Amblygonite, however, is known as a pocket phase in other pegmatites (Palache et al., 1951).

Because of limited access to the Stewart pegmatite and the lack of observable amblygonite, it is difficult to es-

tablish the crystallization sequence among the primary phosphates. Moore (1973, 1982) proposed the sequence apatite → triphylite → amblygonite. In contrast, London and Burt (1982a) suggested the lithiophilite crystallized after montebrazite in pegmatites of the White Picacho district. This discrepancy may be a result of differing crystallization conditions at different pegmatites. Our observations at the Stewart pegmatite suggest that lithiophilite formation proceeded and may have been in part concomitant with the formation of amblygonite, which reflects the increasing activity of phosphorus and fluorine in the pegmatite magma system (London and Burt, 1982a, 1982b, 1982c).

Conditions of lithiophilite alteration

Secondary phosphates generally result from the solution, recrystallization, or oxidation of parent phosphate minerals, or by their metasomatic replacement (Černý, 1970). However, relating the phosphate paragenesis to the overall geologic history of a particular pegmatite is complicated because one cannot always directly link the occurrence of specific secondary phosphates to unique alteration conditions. A further hinderance is the lack of thermodynamic data for most phosphate minerals. Thus, while at the present time the phosphate mineralogy of a pegmatite at best gives a general indication of the alteration history, it does provide evidence regarding this history that is often less clearly reflected in other pegmatite mineral assemblages.

From our observations, all Stewart lithiophilite crystals were initially altered in a late-stage hydrothermal environment, and later under near-surface weathering conditions. Secondary phosphate formation took place entirely within the altered primary crystals, with released components, if any, being carried off by hydrothermal or groundwater solutions. Oxidation and cation leaching occurred in conjunction with hydration and limited introduction of some components from outside sources.

Referring to Figure 10, an indication of the particular conditions of lithiophilite alteration can be gained from several considerations. Both sicklerite and purpurite form under hydrothermal conditions during the final stages of pegmatite consolidation (Moore, 1973; Leavens and Simpson, 1975; Fontan et al., 1976). Temperatures during this stage of alteration are assumed to have been approximately 300–500°C on the basis of secondary fluid inclusions in some unaltered lithiophilite. Pressure-corrected homogenization temperatures (using the salinity equations of Potter et al., 1978) fall in the range of 275–350°C for these inclusions. Such temperatures for the hydrothermal alteration of lithiophilite agree with those of late-stage gem pocket formation in the nearby Himalaya pegmatite at Mesa Grande (Taylor et al., 1979). Subsequently-formed secondary phosphates apparently crystallized at even lower temperatures. Hureaulite and phosphosiderite crystallized in the range of about 150–200°C, which seems to roughly be the upper stability limit for hydrated secondary phosphates (Moore, 1973). The final alteration products like

stewartite and the manganese oxides formed under supergene weathering conditions.

Internally-generated hydrothermal fluids seem to have been responsible for some of the lithiophilite replacement. The changing chemistry of these residual fluids is reflected in the compositions of the several hureaulites—types I and II contain some iron while types III and IV are iron-free. A similar manganese enrichment of late-stage pegmatitic fluids was noted by Moore and Araki (1973), Fransolet (1976), and Foord (1976). On the other hand, the presence of stewartite and phosphosiderite indicates at least some local enrichment of iron in these late pegmatitic fluids.

The lack of extensive metasomatism among the secondary phosphates suggests that the conditions conducive to such phosphate alteration apparently did not exist for extended periods during the crystallization of the Stewart pegmatite.

Summary

The Stewart pegmatite is an outstanding example of a complex, lithium-rich granitic pegmatite which exhibits a vertical asymmetry in terms of many of its internal features. The sequence of primary mineral formation is difficult to ascertain, but assuming that crystallization generally proceeded from the border zone towards the core, then this sequence reflects an increase in Li-species (spodumene follows microcline) and in volatile content (lepidolite and amblygonite occur along with spodumene). Lithiophilite and presumably amblygonite represent primary pegmatite minerals.

Secondary alteration of lithiophilite involved oxidation, hydration, and cation leaching but little metasomatism. As a result of this study, most of the phosphate minerals first described from this area by Schaller (1912) have been more fully characterized. The phosphate assemblage at the Stewart pegmatite represents a classic lithiophilite alteration sequence similar to that reported from other pegmatite localities. No new phosphate mineral assemblages or paragenetic relationships were noted. Further study of the possible alteration of amblygonite, as well as the phosphate mineralogy of the other important Pala pegmatites, is needed.

The phosphate mineralogy of the Stewart pegmatite provides clues regarding mineral alteration during its late- and post-crystallization history in both hydrothermal and near-surface weathering environments. The limited nature of the phosphate assemblage appears to be primarily due to the lack of metasomatism which is so apparent in the phosphate mineralogy of other pegmatite localities. R. H. Jahns (oral comm., 1978) has suggested that the extent of metasomatism can be related to the depth of pegmatite formation. In shallow pegmatites, such as the Stewart, there apparently was little opportunity for residual pegmatitic fluids to interact with the primary phosphates under elevated temperature and pressure conditions for an extended period. Such conditions that favor extensive metasomatism are more likely to exist in pegmatites formed at greater depths.

Despite its notoriety as a gem producer, certain aspects

of the geology of the Stewart pegmatite have yet to receive careful study. There is little published information regarding the lithium aluminosilicate minerals of the pegmatite which Stewart (1978) and London and Burt (1982a, 1982b, 1982c) have shown to provide key information on the geologic evolution of complex granitic pegmatites. In addition, further laboratory experimental studies of pegmatite crystallization, such as those of Shigley and Brown (1982) to be described in detail in a forthcoming article, are needed to better understand granitic pegmatite genesis.

Acknowledgments

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