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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 ($LiAlSi_2O_6$), montebrasite ($LiAlPO_4(OH,F)$), and lithiophilite ($Li(Mn,Fe)PO_4$) 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 Spodumene has been replaced by eucryptite, albite, and micas.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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APPENDIX 2. POWDER DIFFRACTION DATA ON WHITE PICACHO MINERALS

Indexed reflections and refined cell parameters for spodumene, montebrasite, lithiophilite, and the major secondary phases are tabulated below. Powder patterns were obtained on an IRDAB XDC 700 Guinier camera, utilizing quartz-monochromated CuKα radiation generated at 40 kV and 18 mA. Patterns were indexed and refined using the program of Appleman and Evans (1973). Cell parameter refinements were based on the maximum number of observed indexed reflections for each mineral; however, only the ten most intense lines for each mineral are given below.

Mineral Crystal system Space group Cell parameters	hkl	d(obs)	I/I_o
spodumene	110	6.117	3
monoclinic	$\bar{1}11$	4.367	4
C2/c	020	4.191	2
a_o: 9.493*esd*0.019 Å	111	3.441	1
b_o: 8.383*esd*0.015 Å	$02\bar{1}$	3.186	10
c_o: 5.233*esd*0.006 Å	$\bar{2}21$	2.918	10
β : 110° 26'	310	2.793	6
	$\bar{2}02$	2.563	3
	002	2.448	5
	221	2.353	1
lithiophilite	011	4.279	3
orthorhombic	111	3.470	6
Pmcn	200	3.007	10
a_o: 6.057*esd*0.012 Å	031	2.782	5
b_o: 10.451*esd*0.020 Å	131	2.532	5
c_o:4.698*esd*0.009 Å	211	2.464	4
	222	1.746	3
	331	1.636	2
		1.517	4
		1.505	3

Mineral Crystal system Space group Cell parameters	hkl	d(obs)	I/I_o
montebrasite	110	4.681	7
triclinic	$\bar{1}01$	3.337	6
$P\bar{1}$	$1\bar{1}0$	3.283	5
a_o: 5.203 esd 0.008 Å	$12\bar{1}$	3.220	9
b_o: 7.179 esd 0.011 Å	120	3.171	10
c_o: 5.046 esd 0.008 Å	$1\bar{1}1$	2.970	5
α: 112° 27'	$0\bar{1}2$	2.499	3
β: 97° 51'	$21\bar{1}$	2.400	5
γ: 67° 50'	211	2.132	3
	012	1.963	4
eucryptite	110	6.741	2
rhombohedral	012	4.199	2
$R\bar{3}$	211	3.961	6
a_o: 13.448 esd 0.018 Å	300	3.892	1
c_o: 8.985 esd 0.012 Å	220	3.377	8
	122	3.154	2
	330	2.742	10
	410	2.551	5
	303	2.378	2
	113	2.251	2

Mineral Crystal system Space group Cell parameters	hkl	d(obs)	I/I_o
albite	020	6.381	1
triclinic	$20\bar{1}$	4.032	7
$C\bar{1}$	111	3.779	4
a_o : 8.131*esd*0.007 Å	130	3.685	1
b_o : 12.784*esd*0.010 Å	$13\bar{1}$	3.665	6
c_o : 7.159*esd*0.006 Å	$11\bar{2}$	3.507	1
α : 94° 9'	040	3.192	10
β : 116° 37'	$1\bar{3}1$	2.962	3
γ : 87° 42'	$24\bar{1}$	2.560	1
	$2\bar{4}\bar{1}$	2.443	1
lithian muscovite	002	10.067	1
monoclinic	110	4.487	2
C2/c	$11\bar{3}$	3.881	2
a_o : 5.191*esd*0.008 Å	023	3.739	2
b_o : 9.004*esd*0.010 Å	$11\bar{4}$	3.497	5
c_o : 20.176*esd*0.020 Å	006	3.349	10
β : 95° 49'	114	3.202	5
	025	2.992	5
	$13\bar{1}$	2.591	5

Mineral Crystal system Space group Cell parameters	hkl	d(obs)	I/I_o
lepidolite	003	10.067	3
monoclinic ($2M_2$)*	101	4.485	3
	104	3.861	1
C2/c	108	2.868	2
a_o: 9.113*esd*0.011 Å	111	2.642	1
b_o: 5.294*esd*0.005 Å	112	2.561	10
	114	2.461	1
c_o: 20.227*esd*0.038 Å	213	2.128	5
β : 97° 15'			
hureaulite	200	8.770	3
monoclinic	110	8.010	3
C2/c	$\bar{3}11$	4.563	2
a_o: 17.587*esd*0.085 Å	312	3.256	2
b_o: 9.059*esd*0.043 Å	$\bar{5}11$	3.[illegible]4	3b
c_o: 9.607*esd*0.067	$\bar{2}22$	3.162	10
β : 97° 44'	402	3.001	7
	$\bar{3}31$	2.623	2
	$\bar{6}23$	2.053	2

**May contain domains of 3T hexagonal structure, as evidenced by a reflection at d = 2.642 Å, a distinctive d(112) reflection of 3T lepidolite.*

Mineral Crystal system Space group Cell parameters	hkl	d(obs)	I/I_o
triploidite	122	3.148	1
monoclinic	140	3.204	3b
$P2_1/a$	212	3.162	10
a_o: 12.673*esd*0.033 Å	$\bar{4}11$	3.080	2
b_o: 13.279*esd*0.028 Å	330	3.001	7
c_o: 9.894*esd*0.023 Å	$\bar{3}13$	2.885	4
β : 108°	$\bar{1}33$	2.638	3
	150	2.594	2
	$\bar{4}13$	2.567	2
	$\bar{4}43$	2.053	2
robertsite	200	8.61	10
monoclinic	002	5.62	5
A2/a	213	3.24	2
a_o: 17.300*esd*0.012 Å	160	3.19	1
b_o: 19.498*esd*0.019 Å	233	2.936	1
c_o: 11.246*esd*0.011 Å	600	2.866	1
β : 96° 19'	$\bar{2}04$	2.745	5
	$\bar{6}22$	2.578	4
	$\bar{1}82$	2.229	1
	800	2.149	1

Mineral Crystal system Space group Cell parameters	hkl	d(obs)	I/I_o
fillowite	024	5.667	1
rhombohedral	214	4.546	1
$R\bar{3}$	036	3.780	1
a_o: 15.318*esd*0.018 Å	223	3.708	1
c_o: 42.930*esd*0.420 Å	312	3.627	5
	134	3.485	1
	226	3.348	5
	232	3.016	10
	413	2.839	1
	330	2.551	4
wyllieite	020	6.209	5
monoclinic	121	3.573	3
$P2_1/n$	310	3.441	5
a_o: 11.845*esd*0.029 Å	$\bar{1}12$	3.054	1
b_o: 12.339*esd*0.031 Å	131	3.008	1
c_o: 6.393*esd*0.012 Å	$\bar{3}12$	2.854	3
β : 114° 31'	400	2.684	10
	112	2.509	5
	$\bar{3}13$	2.080	1
	$\bar{5}32$	1.963	1

Mineral Crystal system Space group Cell parameters	hkl	d(obs)	I/I_o
brazilianite	020	5.083	8
monoclinic	121	3.755	3
$P2_1/m$	012	3.290	2
a_o : 11.246*esd*0.042 Å	$20\bar{2}$	3.169	2b
b_o : 10.084*esd*0.024 Å	320	2.985	10
c_o : 7.061*esd*0.024 Å	022	2.877	5
β : 97° 42'	$23\bar{1}$	2.742	3
	410	2.689	7
	412	2.009	3
	150	1.981	4
kulanite	100	8.897	2
triclinic	120	5.011	2
$P\bar{1}$	011	4.504	2
a_o : 9.005*esd*0.040 Å	031	3.104	10
b_o : 12.209*esd*0.085 Å	131	3.040	7
c_o : 4.936*esd*0.007 Å	211	2.928	3
α : 90° 35'	$\bar{1}31$	2.829	2
β : 100° 2'	221	2.693	2
γ : 90° 20'	$\bar{3}20$	2.662	2
	$\bar{1}02$	2.455	2

Mineral Crystal system Space group Cell parameters	hkl	d(obs)	I/I_o
carbonate-apatite	002	3.454	2
hexagonal	211	2.806	10
$P6_3/m$	112	2.783	4
a_o: 9.371esd0.012 Å	300	2.710	6
c_o: 6.896esd0.009 Å	202	2.630	2
	310	2.254	2
	400	2.026	3
	222	1.939	3
	213	1.840	3
	321	1.800	2
Mn-chlorapatite	100	7.99	1
hexagonal	200	4.004	1
$P6_3/m$	111	3.808	1
a_o: 9.475esd0.040 Å	002	3.383	3b
c_o: 6.926esd0.030 Å	300	2.757	10
	202	2.663	5
	221	2.217	2
	312	1.906	1
	410	1.806	2b
	402	1.770	1