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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 Spodumene has been replaced by eucryptite, albite, and micas.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 1. ELECTRON MICROPROBE ANALYSES OF PHOSPHATES AND CARBONATES FROM THE WHITE PICACHO PEGMATITES, ARIZONA

Representative analyses of most White Picacho phosphates (primary and secondary) and secondary carbonates are listed below. Analyses (1) through (4) were performed on a Cameca MS-46 electron microprobe in the Center for Solid State Science, Arizona State University. These analyses were conducted using a beam voltage of 15 kV, a sample current of 30 nA, and a beam diameter of 2 microns. Each spot was analyzed for 20 seconds of counting time. The standards used were apatite for Ca and P, olivine for Fe and Mg, and rhodonite for Mn. Count data were reduced and corrected by the Heinrich Frame 3P program (Heinrich *et al.*, 1972). The remaining analyses were obtained on an ARL-SEMQ electron microprobe in the Division of Mineralogy, Smithsonian Institution, Washington, D. C. Individual analyses were counted for 10 seconds at a beam voltage of 15 kV, a sample current of 25 nA, and a beam diameter of 2 microns. The standards were omphacite for Si, Al, Fe, and Mg; hornblende for Si, Al, Fe, Mg, Ca, and K; apatite for Ca and P; manganite for Mn, anorthoclase for Na and Al; and benitoite for Ba. The data were corrected and reduced using standard background and Bence-Albee correction factors (Albee and Ray, 1970). Each analysis reported below represents an average across six analyzed spots in an individual grain.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
SiO_2	n.d.*	n.d.	n.d.	n.d.	---	0.03	0.01	0.05	0.03	---
Al_2O_3	n.d.	n.d.	n.d.	n.d.	---	---	---	---	---	---
FeO	0.25	0.88	6.31	0.57	---	0.36	0.34	0.33	0.41	---
MnO	44.11	44.36	38.94	44.68	45.23	63.61	62.90	63.68	63.26	63.95
MgO	---	---	---	---	---	0.11	0.16	0.14	0.24	---
CaO	0.02	---	---	---	---	0.02	0.06	0.05	0.03	---
Na_2O	n.d.	n.d.	n.d.	n.d.	---	---	---	---	---	---
K_2O	n.d.	n.d.	n.d.	n.d.	---	0.01	0.01	0.01	0.01	---
P_2O_5	46.62	44.28	41.10	43.92	45.25	32.04	31.79	31.90	31.95	31.99
Total	90.99	89.52	86.35	89.17	90.48	96.17	95.23	96.16	95.93	95.94

(1) lithiophilite, Midnight Owl; (2) lithiophilite, Midnight Owl; (3) lithiophilite, White Ridge; (4) lithiophilite, Homestead; (5) $LiMnPO_4$; (6) through (9): triploidite, Midnight Owl; (10) $Mn_2PO_4(OH)$
*n.d. = not determined

	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)
SiO_2	0.01	0.02	---	---	0.01	---	---	---	0.03	---
Al_2O_3	---	---	---	---	24.84	25.04	22.26	---	---	---
FeO	0.18	0.18	0.22	---	0.03	0.01	---	0.01	---	---
MnO	46.68	46.10	46.87	48.66	30.41	30.25	30.98	39.57*	39.32*	36.05*
MgO	0.07	0.18	0.11	---	---	---	---	0.03	0.03	---
CaO	0.57	0.80	0.24	---	0.14	0.14	---	16.19	16.31	19.21
Na_2O	---	---	---	---	---	---	---	---	---	---
K_2O	---	0.01	---	---	---	---	---	0.03	0.03	---
P_2O_5	37.80	37.83	37.98	38.98	30.61	30.33	31.02	33.23	33.09	32.41
Total	85.31	85.12	85.42	87.64	86.04	85.78	84.26	89.09	88.72	87.67

(11) through (13): hureaulite, Midnight Owl; (14) $Mn_5(PO_4)_2(PO_3)(OH)_2 \cdot 4H_2O$; (15) and (16): eosphorite, Midnight Owl; (17) $MnAlPO_4(OH) \cdot H_2O$; (18) and (19): robertsite, Midnight Owl; (20) $Ca_3Mn^{3+}_4(OH)_6(H_2O)_3(PO_4)_4$

* wt% Mn_2O_3

	(21)	(22)	(23)	(24)	(25)	(26)*	(27)*	(28)*	(29)*	(30)
SiO_2	0.01	---	---	---	---	0.13	---	---	---	---
Al_2O_3	---	---	---	---	---	2.56	2.36	2.78	2.71	2.0
FeO	1.77	2.05	1.80	2.26	9.69	3.14	3.10	2.88	2.86	13.3
MnO	46.07	47.85	47.19	45.66	39.58	42.13	41.64	41.48	41.26	32.0
MgO	0.02	0.09	0.27	0.02	---	0.04	0.02	0.04	---	---
CaO	3.78	2.99	3.64	3.87	3.63	1.69	1.86	1.97	1.87	2.3
Na_2O	6.51	6.86	6.58	6.43	5.44	6.48	6.47	6.56	6.50	7.8
K_2O	0.04	0.04	0.02	0.03	---	1.83	1.83	1.87	1.87	1.1
P_2O_5	39.91	40.18	40.52	40.18	39.68	39.21	39.40	39.53	38.99	39.5
Total	98.11	100.07	100 01	98.45	98.02	97.21	96.68	97.12	96.08	98.0

(21) through (24): fillowite, Midnight Owl; (25) fillowite, Branchville, Connecticut (Brush and Dana, 1879a); (26) through (29): dickinsonite, Midnight Owl; (30) dickinsonite, Branchville, Connecticut (Moore and Ito, 1979). *also contain Ba up to 0.25 wt% BaO.

	(31)	(32)	(33)	(34)	(35)	(36)	(37)	(38)	(39)	(40)
SiO_2	0.01	0.29	0.02	0.03	---	---	---	---	---	---
Al_2O_3	---	0.14	---	---	---	---	---	---	---	---
FeO	---	1.45	1.53	0.60	---	2.35	3.04	2.52	1.89	---
MnO	19.36	18.04	15.33	18.72	19.65	53.68	55.05	53.86	52.99	61.71
MgO	0.16	0.26	0.19	0.09	---	0.02	0.12	0.22	0.19	---
CaO	29.76	30.15	33.41	30.09	31.07	0.07	0.10	1.69	2.12	---
Na_2O	---	---	---	---	---	---	---	---	---	---
K_2O	0.01	0.01	0.01	0.02	---	---	---	---	---	---
P_2O_5	37.47	37.81	37.93	37.79	39.31	---	---	---	---	---
Total	86.78	88.50	88.42	87.35	90.03	56.12	58.38	58.94	57.94	61.71

(31) fairfieldite, Midnight Owl; (32) fairfieldite, Homestead; (33) fairfieldite, White Ridge; (34) fairfieldite, White Ridge; (35) $Ca_2Mn(PO_4)_2 \cdot 2H_2O$; (36) rhodochrosite, Midnight Owl; (37) rhodochrosite, Midnight Owl; (38) rhodochrosite, Midnight Owl; (39) rhodochrosite, White Ridge; (40) $MnCO_3$

	(41)	(42)	(43)	(44)	(45)	(46)	(47)	(48)
SiO_2	---	---	---	---	---	---	---	---
Al_2O_3	---	---	---	---	---	---	---	---
FeO	---	0.05	---	---	---	---	0.02	---
MnO	6.65	6.14	4.74	1.22	5.13	6.74	6.56	7.72
MgO	0.06	0.10	0.07	0.07	0.03	0.04	0.03	0.05
CaO	48.42	47.87	49.64	52.97	50.67	49.00	49.41	48.25
Na_2O	0.02	0.30	0.02	0.03	---	---	---	---
K_2O	0.01	0.02	---	0.02	---	0.01	---	---
P_2O_5	40.75	39.34	40.03	40.34	41.77	41.19	41.24	41.79
Total	95.91	93.82	94.50	94.65	97.60	96.98	97.26	97.81

(41) through (44): rim of fibrous secondary apatite surrounding altered lithiophilite from the Homestead pegmatite. Analyses proceed outward from contact with the lithiophilite nodule (41) to the outer contact with coarse-grained albite (44). (45) through (48): coarse-grained, anhedral primary apatite in contact with altered lithiophilite from the Midnight Owl pegmatite. Analyses proceed from the apparent crystal core (45) to rim (48).

	(49)	(50)	(51)	(52)	(53)	(54)	(55)
SiO_2	---	---	---	0.03	0.01	0.03	---
Al_2O_3	---	---	---	0.01	---	---	---
FeO	---	0.01	---	---	0.07	0.08	0.53
MnO	5.34	6.81	5.23	13.86	1.27	0.52	1.74
MgO	---	0.01	---	0.01	---	0.03	0.02
CaO	48.83	47.34	48.58	41.70	53.98	54.28	51.99
Na_2O	0.03	0.01	0.05	0.03	---	0.01	0.22
K_2O	---	---	0.01	0.03	0.01	0.01	0.04
P_2O_5	40.46	39.75	39.51	40.52	41.81	40.67	40.52
Total	94.66	93.93	93.38	96.19	97.15	95.63	95.06

(49) through (52): secondary apatite in lithiophilite, Midnight Owl; (53) through (55): secondary apatite in montebrasite, Midnight Owl

	(56)	(57)	(58)	(59)	(60)
SiO_2	0.04	0.02	0.02	---	---
Al_2O_3	17.54	17.53	17.23	14.30	13.33
FeO	12.10	11.92	12.65	10.50	5.54
MnO	9.46	9.22	9.99	6.32	15.84
MgO	1.21	1.27	0.88	3.08	---
CaO	0.12	0.12	0.07	0.77	---
BaO	22.69	23.05	21.92	23.66	23.35
Na_2O	---	---	---	0.02	---
K_2O	0.01	0.01	0.01	---	---
P_2O_5	32.89	33.43	33.36	33.28	32.74
Total	96.06	96.56	96.13	94.07*	94.54**

(56) through (58): kulanite, Midnight Owl; (59) kulanite, Yukon Territory, Canada (Mandarino and Sturman, 1976); (60) bjarebyite, Rwanda (von Knorring and Fransolet, 1975)

* includes 2.14 wt% Fe_2O_3

** includes 3.74 wt% Fe_2O_3

	(61)	(62)	(63)	(64)	(65)	(66)	(67)	(68)
SiO_2	0.02	---	---	---	0.05	0.04	0.03	---
Al_2O_3	34.25	33.69	34.66	30.54	46.18	46.96	47.19	42.25
FeO	16.80	18.34	15.42	21.53	---	---	0.05	---
MnO	0.34	0.56	0.03	---	---	---	---	---
MgO	2.56	1.42	3.50	---	0.14	0.06	0.12	---
CaO	---	---	---	---	0.03	0.11	0.10	---
Na_2O	---	---	---	---	6.51	7.73	7.70	8.56
K_2O	---	---	---	---	---	---	---	---
P_2O_5	42.02	42.09	42.40	42.53	38.67	38.69	39.05	39.23
Total	96.00	96.11	96.04	94.60	91.60	93.58	94.24	90.04

(61) through (63): scorzalite, Midnight Owl; (64) $Fe^{2+}Al_2(PO_4)_2(OH)_2$; (65) through (67): brazilianite, Independence; (68) $NaAl_3(PO_4)_2(OH)_4$

	(69)	(70)	(71)	(72)	(73)	(74)	(75)	(76)	(77)	(78)
SiO_2	---	---	0.01	---	0.08	0.42	0.03	---	---	---
Al_2O_3	10.01	10.07	9.57	11.49	7.9	51.17	51.89	52.48	50.98	47.[illegible]1
FeO	10.44	9.05	7.04	2.23	29.2	0.07	---	---	---	---
MnO	27.68	29.00	32.24	33.79	4.3	0.29	---	---	---	---
MgO	0.27	0.31	0.28	0.09	1.97	0.06	0.01	---	---	---
CaO	0.43	0.46	0.51	5.53	2.5	---	---	---	---	---
Na_2O	5.72	6.24	5.62	3.75	8.0	0.32	0.01	0.01	---	---
K_2O	0.04	0.04	0.02	0.02	0.05	0.11	---	---	---	---
P_2O_5	45.13	45.43	44.32	42.09	43.8	40.83	40.24	40.75	35.51	44.10
Total	99.73	100.61	99.63	99.00	97.8	93.27	92.17	93.24	86.67	91.61

(69) through (72): wyllieite, Midnight Owl; (73) wyllieite, Custer, SD (Moore and Ito, 1979, p. 230, analysis #1); (74) through (76): augelite (tentative), Midnight Owl; (77) $Al_2PO_4(OH)_3$; (78) $Al_3(PO_4)_2(OH)_3$