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II. Crystal Structure

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Introduction

The chemical and crystallographic data presented in Part I suggest that fluorapophyllite and natroapophyllite are isostructural. Crystal structures of tetragonal potassium-rich fluorapophyllite have been determined by Taylor and Náray-Szabó (1931), and refined by Colville *et al.* (1971), Chao (1971), Prince (1971), and Bartl and Pfeifer (1976); and that of tetragonal potassium-rich hydroxyapophyllite by Rouse *et al.* (1978). Crystal structures of orthorhombic potassium-rich apophyllite (Sahama, 1965; Belsare, 1969), however, have not been determined because they are complexly twinned. It is well known that minor amounts of Na replace K in apophyllite, but no reports on the crystal structure of natural natroapophyllite with $Na/K \gg 1$ have been published.

In this section the results of a crystal structure analysis of natroapophyllite (SA-1b) are given. The differential thermal analysis (DTA), thermogravimetric analysis (TGA) and IR absorption spectrum of the new mineral are also reported. Comparisons are made with tetragonal apophyllites of other workers. According to the redefinitions of Dunn *et al.* (1978) we refer to the latter as 'fluorapophyllite.'

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Experimental methods and results

A crystal 0.2 × 0.3 × 0.3 mm was mounted on a Syntex P$\bar{1}$ automated single-crystal diffractometer equipped with a graphite monochromator, at Kyūshū University. Mo$K\alpha$ radiation was used to measure 984 crystallographically-independent reflections up to $2\theta = 60°$, of which 563 reflections were judged to be significant ($I \geqq 3_I$). No absorption corrections were made, since the size and nature of the crystal was small enough for the effect to be negligible. The unit cell parameters a = 8.875(4), b = 8.881(6), c = 15.79(1)Å, V = 1263.9Å^3 were refined from the data for the 15 strong reflections used to orient the crystal on the Syntex P$\bar{1}$.

The crystal was from the Sampo Mine and was designated SA-1b. This was the most Na-rich among the specimens found there (Tables 1 and 2). Ten other specimens listed in Table 1 contain less Na, and are intermediate in composition between fluorapophyllite and natroapophyllite. The specimen which gave the sharpest reflections on Weissenberg photographs was SA-2, which originated in a druse in the white skarn. SA-1 and SA-3 specimens, on the other hand, yielded slightly diffuse spots, but showed more Na enrichment than SA-2. Figure 1(a) shows an optical micrograph of SA-1, where zoning due to Na–K substitution can be seen. The crystal (SA-1b) from SA-1 used for the structure determination was selected because it had the smallest cell parameters of

Comparison of Observed and Calculated Structure Factors for Natroapophyllite

k	*l*	F_{obs}	F_{calc}
		h=0	
0	2	-206.36	229.64
0	4	1125.58	1134.35
0	6	127.94	28.73
0	10	2175.30	2154.08
1	1	684.14	747.77
1	3	-546.00	575.76
1	5	1304.65	1384.71
1	7	-283.25	282.53
1	9	411.67	394.31
2	0	-986.29	1022.83
2	2	118.78	86.86
2	10	-432.18	434.80
3	1	-797.20	796.23
3	3	144.92	126.54
3	5	-414.34	441.81
3	7	265.70	266.97
3	9	-366.45	375.15
4	0	306.25	307.85
4	2	665.35	654.07
4	4	-364.73	349.47
4	6	259.02	292.56
4	8	-252.92	251.58
4	10	423.88	475.54
5	1	-498.49	532.14
5	3	-137.00	130.17
5	5	-177.26	170.11
5	9	-230.31	251.52
6	0	-1431.63	1510.37
6	6	-369.31	385.15
6	8	424.74	470.26
6	10	-874.19	929.59
7	1	-178.21	219.04
7	3	654.76	705.89
7	5	-687.29	714.08
7	7	389.92	433.64
8	0	453.07	492.88
8	2	473.11	522.09
8	4	431.32	457.29
8	6	323.90	336.41
8	8	451.93	517.09
8	10	226.68	264.71
9	1	412.72	436.65
9	5	343.74	334.93
9	9	156.18	144.16
10	2	-162.28	142.75
		h=1	
0	0	87.10	0.00
0	1	769.81	781.05
0	3	-603.33	599.74
0	5	1426.00	1409.73
0	7	-313.56	299.77
0	9	439.62	408.18
1	0	315.79	291.86
1	4	438.29	399.91
1	6	585.30	575.32
1	10	294.61	315.84
2	0	-308.06	309.02
2	1	-535.22	532.01
2	2	868.46	900.51
2	3	180.41	168.30
2	4	363.58	373.03
2	5	-946.60	966.02
2	6	450.69	440.70
2	8	486.46	493.13
2	9	-277.15	274.10
2	10	150.93	139.19
3	0	167.15	129.27
3	1	-348.32	339.13
3	2	495.05	514.76
3	3	1257.71	1340.96
3	5	843.75	839.30
3	6	-186.32	217.81
3	7	913.97	922.99
3	8	373.22	395.52
3	9	634.15	666.01
4	1	409.95	439.88
4	2	207.03	220.04
4	4	263.98	279.43
4	5	442.29	473.39
4	6	-420.35	427.33
4	8	533.59	555.29
4	10	-175.35	145.36
5	0	365.11	371.32
5	1	-405.94	430.13
5	2	-220.96	246.05
5	3	-369.02	381.02
5	4	410.43	433.38
5	5	-218.67	253.38
5	6	310.73	344.84
5	7	-307.01	347.49
5	9	-204.83	202.96
6	0	140.05	111.30
6	1	-356.91	366.16
6	2	-330.19	354.79
6	4	-319.60	340.39
6	5	-417.11	461.51
6	6	-403.65	431.86
6	8	-266.94	288.43
6	10	-134.90	143.75
7	0	-207.41	217.57
7	1	-141.77	112.63
7	2	520.52	564.55
7	4	-192.91	223.55
7	6	-181.08	191.28
7	8	204.55	220.81
7	9	-154.94	182.60
8	0	125.65	126.93
8	1	191.00	189.92
8	3	122.21	104.76
8	4	-268.18	288.36
8	5	161.81	163.99
8	7	184.51	180.55
8	8	-220.96	222.84
8	10	148.83	126.18
9	0	167.72	156.02
9	1	128.89	92.51
9	3	-353.66	385.47
9	6	335.34	359.38
9	7	-173.25	213.06
9	9	-171.15	154.16
10	0	323.04	341.91
10	1	-135.38	153.79
		h=2	
0	0	-1041.72	1033.85
0	2	109.05	71.39
0	4	-119.06	107.76
0	10	-469.01	427.19
1	0	306.53	278.68
1	1	-571.09	530.51
1	2	-948.51	901.43
1	3	185.47	200.45
1	4	-392.97	352.88
1	5	-1025.21	973.94
1	6	-507.93	443.47
1	8	-535.98	501.99
1	9	-284.11	268.39
1	10	-159.99	129.34
2	0	-1602.12	1647.85
2	2	431.42	427.25
2	4	444.20	418.39
2	6	414.36	372.29
2	8	660.29	631.18
2	10	-666.01	615.91

Comparison of Observed and Calculated Structure Factors for Natroapophyllite(Cont.)

k	*l*	F_{obs}	F_{calc}
3	0	279.53	259.98
3	1	309.39	327.73
3	2	274.48	338.98
3	3	332.10	328.90
3	4	854.44	849.46
3	5	-147.11	141.84
3	7	180.89	204.39
3	8	908.44	888.24
3	9	162.85	151.42
3	10	-151.60	119.75
4	0	1563.10	1607.36
4	1	239.56	251.09
4	2	248.81	254.02
4	4	405.37	448.69
4	5	-217.71	216.87
4	6	444.01	459.81
4	7	-234.69	235.25
4	9	366.64	400.40
4	10	824.58	825.98
5	0	-117.06	104.53
5	1	730.89	769.51
5	2	-382.09	417.03
5	3	-349.56	367.81
5	4	-406.52	432.76
5	5	660.58	675.44
5	7	-289.74	297.18
5	8	-583.68	615.21
5	9	280.49	300.28
6	0	686.53	707.34
6	2	-140.91	127.74
6	3	-152.93	182.69
6	4	219.52	236.37
6	5	198.54	223.16
6	6	188.80	226.00
6	9	-216.66	226.58
6	10	357.86	371.39
7	0	-266.56	269.84
7	2	483.13	518.58
7	3	-239.85	268.27
7	5	157.03	149.54
7	6	290.50	305.47
7	7	-137.86	141.44
7	8	258.16	288.36
8	0	229.64	214.12
8	2	-151.50	179.06
8	3	186.99	207.41
8	5	-262.93	280.75
8	8	-272.86	305.53
8	10	138.62	109.53

k	*l*	F_{obs}	F_{calc}
9	1	-260.93	226.48
9	2	-364.35	403.70
9	3	-253.39	260.03
9	6	-160.76	158.96
9	8	-202.54	223.82
9	9	-231.45	233.55
10	0	-230.11	255.66
10	3	-244.14	244.98
10	5	259.21	291.20

h=3

k	*l*	F_{obs}	F_{calc}
0	1	-889.74	841.68
0	3	174.68	200.19
0	5	-478.35	468.10
0	7	272.76	252.99
0	9	-405.18	394.09
1	0	167.62	174.76
1	1	384.10	363.76
1	2	554.49	505.97
1	3	-1406.73	1340.59
1	5	-943.45	848.62
1	6	-230.40	199.16
1	7	-1023.78	958.67
1	8	422.93	409.20
1	9	-690.63	650.44
1	10	-132.61	104.74
2	0	-285.07	258.17
2	1	316.84	298.28
2	2	-287.26	317.56
2	3	341.64	333.52
2	4	-895.18	832.75
2	5	-171.35	129.97
2	7	198.63	198.82
2	8	-957.76	895.59
2	9	158.66	161.03
3	0	169.34	177.83
3	2	408.61	403.77
3	6	249.20	240.77
3	10	252.53	258.20
4	0	228.68	226.34
4	1	-352.14	345.98
4	2	-355.95	368.08
4	3	-296.99	308.97
4	5	218.57	222.69
4	8	-141.39	126.70
4	9	-153.22	132.08
5	0	231.35	236.20
5	1	438.00	458.32
5	3	-669.07	678.26
5	4	213.99	207.32
5	6	304.91	316.43
5	7	-563.46	551.19
5	9	-143.39	109.06
5	10	211.42	215.53
6	0	238.80	261.64
6	1	257.78	277.07
6	4	357.10	377.95
6	5	313.12	333.66
6	6	473.30	484.78
6	9	192.62	168.60
6	10	142.53	111.43
7	0	372.55	398.67
7	1	136.90	131.00
7	2	-173.44	178.01
7	3	763.52	816.86
7	4	269.52	267.94
7	7	614.97	648.41
7	9	307.39	313.15
8	0	-452.79	485.34
8	2	395.93	424.20
8	3	-175.83	203.49
8	4	174.02	188.52
8	7	-159.13	166.00
8	8	551.72	550.17
8	10	-214.85	233.35
9	1	-178.98	199.27
9	5	-230.78	218.61
9	7	-186.71	225.60
10	0	-143.01	123.91
10	2	-190.90	206.01
10	3	151.41	140.25

h=4

k	*l*	F_{obs}	F_{calc}
0	0	310.16	298.84
0	2	753.40	665.57
0	4	-401.75	358.84
0	6	298.04	281.44
0	8	-290.89	247.28
0	10	477.69	469.08
1	0	-109.33	86.53
1	1	439.62	436.63
1	2	-217.43	238.98
1	4	-324.37	285.28
1	5	501.35	493.53
1	6	460.42	443.12
1	8	-580.53	547.56
1	9	130.32	113.97
1	10	159.52	139.31

Comparison of Observed and Calculated Structure Factors for Natroapophyllite(Cont.)

k	*l*	F_{obs}	F_{calc}
2	0	1626.64	1620.64
2	1	-249.39	255.50
2	2	274.48	257.31
2	4	453.93	447.47
2	5	221.15	223.33
2	6	493.52	443.83
2	7	242.99	255.08
2	9	-388.68	395.05
2	10	890.02	844.41
3	0	-221.81	224.22
3	1	-353.47	359.81
3	2	360.82	351.30
3	3	-326.57	306.23
3	5	217.90	222.77
3	7	-157.03	144.42
3	8	149.40	142.68
3	9	-160.18	155.13
4	0	-830.68	873.07
4	2	-419.11	439.26
4	4	-158.75	159.70
4	6	-694.64	671.86
4	10	-881.06	816.47
5	0	373.98	398.55
5	1	-507.36	522.21
5	2	-330.10	332.21
5	3	186.32	187.83
5	5	-668.78	707.61
5	8	-342.79	347.98
5	9	-175.26	207.03
5	10	200.16	191.52
6	2	438.38	440.39
6	4	173.54	185.05
6	5	290.98	303.39
6	6	211.61	206.18
6	8	330.57	338.73
7	2	295.37	292.54
7	3	178.50	195.52
7	6	-182.70	167.51
7	7	145.49	141.17
7	8	281.82	279.84
8	0	-263.98	268.66
8	2	199.01	205.21
8	3	207.22	249.34
8	5	-309.68	330.75
8	8	164.95	129.89
8	9	231.55	217.63
9	1	249.48	235.54
9	3	169.72	205.08

h=5

k	*l*	F_{obs}	F_{calc}
0	1	-552.96	530.55
0	3	-130.32	129.89
0	5	-213.32	180.18
0	9	-265.80	273.28
1	0	377.70	353.41
1	1	437.81	431.60
1	2	-234.22	240.20
1	3	399.74	380.40
1	4	461.75	446.21
1	5	263.89	231.57
1	6	345.17	340.54
1	7	358.72	359.14
1	9	250.53	190.27
2	0	139.29	122.83
2	1	778.11	782.40
2	2	427.98	434.90
2	3	-387.15	383.48
2	4	455.84	440.69
2	5	717.15	688.36
2	7	-303.10	291.15
2	8	630.62	595.75
2	9	321.32	301.40
3	0	251.20	244.78
3	1	-470.53	464.52
3	3	701.12	673.48
3	4	234.60	204.18
3	6	327.62	316.31
3	7	574.71	566.15
3	10	216.09	213.33
4	0	-393.73	385.18
4	1	-526.63	519.29
4	2	350.61	329.09
4	3	205.50	178.18
4	5	-702.17	708.37
4	8	355.67	344.74
4	9	-215.23	203.79
4	10	-220.67	189.79
5	0	-469.96	500.03
5	2	664.58	685.68
5	4	-273.05	279.67
5	6	-246.62	241.43
5	8	365.59	358.26
5	10	-193.38	188.42
6	1	227.82	253.82
6	3	281.44	271.59
6	4	-401.65	424.36
6	6	-185.18	180.70
6	7	245.19	255.92
6	8	-378.94	383.58

k	*l*	F_{obs}	F_{calc}
7	0	136.33	152.38
7	1	-304.43	285.99
7	3	-283.83	297.22
7	5	-225.06	226.07
7	7	-225.06	231.07
7	9	-235.55	235.04
8	1	-279.63	293.89
8	2	-187.66	192.06
8	5	-181.17	191.15
9	1	213.90	223.74
9	2	157.89	152.24

h=6

k	*l*	F_{obs}	F_{calc}
0	0	-1505.86	1502.77
0	6	-416.06	371.72
0	8	479.12	472.52
0	10	-1001.17	948.43
1	0	-141.39	124.17
1	1	-374.65	351.99
1	2	365.49	359.54
1	4	357.96	347.21
1	5	-476.35	470.43
1	6	458.99	420.56
1	8	320.65	297.86
1	10	190.52	144.75
2	0	729.36	708.80
2	1	126.60	114.71
2	2	-152.46	121.67
2	3	191.67	171.94
2	4	238.61	249.76
2	5	-223.63	198.60
2	6	232.40	234.33
2	9	229.83	247.59
2	10	401.46	375.01
3	0	-233.45	258.42
3	1	289.46	275.93
3	4	-401.94	375.25
3	5	369.59	326.79
3	6	-511.65	477.38
3	9	203.88	178.11
4	0	-153.89	148.11
4	2	452.41	441.03
4	3	142.15	142.39
4	4	200.35	184.75
4	5	-304.62	305.92
4	6	176.88	205.78
4	8	336.58	331.11
4	9	133.47	125.64

Comparison of Observed and Calculated Structure Factors for Natroapophyllite

k	*l*	F_{obs}	F_{calc}
5	1	241.09	254.18
5	3	262.93	262.15
5	4	419.49	415.76
5	6	183.84	157.37
5	7	269.13	259.01
5	8	388.20	384.90
6	0	697.31	712.00
6	0	373.51	359.47
6	8	-205.12	188.25
6	10	511.17	478.54
7	2	-280.39	297.25
7	3	-390.97	403.32
7	5	338.40	340.03
7	7	-200.92	176.56
7	8	-264.36	216.43
8	2	-203.97	220.62
8	6	-189.85	192.90
		h=7	
0	1	-222.77	222.52
0	3	703.22	688.36
0	5	-753.88	704.08
0	7	431.51	413.84
1	0	-245.09	233.22
1	1	131.94	119.65
1	2	575.29	563.21
1	4	-217.52	215.99
1	6	-207.41	191.19
1	8	220.57	219.27
1	9	190.90	182.00
2	0	261.03	259.39
2	2	-519.86	513.07
2	3	-266.84	253.71
2	4	-148.35	115.84
2	5	140.63	137.53
2	6	-319.89	295.49
2	7	-147.21	137.26
2	8	-296.52	283.08
3	0	388.48	397.50
3	2	-194.34	170.71
3	3	-844.90	817.88
3	4	310.44	264.23
3	5	-128.32	131.32
3	7	-675.56	664.92
3	9	-333.53	315.11
4	2	-297.66	305.49
4	3	187.09	196.57
4	6	169.72	191.93
4	7	167.91	155.27

k	*l*	F_{obs}	F_{calc}
4	8	-273.71	269.25
5	0	150.83	166.40
5	1	269.61	291.53
5	3	303.96	303.68
5	4	154.36	148.39
5	5	238.80	229.06
5	7	264.75	230.38
5	9	256.06	244.86
6	2	264.55	285.12
6	3	-398.98	400.76
6	4	166.19	146.66
6	5	361.39	344.21
6	6	190.43	119.65
6	7	-168.39	184.43
6	8	184.89	218.08
7	0	282.20	269.08
7	2	-227.25	247.31
7	6	400.98	374.08
		h=8	
0	0	485.32	512.45
0	2	526.53	523.23
0	4	464.04	443.28
0	6	374.75	326.22
0	8	528.06	504.45
0	10	256.25	273.39
1	0	-162.38	128.05
1	1	174.49	176.49
1	4	298.90	297.05
1	5	186.61	167.03
1	7	206.36	197.18
1	8	251.96	228.68
1	10	-143.20	125.31
2	0	227.16	210.30
2	2	-180.22	170.44
2	3	-191.95	210.49
2	4	-167.72	158.57
2	5	269.80	275.95
2	8	-348.89	296.34
3	0	487.32	483.53
3	2	-461.37	437.32
3	3	-212.85	196.40
3	4	-192.24	186.61
3	7	-164.09	170.24
3	8	-606.01	561.02
3	10	261.88	232.02
4	0	-248.05	249.38
4	2	224.39	202.59
4	3	-259.50	257.54

k	*l*	F_{obs}	F_{calc}
4	5	339.92	332.75
4	8	145.78	121.75
4	9	-223.82	217.46
5	1	-314.17	284.93
5	2	202.92	203.77
5	5	-183.56	175.14
5	8	153.31	127.41
6	0	-156.75	140.49
6	2	-207.69	219.96
6	3	156.94	135.91
6	6	-199.39	184.54
		h=9	
0	1	449.54	439.78
0	5	364.16	358.77
1	0	211.99	166.71
1	1	-141.39	93.14
1	3	398.31	382.99
1	4	146.16	147.75
1	6	362.06	359.77
1	7	218.09	217.53
1	8	-132.80	129.06
1	9	179.74	158.03
2	1	-239.65	230.07
2	2	388.48	405.77
2	3	-253.58	254.10
2	6	160.85	153.25
2	8	254.73	216.64
2	9	-266.84	236.93
3	1	175.07	190.58
3	5	217.33	222.13
3	7	222.29	212.64
4	1	246.62	237.84
4	3	182.03	198.37
4	6	159.32	122.07
5	1	-226.11	239.31
5	2	192.62	145.28
5	3	171.82	150.84
		h=10	
0	0	143.30	125.06
0	2	-192.14	142.58
1	0	-346.13	340.69
2	0	-267.32	283.83
2	3	247.57	253.59
3	2	234.12	206.88