Powder Diffraction Data for Synthetic Potassium-Richterite, Nickel-Potassium-Richterite and Cobalt-Potassium-Richterite

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Abstract

Indexed X-ray powder diffraction data derived from Rietveld crystal structure refinements are reported for synthetic potassium-richterite (KRC: K[CaNa]Mg₅Si₈O₂₂(OH)₂), nickel-potassium-richterite (NIKRC:K[CaNa] Ni₅Si₈O₂₂(OH₂) and cobalt-potassium-richterite (COKRC:K[CaNa]Co₅Si₈O₂₂ (OH₂). The following dimensions were obtained: KRC: a = 10.0547(8), b = 17.997(1), c = 5.2746(4)Å, β = 104.832(5)°; NIKRC: a = 10.0297(7), b = 17.942(1), c = 5.2576(4)Å, β = 104.982(5)°; COKRC: a = 10.1166(9), b = 18.066(1), c = 5.2752(4)Å, β = 104.846(6)°.

Introduction

Amphiboles are common rock forming silicate minerals found in a wide variety of igneous and metamorphic rocks. They can be orthorhombic or monoclinic and have the general formula $A_{0.1}B_2C_5T_8O_{22}W_2$, where A = Na,K; B = Ca, Na,Li, Mg Fe²⁺, Mn; C = Mg, Fe²⁺, Mn, Al, Fe³⁺, Ti, Li; T = Si, Al, Ti; W = OH, F Cl, O²⁻. The structural chemistry of natural amphiboles is often extremely complex and its interpretation is facilitated by a knowledge of the physical and chemical characteristics of end members.

Richterite is a common sodic-calcic amphibole with the ideal formula Na[CaNa]Mg₅Si₈O₂₂(OH)₂; divalent cations (Ni, Co, Fe²⁺, Mn) can readily substitute for Mg in octahedral coordination (see Hawthorne, 1983, for structural details). Here we report X-ray powder diffraction data derived from Rietveld Crystal structure refinements of potassium-richterite, nickel-potassium-richterite and cobalt-potassium-richterite.

Synthesis

Mixtures of amphibole stoichiometry were prepared as silicate gels with the method of Hamilton and Henderson (1969). Approximately 10 percent water by weight was added to the charge. Hydrothermal syntheses were done in coldseal, externally heated Tuttle-type pressure vessels at 750° C and 1 kbar; reaction times were up to 30 days. The crystals are violet pink and acicular, 5-10 μ m along c and 2-5 μ m in diameter. Extraneous phases were not detected by optical microscopy, by scanning electron microscopy or by X-ray diffraction.

X-Ray Studies

Samples were ground under ethanol to less than 2 μ m grain size and were mounted in standard aluminum sample holders with 20 x 15 x 1.6 mm cavities. In order to minimize preferred orientation, the powder was back loaded and gently pressed against a frosted glass slide covering the front of the holder. The already textured surface was then serrated with a razor blade in a direction parallel to the path of the X-ray beam. This technique tends to randomize the orientation of anisotropic crystals that are aligned during filling, but maintains a reasonably flat surface. Step-scan powder diffraction data were collected with a Philips automated diffractometer system PW1710, using a PW1050 Bragg-Brentano goniometer equipped with incident- and diffracted-beam Soller slits, 0.5° divergence and anti-scatter slits, a 0.2 mm receiving slit and a curved graphite diffracted-beam monochromator. The normal focus Cu X-ray tube was operated at 40 kV and 40 mA, using a take-off angle of 6°. The profiles were taken using a step interval of $0.1^{\circ} 2\theta$, with a step counting time of 5 s. As discussed by Hill and Madsen (1986), these are approximately the optimum conditions for reducing serial correlation during Rietveld refinement without adversely affecting the accuracy of the results. Information pertinent to data collection is given in Table 1.

Table 1.

Data Collection and Details of Structure Refinement

	KRC	NIKRC	COKRC
2θ Scan range (°)	9-100	9-100	9-100
Step interval (°2 θ)	0.100	0.100	0.100
Integration time/step (s)	5	5	5
Maximum step intensity (counts)	2705	4519	2503
No. of unique reflections	526	522	533
No. of structure parameters	35	19	35
No. of experimental parameters	13	13	13
N - P	863	860	860
R _p	9.0	5.5	7.5
R _{wp}	11.9	7.4	9.9
R _B	4.0	1.9	2.5
Durbin-Watson d-statistic	1.77	1.97	1.86
U	0.018	0.173	0.204
V	0.064	-0.067	-0.127
W	0.030	0.063	0.044
γι	0.467	0.572	0.674
γ_2	0.001	-0.0002	-0.001

N - P: no. of observations (steps) - no. of least-squares parameters.

Structures were refined in space group C2/m with the LHPM1 program (DBW 3.2, originally written by Wiles and Young, 1981; modified by Hill and Howard, 1986). Scattering factors for neutral atoms and anomalous dispersion coefficients were obtained from International Tables for X-ray Crystallography, volume IV, 1974. The peaks were defined as pseudo-Voigts with the percentage Lorentzian character var-

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ied according to the relation $\gamma = \gamma_1 + \gamma_2 \theta$, where γ_1 and γ_2 are refinable parameters. The peak full-width at half-maximum height (FWHM) was varied as a function of 2θ using the expression of Cagliotti et al. (1958), $H_k = (U \tan^2 \theta + V \tan \theta +$ W)^{0.5}, where U, V and W are refinable parameters. Backgrounds were fitted with a simple polynomial function. The profile step intensity was calculated over the interval of four FWHM on either side of each peak centroid; peak assymetry was corrected as a function of 2θ using the semi-empirical relation of Rietveld (1969). Refinement results were significantly improved by using a preferred orientation correction (for platey crystallites) of the form $I_{calc} = I_{calc}[P1]$ + $(1 - P2)\exp(Pl\alpha_k^2)$], where P1 and P2 (not refined) are refinable parameters, and α_k is the acute angle between the scattering vector and the normal to the crystallites. The monochromator polarization correction was experimentally derived for the instrument used. Initial structural parameters were taken from the single crystal study of postassium-fluorrichterite (Cameron et al., 1983); isotropic displacement factors were fixed at values approximately correct for amphiboles. Information pertinent to structure refinements is given in Table 1. As hydrothermal mineral synthesis products are small in volume, and portions of the sample are required for other analytical techniques, the cell dimensions (Table 2) were refined as part of the structure refinement without reference to an internal standard. However, in our experience with other Rietveld refinements in which the Rietveld-derived call dimensions were compared with those corrected by the addition of an internal standard, such systematic errors are generally between 0.05 and 0.1%. (Rietveld cell larger than corrected cell.)

Table 2.

Cell Dimensions for Synthetic Richteritic Amphiboles

	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)
KRC	10.0547(8)	17.997(1)	5.2746(4)	104.832(5)	922.66
NIKRC	10.0297(7)	17.942(1)	5.2576(4)	104.982(5)	913.94
COKRC	10.1166(9)	18.066(1)	5.2752(9)	104.846(6)	931.51

Indexed X-ray powder patterns are given in Tables 3-5; 2θ to d conversions were done using the wavelength for CuK α_1 ($\lambda = 1.5406$ Å). The intensities in Tables 3-5 (I_{obs} and I_{cale}) are integrated intensities, and that I_{obs} is the "observed" intensity calculated at the end of the refinement after apportioning each observed step intensity between the contributing peaks according to the calculated Bragg intensities. The 2θ and d values are calculated from the refined cell parameters.

Table 3.

X-Ray Data for Potassium Sodium Calcium Magnesium Silicate Hydroxide

42-1481 Potassium Soo sium Silicate I	dium Calcium M Hydroxide	KNa lagne- Pota	CaMg5Si8 assium-rich	O ₂₂ (OH) ₂ nterite, syn
Rad. CuKa ₁ Cut off Ref Raudsepp	λ 1.5406 int. o, M. et. al. Powde	Filter Mono I/ r Diffraction 7, !	d-sp (I _{cor.} 53 (1992)	Calculated
Sys. Monoclin	nic	S.G. C2/m	n(12)	
a 10.0548(8)	b 17.997(1)	c 5.2746(4)	A 0.558	7 C 0.2931
α Ref Ibid.	β 104.832(5)	γ	Z	mp
D _v	\mathbf{D}_{m}	SS/FOM F ₃₀	= 1000(.0)	00,41)

Reference states that d and 2θ are observed but they are calculated. Reference also reports: a = 9.899(2), b = 17.945(4), c = 5.279(1), β = 105.60(2). Unit cell data determined by Rietveld or profile fit analysis. PSC: mC?.

d(Å)	I/I_o	hk <i>l</i>	$2\theta(^{\circ})$	d(Å)	I/I_o	hk <i>l</i>	$2\theta(^{\circ})$
8.9989	4	020	9.821	2.0332	11	351	44.526
8.5525	40	110	10.335	2.0140	4	370	44.974
4.8907	9	$11\overline{1}$	18.124	1.9587	7	190	46.316
4.8598	10	200	18.240	1.9555	3	421	46.397
4.4992	21	040	19.716	1.9451	6	$35\overline{2}$	46.659
4.0011	17	111	22.200	1.9327	22	510	46.977
3.8777	17	$13\overline{1}$	22.916	1.8978	8	$46\overline{1}$	47.894
3.7141	2	$22\overline{1}$	23.940	1.8669	2	242	48.738
3.3871	87	131	26.291	1.8608	10	$19\overline{1}$	48.908
3.3754	1	150	26.383	1.8571	4	$44\overline{2}$	49.012
3.3737	2	$04\overline{1}$	26.397	1.8493	5	530	49.232
3.3016	85	240	26.984	1.8410	ĩ	$17\overline{2}$	49,469
3.1887	81	310	27 959	1 8302	<1	441	49.781
3.0740	14	311	29.024	1.7997	5	0100	50.683
3.0214	<1	241	29.541	1.7976	4	191	50.747
2.9641	68	221	30.125	1 7840	. 9	312	51.161
2 9373	19	151	30 407	1 7726	3	$51\frac{1}{2}$	51 515
2 8507	28	330	31 354	1 7438	Ĩ	113	59 499
2 7679	48	331	39 317	1 7949	1	179	53 079
2 7060	100	151	33 077	1 7178	_1	339	53 985
2.7000	-1 -	1191	34 341	1.6877	9	2100	54 313
2 5853	45	061	34 669	1.6868	ī	$\overline{089}$	54 844
2.5055	9	941	34.818	1.6844	5	989	54 498
9 5595	1	211	35 190	1.6835	1	202	54 450
9 5404	7	009	35.123	1.6818	-1 -8	122	54 510
9 6/10	66	902	35.904	1.6701	7	133	54 022
9 4855	1	170	36 109	1.6660	20	461	55 080
9 4 4 5 4	_1	999	36 799	1.0000	55	480	55 691
9 / 900		400	36.064	1.6449	~1	691	55 979
2.4299	3	261	30.304	1.6900	6	600	56 783
9 41 49	-1	129	37.104	1.0200	~1	591	56.765
9 40 91	17	350	37.212	1.0108	19	1110	57.900
9 2646	90	491	39.094	1.0134	14 ~1	1 <u>11</u> 0 959	57.057
2.3040	29	44 <u>1</u> 251	30.024	1.0040	1	552	57.570
9 90 4 9	90	$\frac{351}{171}$	30.143	1.5904	1	552 690	57.701
9 90 90	16	1/ <u>1</u> 919	39.237	1.5945	1	520	- 07.704 - 50 500
2.2920	10	291 291	39.202 30.506	1.5756	4 10	159	- 90.920 - E0 E 40
2.2792	<i>)</i>	090	39.500	1.5755	10	193	50.548
2.2497	2	040	40.040	1.5097	0	402	50.111
2.2181	10	042	40.042	1.5015	4	Z <u>IU</u> I	59.125
2.2120	12	242	40.747	1.5599	10	00Z	59.183
2.1/00	3	1/1	41.408	1.5405	<1	422	59.750
2.1088	48	201	41.008				
2.1570	8 C	33 <u>7</u>	41.840				
2.12/3	0	102	42.409				
2.0019	24	202	44.099				
2.0415	L	280	44.330				
2.0388	b	402	44.397				~ ~

Table 4. X-Ray Data for Potassium Sodium Calcium Nickel Silicate Hydroxide

42-1480KNaCaNi ₅ Si ₈ O 22(OH) 2Potassium Sodium Calcium NickelNickel-potassium-richter- ite, syn							
Rad. C Cut of Ref Ra	CuKα _l f iudsep	λ i1 op, M. <i>e</i>	1.5406 nt. et. al. Powder	Filter Mor	ao (I/I _{cor.} 7, 54 (1	i-sp Cal 992)	culated
Sys. M	Sys. Monoclinic S.G. C2/m(12)						
a 10.02	297(7)	b = 17	7.942(1)	c 5.2576(4	4) A (0.5590 (℃ 0.2930
α Ref Ibi	id.	ρπ	982(5)	γ	L	1	np
D_x D_m SS/FOM $F_{30} = 1000(.000,46)$							
Reference states that d and 2θ are observed but they are calculated. Reference also reports: $a = 9.816(2)$, $b = 17.918(3)$, $c = 5.292(1)$, $\beta = 105.18(2)$. Unit cell data determined by Biotrophysical an provide and provide a provide and provide a provide and provide a p							
d(Å)	I/I _o	hk <i>l</i>	2θ(°)	d(Å)	I/I _o	hk <i>l</i>	2 θ (°)
8.5253	100	110	10.368	1.9265	<1	510	47.137
5.0890	2	130	17.412	1.8931	7	$46\overline{1}$	48.020
4.8784	3	111	18.170	1.8588	1	24 <u>2</u>	48.964
4.8443	7	200	18.299	1.8552	1	191	49.065
4,4655	1	$040 \\ 021$	20.074	1.8355	<1	441	49.119
4.0701	<1	201	21.819	1.7942	2	0100	50.850
3.9830	4	111	22.302	1.7916	2	191	50.929
3.8670	3	131	22.980	1.7694	3	512	51.615
3.3732	26	$131 \\ 041$	26.401 96.400	1.7402	1	551 179	52.546 53.909
3.2913	14	240	27.070	1.6825	1	2100	55.292 54.494
3.1785	42	310	28.050	1.6796	2	282	54.596
3.0681	3	$31\overline{1}$	29.081	1.6790	2	$39\overline{1}$	54.617
3.0142	2	241	29.613	1.6760	2	133	54.723
2.9511	12	221	30.201	1.6596	16	023 461	55.100 55.310
2.7621	14	$33\overline{1}$	32.387	1.6456	2	480	55.822
2.6959	49	15 <u>1</u>	33.205	1.6148	3	600	56.983
2.6010	1	$11\overline{2}$	34.454	1.6084	7	1 <u>11</u> 0	57.230
2.5768	33	061	34.787	1.5700	10	153	58.765
2.5041	1 39	241	34.905 35 384	1.5626	3 7	$\frac{402}{602}$	59.071 59 304
2.4222	5	400	37.086	1.5560	<1	21 <u>0</u> 1	59.346
2.4099	1	$26\overline{1}$	37.282	1.5288	<1	$35\overline{3}$	60.511
2.4066	<1	132	37.335				
2.4005	2	350 491	37.434				
2.3519	18	$\frac{421}{351}$	38.237				
2.2951	2	112	39.221				
2.2881	11	$31\overline{2}$	39.346				
2.2873	2	171	39.361				
2.2097	<1 9	331 949	39.679 40.861				
2.1711	3	171	41.562				
2.1605	25	261	41.775				
2.1523	3	33 <u>2</u>	41.942				
2.1473	<br 1	44 <u>1</u> 159	42.044				
2.1200	1 19	192 202	44.313				
2.0351	8	$40\overline{2}$	44.482				
2.0252	9	351	44.712				
2.0077	<1	37 <u>0</u>	45.123				
1.9790	1	371	45.814				
1.9526	2 1	190 491	40.470 46 598				
1.9405	1	$35\frac{1}{2}$	46.776				

Table	5.			
X-Ray	Data for Potassium	Sodium	Calcium	Cobalt
** *				

X-Ray Data for Potassium Sodium Calcium Cobalt Silicate Hydroxide							
42-147 Potass Silicat	'9 ium S e Hyd	odium lroxide	Calcium Co	K obalt Ca ite	NaCaO obalt-p e, syn	Co ₅ Si ₈ O ₂ otassium	2(OH)2 1-richter-
Rad. C Cut of Ref Ra	CuKα _l f iudsej	λ i pp, M. <i>i</i>	1.5406 nt. et. al. Powde	Filter Mor r Diffraction	no I/I _{cor.} 7, 54 (d-sp Ca 1992)	lculated
Svs. M	onoc	linic		S.G. C2	/m(12)	
a 10.1	166(9) b 18	8.066(1)	c 5.2752(9) A	0.5600	C 0.2920
α		β10	04.846(2)	γ	Z		mp
Ref Ib	1d.						
D _x		D	m	SS/FOM	$F_{30} = 1$	000(.000),42)
Refere lated. c = 5.2 Rietve	ence s Refer 952(9 ld or	tates the ence all β), $\beta = 1$ profile	at d and 26 so reports: 105.39(2). U fit analysis.	are observe a = 9.941(2) Jnit cell dat PSC: mC?.	ed but , b = 1 a deter	they are 8.090(3) rmined l	calcu-), oy
d(Å)	I/I _o	hk <i>l</i>	2 θ (°)	d(Å)	I/I _o	hk <i>l</i>	2 θ (°)
8.5998	100	110	10.278	1.9644	1	421	46.174
5.1276	2	130	17.280	1.9504	2	$35\overline{2}$	46.525
4.8969	3	111	18.101	1.9444	1	510	46.677
4.8894	9	200	18.129	1.9071	8	46 <u>1</u> 581	47.646
4.4404	1	$040 \\ 021$	19.980	1.8705	1	242	48.638
4.0916	2	$20\overline{1}$	21.703	1.8672	2	191	48.729
4.0077	4	111	22.163	1.8635	1	$44\overline{2}$	48.832
3.8862	4	131	22.865	1.8601	<1	530	48.928
3.3948	28 4	$131 \\ 041$	26.230	1.8383	1	441	49.547
3.3177	19	240	26.851	1.8037	2	191	50.563
3.2079	48	310	27.788	1.7802	3	$51\overline{2}$	51.279
3.0889	4	$31\overline{1}$	28.881	1.7538	2	$55\overline{1}$	52.108
3.0323	2	241	29.432	1.7278	<1	172	52.953
2.9735	14	$\frac{221}{151}$	30.028	1.6946	2	2100	54.073
2.9458	<1 13	151 330	30.317 31 175	1.6905	2 9	291 289	54.215 54 978
2.7808	16	331	32.163	1.6823	3	133	54.501
2.7137	60	151	32.981	1.6732	19	461	54.823
2.6099	1	112	34.333	1.6704	1	$02\overline{3}$	54.922
2.5927	37	061	34.567	1.6588	3	480	55.339
2.5832	2	241	34.699	1.6323	<br 5	243	56.317
2.5058	35	200/200/200/200/200/200/200/200/200/200	35.256	1.6296	8	1110	56 794
2.4954	<1	170	35.960	1.6032	<1	$55\overline{2}^{-1}$	57.433
2.4447	6	400	36.732	1.5838	<1	$57\overline{1}$	58.203
2.4251	2	261	37.040	1.5765	12	153	58.499
2.4203	2	35 <u>0</u>	37.116	1.5745	5	402	58.581
2.4100	1 5	13 <u>7</u> 491	37.185 37 800	1.5075	8	002 9101	58 888
2.3679	23	$\frac{121}{351}$	37.969	1.5070	1	<u>210</u> 1	50.000
2.3068	2	112	39.014				
2.3016	3	$17\overline{1}$	39.106				
2.2980	14	312	39.170				
2.2882	2	331 949	39.345 40.676				
2.2103	2 9	242 171	40.070 41 979				
2.1763	29	261	41.458				
2.1632	<1	441	41.721				
2.1623	3	$33\overline{2}$	41.739				
2.1304	1	152	42.394				

44.027

44.238

44.342

45.484

46.127

2.0551

2.0458

2.0412

1.9926

1.9663

14

9

1

2

11

20<u>2</u>

 $40\bar{2}$

351

 $37\overline{1}$

190

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