

Scapolite crystal chemistry: aluminum-silicon distributions, carbonate group disorder, and thermal expansion

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Abstract

Crystal structure parameters have been determined for a compositionally intermediate scapolite ($\text{Na}_{2.47}\text{Ca}_{1.33}\text{K}_{0.20}$) ($\text{Si}_{8.06}\text{Al}_{3.94}$) $\text{O}_{24}\text{Cl}_{0.59}(\text{CO}_3)_{0.37}(\text{SO}_4)_{0.04}$ in space group $P4_2/n$ before and after a heating cycle. In addition, unit-cell parameters have been determined with room-temperature data collected before and after heating, and with data collected at 400°, 600°, 700°, 800°, 900° and 1000°C. Both a and volume increase with temperature while c remains constant. Thermal expansion of a results from rotation of four-membered rings of tetrahedra in the (001) plane. Tetrahedral bond distances suggest that this sample has a highly ordered Si-Al distribution with T1 and T3 occupied by Si^{4+} and T2 occupied by Al^{3+} . The irreversible change in tetrahedral bond distances after the sample was heated to 1000°C suggests a slight amount of disordering has taken place. This change also affected the unit-cell parameters. The carbonate group was refined as a rigid body with realistic bond distances and angles using the least-squares computer program RFINE4. The refinement confirms the model of Papike and Stephenson (1966) and suggests that the group tilts only slightly out of the (001) plane. Normalized primitive reflections which violate $I4/m$ symmetry decrease in intensity with temperature up to 1000°C but do not disappear.

Introduction

Scapolites, a group of rock-forming silicates that exhibit many structural complexities, can, as a first approximation, be considered as solid solutions between marialite, $\text{Na}_4\text{Al}_3\text{Si}_2\text{O}_{24}\text{Cl}$, and meionite, $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$. These formulae are written in the form most consistent with the scapolite structure, but can also be written as marialite, $3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaCl}$ and meionite, $3\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot \text{CaCO}_3$ to show an analogy with plagioclase feldspar chemistry. Three coupled substitutions are evident in this solid solution series: $\text{Na}^{1+} \rightleftharpoons \text{Ca}^{2+}$; $\text{Si}^{4+} \rightleftharpoons \text{Al}^{3+}$; $\text{Cl}^{-} \rightleftharpoons \text{CO}_3^{2-}$. All three substitutions are active in the more sodic part of the series [$\text{Ca}/(\text{Ca} + \text{Na}) < 0.75$] while in the less sodic part [$\text{Ca}/(\text{Ca} + \text{Na}) > 0.75$], the substitution is $\text{NaSi} \rightleftharpoons \text{CaAl}$, the same as in the plagioclase feldspars (Evans *et al.*, 1969). At $\text{Ca}/(\text{Ca} + \text{Na}) > 0.75$ the anion site is filled with CO_3^{2-} (Papike, 1964; Evans *et al.*, 1969).

The first reasonably complete structure models of scapolite were reported by Pauling (1930) and Schiebold and Seumel (1932). The structure of a Na-rich scapolite was first refined by Papike and Zoltai (1965)

and that of a Ca-rich scapolite by Papike and Stephenson (1966). Lin and Burley (1973a, 1973c, 1975) reported three additional structural refinements. The space group of scapolite is a function of composition. The theoretical end-members, marialite and meionite, display diffraction symmetry consistent with space group $I4/m$, but intermediate compositions have reflections that violate this symmetry and reduce the space group to a primitive type. Papike and Stephenson (1966) reported diffuse reflections violating the body-centered symmetry but did not treat them in the structural refinement. Lin and Burley (1973a, 1973b, 1973c, 1975) state that the true space group is $P4_2/n$, and their three refinements are reported in this space group, even though they did not observe reflections violating $I4/m$ symmetry in their meionite-rich scapolite. Ulbrich (1973) also states that the space group for intermediate compositions is $P4_2/n$. Phakey and Ghose (1972) and Buseck and Iijima (1974), however, conclude from electron diffraction studies that the space group for intermediate compositions is $P4$ or $P4/m$.

Infrared spectra (Papike, 1964; Schwarcz and Speelman, 1965) suggest that the carbonate group is,

K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	
8	400	402	5	46	5	8	49	64	7	656	670	6	67	70	7	56	8	0	56	42	
9	109	109	12	K	0	9	264	285	9	515	506	7	193	205	8	827	804	1	462	450	
10	629	620	12	K	0	10	55	46	8	32	10	8	32	10	14	K	3	2	30	27	
11	35	19	12	K	4	13	K	1	13	K	5	13	K	5	14	K	3	4	305	283	
11	K	4	0	649	624	0	370	357	0	247	245	0	271	284	0	52	11	5	262	269	
0	76	54	2	529	516	1	78	83	1	78	83	0	157	142	1	459	456	6	50	26	
1	156	151	4	479	474	2	407	402	2	407	402	1	798	775	2	52	10	1	462	450	
2	50	54	6	143	148	3	28	37	3	28	37	2	38	67	3	424	424	2	30	27	
3	326	325	8	487	476	4	53	4	4	270	258	3	38	67	4	51	34	3	109	83	
4	56	55	10	169	158	5	159	153	5	50	27	4	278	256	5	470	468	5	109	83	
5	51	52	12	K	1	48	48	6	542	541	5	57	62	6	108	93	0	199	216		
6	91	90	0	101	94	6	93	104	6	542	541	5	57	62	6	108	93	1	61	65	
7	248	247	1	274	276	7	53	2	7	113	111	6	740	725	7	52	41	2	33	6	
8	66	67	2	47	37	8	310	302	8	259	244	13	K	6	14	K	4	3	89	90	
9	389	372	3	158	150	9	41	38	9	124	116	0	99	113	0	101	109	4	78	52	
10	61	86	4	48	2	10	41	38	10	34	48	0	206	202	1	120	123	5	66	33	
11	K	5	5	357	355	12	K	5	13	K	2	99	113	113	14	K	0	0	153	141	
0	50	25	6	48	7	0	34	32	0	75	95	0	109	101	4	43	36	1	211	214	
1	37	36	7	120	104	1	51	48	1	607	600	2	100	87	2	55	55	0	39	12	
2	231	224	8	55	17	2	38	15	2	304	49	4	126	136	3	126	137	1	172	146	
3	34	25	9	144	135	3	219	230	3	308	313	2	109	101	4	73	93	0	712	695	
4	111	123	10	84	110	4	51	36	4	79	64	0	K	0	14	K	5	2	290	296	
5	73	44	11	84	110	5	32	43	5	189	181	0	178	169	5	106	122	4	599	595	
6	37	7	12	K	2	6	54	56	6	61	53	2	258	256	6	80	23	0	712	695	
7	82	51	0	47	479	7	219	199	7	367	349	4	204	230	1	112	91	2	290	296	
8	53	57	1	37	29	8	34	1	8	354	349	6	178	169	3	285	281	4	599	595	
9	52	24	0	47	479	12	K	6	13	K	3	354	349	14	K	1	22	4	16	K	1
11	K	6	1	366	346	0	79	52	13	K	3	354	349	14	K	1	22	4	16	K	1
0	60	90	3	102	93	0	54	29	0	28	11	0	50	43	15	K	0	0	118	101	
1	111	99	4	99	85	1	364	377	0	29	68	0	172	181	15	K	0	1	31	13	
2	53	13	5	47	12	2	134	145	1	399	408	1	68	51	1	404	408	1	31	13	
3	235	216	6	174	166	2	245	241	2	49	14	2	38	9	3	219	208	2	39	27	
4	120	100	7	91	78	3	53	8	3	49	94	3	86	91	3	500	490	3	151	180	
5	48	67	8	51	20	4	135	151	4	110	94	4	86	91	5	133	146	4	170	144	
6	40	5	9	45	31	5	52	20	5	52	20	5	216	220	7	133	146	4	170	144	
7	147	140	10	113	149	6	100	96	6	100	96	6	161	164	15	K	1	0	47	59	
8	33	43	11	47	29	7	88	104	7	88	104	7	205	184	15	K	1	0	47	59	
11	K	7	12	K	3	0	56	10	14	K	2	61	46	46	0	461	465	1	54	4	
0	332	337	0	92	82	0	419	411	0	51	13	0	51	13	0	461	465	1	54	4	
1	139	116	1	480	484	1	118	111	1	238	243	1	95	93	2	54	5	2	544	529	
2	153	141	2	122	115	2	111	104	2	48	50	2	245	258	3	61	43	3	54	26	
3	55	4	3	101	89	3	111	104	3	287	289	3	53	51	3	150	155	4	54	26	
4	54	6	4	50	21	4	284	292	4	133	139	4	729	742	4	109	83	5	54	26	
5	54	7	5	214	226	5	565	575	5	213	211	5	52	41	6	146	156	7	54	26	

K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	
11	K	3	11	K	7	12	K	3	13	K	0	13	K	4	14	K	2	15	K	2	
8	373	384	5	61	11	8	74	48	7	600	636	6	63	44	7	57	13	0	60	36	
9	99	99	9	288	281	9	288	281	9	484	471	7	175	191	8	802	795	1	459	437	
10	626	620	10	38	39	10	38	39	13	K	1	8	56	21	14	K	3	2	49	19	
11	58	2	12	K	0	12	K	4	13	K	5	13	K	5	14	K	3	3	275	267	
0	48	54	0	658	636	0	376	359	0	238	243	0	278	275	0	56	17	4	34	24	
1	155	155	2	497	486	1	95	75	1	66	73	1	110	120	1	460	455	5	266	278	
2	51	33	4	511	498	2	197	193	2	403	404	2	784	760	2	57	7	6	63	34	
3	309	319	6	133	134	3	197	193	3	38	36	3	81	51	3	409	412	15	K	3	
4	57	53	8	484	472	4	53	12	4	254	260	4	254	251	4	49	40	0	194	27	
5	54	45	10	179	158	5	153	159	5	41	20	5	254	251	5	460	451	1	66	70	
6	82	68	12	K	1	6	116	99	6	503	513	6	70	39	6	83	86	2	48	22	
7	243	240	0	95	70	7	57	13	7	98	113	7	721	694	7	106	61	3	80	86	
8	96	66	1	270	273	8	323	297	8	256	235	8	13	6	14	K	4	4	39	52	
9	389	371	2	34	42	9	83	27	9	91	86	9	13	6	14	K	4	5	41	38	
10	66	65	3	117	136	10	83	27	10	62	44	10	62	44	0	125	121	0	15	K	4
0	32	27	4	68	8	12	K	5	0	100	81	0	116	103	0	125	121	0	15	K	4
1	33	31	5	335	346	1	40	58	1	605	606	1	206	195	1	62	106	0	134	124	
2	243	231	6	55	4	2	68	31	2	53	38	2	81	89	2	58	47	1	185	192	
3	53	22	7	127	102	3	195	215	3	349	333	3	163	145	3	118	120	2	42	10	
4	126	120	8	38	27	4	34	31	4	55	53	4	53	77	4	84	87	3	137	135	
5	54	41	9	75	58	5	77	43	5	185	185	5	14	K	0	76	27	0	16	K	0
6	58	3	10	126	114	6	73	57	6	33	45	6	339	342	6	118	120	0	702	677	
7	63	44	11	126	114	7	237	197	7	358	336	7	254	242	7	73	29	2	303	299	
8	63	56	12	K	2	8	61	3	8	56	20	8	212	229	8	104	92	4	575	571	
9	57	11	0	456	451	9	61	3	9	340	348	9	170	165	9	306	288	0	16	K	1
0	57	82	1	42	33	12	K	6	10	135	140	10	136	141	10	42	32	0	101	98	
1	102	99	2	343	333	0	61	77	0	59	27	0	37	40	15	K	0	1	52	3	
2	55	15	3	92	78	1	76	32	1	70	54	1	171	167	1	382	386	2	66	25	
3	204	198	4	80	86	2	352	356	2	373	386	2	53	44	3	212	199	3	148	166	
4	95	93	5	52	20	3	122	120	3	55	18	3	54	7	4	513	499	4	123	130	
5	36	72	6	173	176	4	243	247	4	137	107	4	101	94	5	145	156	0	16	K	2
6	59	16	7	96	66	5	57	13	5	55	24	5	225	217	6	15	K	1	0	59	42
7	128	136	8	87	35	6	131	145	6	124	103	6	136	141	7	225	200	1	54	2	
8	70	30	9	135	140	7	96	102	7	96	102	7	225	200	8	44	446	2	527	516	
0	338	343	10	97	35	8	51	24	8	58	23	8	37	58	0	444	446	3	71	32	
1	97	89	11	K	3	9	392	381	9	57	74	9	14	K	2	1	86	8	1	54	2
2	156	148	0	73	67	13	K	4	13	K	4	0	52	5	2	69	57	2	527	516	
3	50	4	1	450	452	0	97	85	1	237	246	1	34	79	3	159	142	4	78	89	
4	48	7	2	65	103	2	125	98	2	50	54	2	227	244	4	78	89	5	57	3	
			3	53	69	3	125	98	3	300	289	3	34	39	5	57	3	6	133	95	
			4	63	86	13	K	0	4	139	123	4	714	727	6	149	135	7	149	135	
			5	541	537	1	108	63	5	202	212	5	56	24							
			6	44	8	3	294	298	6	202	212	6	53	24							
			7	210	231	5	552	555	7	210	231	7	53	24							