

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

LOUISE LEVIEN AND J. J. PAPIKE

*Department of Earth and Space Sciences
State University of New York, Stony Brook, New York 11794*

Abstract

Crystal structure parameters have been determined for a compositionally intermediate scapolite ($\text{Na}_{2.47}\text{Ca}_{1.33}\text{K}_{0.20}$) ($\text{Si}_{8.06}\text{Al}_{3.95}$) $\text{O}_{24}\text{Cl}_{0.89}(\text{CO}_3)_{0.37}(\text{SO}_4)_{0.04}$ 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, $\text{Ca}_4\text{Al}_3\text{Si}_2\text{O}_{24}\text{CO}_3$. 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,

Table with columns labeled K OBS CALC, K OBS CALC, K OBS CALC, K OBS CALC, K OBS CALC, K OBS CALC, K OBS CALC. Rows contain numerical data points and sub-headers like '5 K 1', '6 K 7', etc.

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	11	K	7	10	55	46	13	K	1	8	32	10	14	K	3	2	30	27	
11	35	19	0	649	624	12	K	4	13	K	5	14	K	3	0	52	11	4	305	283	
0	76	54	2	529	516	0	370	357	0	247	245	0	271	284	0	52	11	5	262	269	
1	156	151	4	479	474	1	61	77	1	78	83	1	157	142	1	459	456	6	50	26	
2	50	54	6	143	148	2	203	211	2	407	402	2	798	775	2	52	10	6	50	26	
3	326	325	8	487	476	3	53	4	3	28	37	3	38	67	3	424	424	0	199	216	
4	56	55	10	169	158	4	159	153	4	270	258	4	278	256	4	51	34	1	61	65	
5	51	52	12	K	1	5	48	6	5	50	27	5	57	62	5	470	468	1	33	90	
6	91	90	0	101	94	6	93	104	6	542	541	6	740	725	6	108	93	3	89	90	
7	248	247	1	274	276	7	53	2	7	113	111	7	57	725	7	52	41	4	78	52	
8	66	67	2	47	37	8	310	302	8	259	244	8	124	116	8	146	146	5	66	33	
9	389	372	3	158	150	9	41	38	9	124	116	9	34	48	9	14	K	4	15	K	4
10	61	86	4	48	2	12	K	5	13	K	2	0	99	113	0	101	109	0	153	141	
0	50	25	5	357	355	0	34	32	1	75	95	1	206	202	1	120	123	1	211	214	
1	37	36	6	48	7	1	51	48	2	607	600	2	100	87	2	55	55	0	39	12	
2	231	224	7	120	104	2	38	15	3	34	49	3	126	136	3	126	137	1	172	146	
3	34	25	8	55	17	3	219	230	4	308	313	4	109	101	4	73	93	1	211	214	
4	111	123	9	144	135	4	51	36	5	79	64	5	189	181	5	43	36	3	172	146	
5	73	44	11	84	110	5	32	43	6	189	181	6	342	339	6	106	122	0	712	695	
6	37	7	12	K	2	6	54	56	7	61	53	7	258	256	7	80	23	2	290	296	
7	82	51	0	472	479	8	219	199	8	367	349	8	204	230	8	112	91	4	599	595	
8	53	57	1	37	29	9	34	1	9	354	349	9	178	169	9	285	281	0	16	K	1
9	52	24	2	366	346	12	K	6	13	K	3	14	K	1	14	K	1	22	16	K	1
0	60	90	3	102	93	0	79	52	14	K	4	50	50	43	15	K	0	15	K	0	
1	111	99	4	99	85	1	54	29	0	28	11	1	172	181	0	461	465	0	47	59	
2	53	13	5	47	12	2	364	377	1	29	68	1	68	51	1	54	5	1	54	4	
3	235	216	6	174	166	2	134	145	2	399	408	2	38	9	2	61	43	2	544	529	
4	120	100	7	91	78	3	245	241	3	49	14	3	86	91	3	150	155	2	54	26	
5	48	67	8	51	20	4	53	8	4	110	94	4	216	220	4	106	96	3	54	26	
6	40	5	9	45	31	5	135	151	5	52	20	5	86	91	5	109	83	4	170	144	
7	147	140	10	113	149	6	135	151	6	100	96	6	161	164	6	146	146	4	170	144	
8	33	43	11	47	29	7	88	104	7	88	104	7	205	184	7	133	146	15	K	2	
0	332	337	12	K	3	0	56	10	8	54	101	8	61	46	15	K	1	0	47	59	
1	139	116	0	480	484	1	419	411	9	80	101	9	54	46	0	461	465	0	47	59	
2	153	141	1	122	115	2	118	111	10	80	101	10	54	46	1	54	529	1	544	529	
3	55	4	2	101	89	3	111	104	13	K	4	51	95	13	13	13	96	0	54	26	
4	54	6	3	561	545	1	62	65	0	238	243	0	245	258	0	150	155	0	54	26	
5	54	7	4	50	21	3	284	292	1	48	50	1	53	51	1	109	83	2	544	529	
6	54	6	5	214	226	5	565	575	3	133	139	3	51	15	3	146	156	3	54	26	

11 K 3		11 K 7		12 K 3		13 K 0		13 K 4		14 K 2		15 K 2								
K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	K	OBS	CALC	K	OBS	CALC			
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	484	471	9	484	471	7	175	191	8	802	795	1	459	437
10	626	620	10	38	39	10	38	39	8	56	21	8	56	21	14	K 3		2	49	19
11	58	2	11	K 1		13	K 1		13	K 5		13	K 5		3	275	267	3	275	267
			0	658	636	12	K 4		0	238	243	0	278	275	4	34	24	4	34	24
			2	497	486	0	376	359	1	66	73	0	278	275	0	56	17	5	266	278
			4	511	498	1	95	75	1	66	73	1	110	120	1	460	455	6	63	34
			6	133	134	2	197	193	2	403	404	2	784	760	2	57	7			
			8	484	472	3	53	12	3	38	36	3	81	51	3	409	412	15	K 3	
			10	179	158	4	153	159	4	254	260	4	254	251	4	49	40	0	194	27
						5	54	6	5	41	20	5	460	451	5	460	451	1	66	70
						6	116	99	6	503	513	6	70	39	6	83	86	2	48	22
						7	57	13	7	98	113	7	721	694	7	106	61	3	80	86
						8	323	297	8	256	235	13	K 6		14	K 4		4	39	52
						9	83	27	9	91	86	13	K 6		14	K 4		5	41	38
						12	K 5		10	62	44									
						0	43	18	0	100	81	0	116	103	0	125	121	15	K 4	
						1	40	58	1	605	606	1	206	195	1	62	106	15	K 4	
						2	68	31	2	53	38	2	81	89	2	58	47	0	134	124
						3	195	215	3	349	333	3	163	145	3	118	120	1	185	192
						4	34	31	4	55	53	4	53	77	4	84	87	2	42	10
						5	77	43	5	185	185	14	K 0		5	76	27	3	137	135
						6	73	57	6	33	45				6	83	86	0	16	K 0
						7	237	197	7	358	336	0	339	342	0	73	29	0	702	677
						8	61	3	8	56	20	2	254	242	1	371	372	2	303	299
						12	K 6		9	340	348	6	212	229	2	104	92	4	575	571
						0	61	77	13	K 3		8	170	165	3	306	288	16	K 1	
						1	76	32	0	59	27	14	K 1		4	42	32	0	101	98
						2	352	356	1	70	54	0	37	40	15	K 0		0	101	98
						3	122	120	2	373	386	1	171	167	0	382	386	1	52	3
						4	243	247	3	55	18	2	53	44	1	382	386	2	66	25
						5	57	13	4	137	107	3	54	7	3	212	199	3	148	166
						6	131	145	5	55	24	4	101	94	5	513	499	4	123	130
						12	K 7		6	124	103	5	225	217	7	145	156	16	K 2	
						0	51	24	7	96	102	6	136	141	15	K 1		0	59	42
						1	392	381	8	58	23	7	225	200	0	444	446	1	54	2
						2	97	85	9	57	74	8	37	58	1	86	8	2	527	516
						3	125	98	13	K 4		14	K 2	0	444	446	3	71	32	
						13	K 0		0	55	54	0	52	5	2	69	57			
						1	450	452	1	237	246	1	34	79	3	159	142			
						2	65	103	2	50	54	2	227	244	4	78	89			
						3	53	69	3	300	289	3	34	39	5	57	3			
						4	63	86	4	139	123	4	714	727	6	133	95			
						5	541	537	5	202	212	5	56	13	7	149	135			
						6	44	8	6	294	298	6	56	24						
						7	210	231	5	552	555	6	53							
						0	73	67	1	108	63									
						1	450	452	3	294	298									
						2	65	103	5	552	555									
						3	53	69												
						4	63	86												
						5	541	537												
						6	44	8												
						7	210	231												