

Cr³⁺ coordination in chlorites: a structural study of ten chromian chlorites

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In an effort to provide additional information on the coordination of Cr³⁺ in chlorites, complete structural refinements were undertaken of two chromian chlorites from Day Book Body, North Carolina, and Siskiyou Co., California, both of which have been reported to contain predominantly tetrahedral Cr³⁺. In addition, eight one-dimensional electron density projections were constructed from X-ray intensity data taken from eight different chromian chlorites, three of which were reported to have tetrahedral Cr³⁺. The one-dimensional projections indicate the Cr³⁺ and other heavy atoms to be concentrated in the interlayer octahedral sites. There is good agreement between the number of electrons per formula unit derived from integration of cation electron density peaks and the number calculated from the microprobe analyses under the assumption that all heavy atoms are concentrated in the interlayer. Both three-dimensional studies were done on 11b-4 polytypes in triclinic space group C1. In both structures the Cr³⁺ was preferentially concentrated in the M(4) octahedron on the inversion center within the interlayer. Si and Al were found to be disordered over the two independent tetrahedra. We propose that a combination of cation repulsion and crystal field effects concentrates the Cr³⁺ in the M(4) octahedron, and that a disordered Si,Al distribution in tetrahedral sites provides the most favorable balance of charge around M(4). The cell angle α was found to be triclinic, and it is postulated that repulsion between the tetrahedral and M(4) cations causes this slewing of the structure. As no evidence of Cr³⁺ in tetrahedral coordination was found, we propose that the names kotschubeite and kämmererite be discarded.

Introduction and nomenclature

Chromium-bearing chlorites long have been of considerable mineralogical interest because of their pleasing pink to red to violet colors. There has been lack of agreement as to the structural location of the chromium, however, and as to the most appropriate species or variety names.

Lapham (1958) in the first detailed investigation of chromian chlorites studied the variations in optical, chemical, X-ray, and thermal properties of eight chromium-bearing chlorites in relation to the amount of chromium present. He found that for chlorites containing less than 2% Cr₂O₃, there was no significant change in the properties, and suggested that the prefix "Cr" be added to the accepted Fe-Mg nomenclature. In chlorites having more than 2% Cr₂O₃, however, Lapham observed significant variations in the analyzed properties, reportedly depending on whether the Cr³⁺ was tetrahedrally or octahedrally coordinated. Coordination was determined by plots

of *d* spacings of certain reflections against percent Cr₂O₃. On the basis of his results, Lapham proposed that the name kämmererite be used for chromian chlorites with octahedral Cr³⁺ and that kotschubeite be used when the Cr³⁺ coordination was tetrahedral.

McCormick (1975) described a chlorite containing both octahedral and tetrahedral chromium, where coordination was determined by differing dissolution rates during acid leaching. He proposed that Lapham's classification be revised so that kämmererite include chlorites with Cr^{VI} \geq Cr^{IV}, and kotschubeite include chlorites with Cr^{VI} < Cr^{IV}. Using this nomenclature McCormick classified his specimen as kotschubeite.

Damodaran and Somasekar (1976) studied a "kämmererite" from the Nuggihalli Schist Belt, India, using Lapham's determinative methods. Their results indicated the Cr³⁺ to be tetrahedrally coordinated, and therefore the specimen to be kotschubeite instead of kämmererite.

TABLE 3(a)-1 Observed and Calculated Structure Amplitudes, Day Book Body Chlorite

K	L TOFO		TOFC		K	L TOFO		TOFC		K	L TOFO		TOFC		K	L TOFO		TOFC		K	L TOFO		TOFC		K	L TOFO		TOFC											
	H	C																																					
0	5	897	978		8	-9	250	256		7	-12	143	145		-7	-15	118	119		-7	-8	218	159		-6	-8	925	1029		-1	3	564	515		-5	-5	87	62	
0	6	276	167		8	-10	233	229		7	-12	167	174		7	-16	124	117		2	-4	213	228		-6	-8	362	941		-1	-3	134	119		-5	-5	352	148	
0	6	666	760		8	-11	197	207		7	-12	167	174		7	-17	85	59		2	-4	213	228		-6	-8	244	253		1	4	109	130		-5	-5	172	101	
0	6	169	180		8	-12	213	215		7	-12	291	303		-7	0	175	165		-2	-4	206	143		-6	-8	354	355		-4	-4	193	105		-5	-6	403	269	
0	6	311	321		8	-13	113	94		7	-13	405	433		-9	-1	80	20		2	-4	213	228		-6	-8	228	287		-1	4	157	167		-5	-6	129	127	
0	10	788	845		8	-13	134	117		7	-13	304	327		-9	1	654	632		2	-4	213	228		-6	-8	366	374		-1	-4	370	403		-5	-7	79	78	
0	11	166	214		8	-14	186	163		7	-14	235	234		-9	-2	680	652		-2	-4	213	228		-6	-8	102	102		1	5	213	238		-5	-7	224	208	
0	12	729	790		8	-14	127	115		7	-14	374	370		-9	-2	455	426		-2	-4	213	228		-6	-8	423	225		-1	5	184	178		-5	-7	118	161	
0	13	155	145		8	-14	99	86		7	-14	229	234		-9	-2	685	674		-2	-4	213	228		-6	-8	223	245		-1	-5	132	159		-5	-6	282	264	
0	14	623	632		10	0	99	66		9	-2	406	367		-9	-2	406	367		-2	-4	213	228		-6	-8	448	457		-1	0	80	68		-5	-6	133	141	
0	16	696	673		10	-2	177	167		9	-3	285	296		-9	-3	437	423		2	-4	213	228		-6	-8	321	391		-1	0	326	212		-5	-6	95	67	
0	19	251	211		10	3	147	158		9	-3	345	325		-9	-3	499	511		2	-4	213	228		-6	-8	193	193		-1	0	174	192		-5	-6	114	101	
2	-1	665	571		10	4	105	102		9	-3	16	323	311		-9	-3	685	650		-2	-4	213	228		-6	-8	141	136		-1	7	276	263		-5	-10	106	79
2	-2	91	59		10	-4	149	138		9	-4	144	159		-9	-4	74	45		-2	-4	213	228		-6	-8	152	131		-1	-7	182	176		-5	-10	159	170	
2	-2	125	131		10	-5	97	96		9	-4	310	306		-9	-4	108	117		-2	-4	213	228		-6	-8	152	140		1	8	168	160		-5	-10	71	51	
2	-3	589	590		10	-7	19	22		9	-5	178	192		-9	-5	440	439		-2	-4	213	228		-6	-8	14	141		-1	9	249	262		-5	-11	116	107	
2	-4	504	510		10	9	169	160		9	-5	248	219		-9	-5	695	670		2	-4	213	228		-6	-8	141	322		1	9	171	94		-5	-14	60	45	
2	-4	264	262		10	-10	162	165		9	-5	333	311		-9	-5	333	311		-2	-4	213	228		-6	-8	258	257		-1	9	123	116		-5	-14	89	81	
2	-5	108	137		10	11	118	105		9	-5	154	136		-9	-5	108	117		-2	-4	213	228		-6	-8	14	265		-1	-9	62	75		-5	-17	157	172	
2	-5	551	284		10	12	111	89		9	-5	175	115		-9	-5	373	388		-2	-4	213	228		-6	-8	15	155		1	10	191	190		-5	-14	146	147	
2	-6	459	297		10	-12	124	106		9	-5	199	459		-9	-6	181	373		-2	-4	213	228		-6	-8	15	164		1	-10	69	58		-5	-14	131	116	
2	-6	304	313		10	-12	124	106		9	-5	199	459		-9	-6	181	373		-2	-4	213	228		-6	-8	15	155		-1	-10	83	73		-5	-16	85	76	
2	-7	205	223		10	0	500	468		9	-6	500	468		-9	-6	326	348		-2	-4	213	228		-6	-8	16	90		-1	-10	140	156		-7	-7	193	200	
2	-8	77	67		10	0	361	323		9	-7	885	874		-9	-7	885	874		-2	-4	213	228		-6	-8	0	104		1	-11	173	170		-7	-7	154	163	
2	-8	221	238		10	1	206	167		9	-7	390	364		-9	-7	390	364		-2	-4	213	228		-6	-8	0	85		-1	-11	143	151		-7	-7	164	167	
2	-9	187	218		10	-1	65	38		9	-7	914	934		-9	-7	914	934		-2	-4	213	228		-6	-8	1	167		-1	-12	86	72		-7	-7	172	162	
2	-9	141	148		10	-1	170	234		9	-7	389	367		-9	-7	389	367		-2	-4	213	228		-6	-8	-1	215		-1	-13	69	73		-7	-7	63	63	
2	-10	124	138		10	-1	459	364		9	-8	355	360		9	-8	267	286		-2	-4	213	228		-6	-8	-1	225		-1	-13	75	59		-7	-7	205	201	
2	-10	75	63		10	-1	676	575		9	-8	228	203		9	-8	79	68		-2	-4	213	228		-6	-8	-1	195		-1	-13	160	173		-7	-7	63	63	
2	-11	71	63		10	-1	171	148		9	-8	167	167		9	-8	167	167		-2	-4	213	228		-6	-8	2	232		-1	-14	147	146		-7	-7	256	272	
2	-11	126	156		10	-2	593	585		9	-8	451	433		9	-8	144	160		-2	-4	213	228		-6	-8	-1	2		-1	-14	81	43		-7	-7	355	315	
2	-12	104	120		10	-2	347	306		9	-9	797	812		9	-9	797	812		-2	-4	213	228		-6	-8	-2	181		-1	-15	82	64		-7	-7	246	234	
2	-12	132	141		10	-2	132	134		9	-9	735	748		9	-9	735	748		-2	-4	213	228		-6	-8	3	93		-1	-16	80	89		-7	-7	184	175	
2	-13	104	111		10	-2	724	709		9	-9	203	189		9	-10	367	364		-4	-4	213	228		-6	-8	-3	271		-1	-17	118	75		-7	-7	175	167	
2	-13	64	46		10	-3	224	196		9	-10	393	392		9	-10	393	392		-4	-4	213	228		-6	-8	-3	111		-1	-18	77	61		-7	-7	187	194	
2	-15	73	74		10	-3	646	607		9	-10	441	459		9	-10	441	459		-4	-4	213	228		-6	-8	-3	66		-1	-18	113	94		-7	-7	187	202	
2	-16	100	92		10	-3	531	544		9	-10	305	369		9	-10	305	369		-4	-4	213	228		-6	-8	4	77		-1	-19	123	85		-7	-7	187	194	
2	-17	110	105		10	-3	499	508		9	-10	465	458		9	-11	465	458		-4	-4	213	228		-6	-8	-4	193		-1	-20	129	178		-7	-7	187	194	
2	-17	99	68		10	-3	369	386		9	-11	206	200		9	-11	206	200		-4	-4	213	228		-6	-8	-4	190		-3	-20	219	7		-7	-7	79	79	
2	-19	116	108		10	-4	81	74		9	-11	420	432		9	-11	420	432		-4	-4	213	228		-6	-8	-4	263		-3	-21	902	7		-7	-7	227	240	

TABLE 3(a)-2

K	L	1,FO	10FC	K	L	1,FO	10FC	K	L	1,FO	10FC	K	L	1,FO	10FC	K	L	1,FO	10FC	
0	-7	74	741	0	3	104	110	1	-4	73	49	-7	-4	143	130	-1	-1	271	242	
0	8	276	277	0	-3	431	325	-1	4	94	68	7	5	133	222	1	-2	199	216	
0	-8	661	655	0	4	451	485	-1	-4	162	164	7	-5	40	106	1	3	169	165	
0	9	441	427	0	-4	640	641	1	12	143	132	-7	5	115	122	-1	4	162	171	
0	-9	379	374	0	4	374	367	1	-10	143	148	7	6	79	65	-1	-4	124	194	
0	10	305	308	0	-4	632	619	1	11	94	86	-7	6	158	148	1	-5	142	162	
0	-10	1616	1019	0	5	398	424	1	-11	107	95	-7	-6	177	170	3	0	346	371	
0	11	276	297	0	-5	358	360	-1	11	135	124	7	7	221	229	3	1	199	210	
0	-11	313	315	0	6	925	936	-1	-11	121	127	7	-7	153	157	3	-1	5-1	574	
0	12	226	234	0	-6	779	676	1	-13	96	109	-7	7	93	68	3	3	365	269	
0	-12	86	58	0	6	921	939	-1	-13	75	65	-7	8	202	265	3	-3	100	65	
0	14	167	178	0	-6	635	610	1	-14	103	86	9	0	324	332	3	-4	348	392	
0	-14	192	181	0	7	307	308	1	-15	86	60	-9	0	234	333	3	-5	348	374	
0	15	157	146	0	-7	384	383	-1	-15	115	108	9	1	466	480	3	-6	92	65	
0	-15	265	239	0	7	209	227	1	-16	108	91	-9	1	356	366					
0	17	123	135	0	-7	365	359	3	0	458	495	0	2	94	58					
2	0	191	182	0	-8	403	396	-3	0	435	377	0	-2	102	93					
2	0	249	235	0	-8	385	369	3	1	759	713	-9	2	106	60					
2	1	272	262	0	9	396	369	-2	1	700	565	9	3	333	347					
2	-1	395	375	0	-9	422	437	-2	-1	50	16	9	-7	472	499					
-2	1	295	306	0	-9	136	139	3	-2	210	170	-9	0	3	377	359				
-2	-1	331	309	0	10	510	500	-3	-2	155	125	-10	-3	484	476					
2	2	247	238	0	-10	821	840	3	3	685	666	-10	-4	375	401					
2	-2	166	143	0	10	461	464	3	-3	735	699	-10	-4	231	322					
-2	2	335	335	0	-10	754	765	-3	3	663	659	-9	-5	259	276					
2	3	74	97	0	-11	409	406	-3	-3	705	701	-9	-5	199	189					
-2	-3	525	482	0	11	101	94	3	4	412	398	9	-7	296	285					
2	3	702	700	0	-11	340	335	3	-4	763	726	-9	-7	323	297					
-2	-3	76	115	0	12	158	143	-3	4	376	364									
2	4	146	138	0	-12	201	210	-3	-4	707	668									
2	-4	204	196	0	12	188	182	3	5	447	453									
-2	4	112	126	0	-12	133	137	3	-5	550	564									
-2	-4	485	480	0	-13	129	134	-3	5	408	429									
2	-5	227	222	0	-13	131	114	-3	-5	510	501	0	0	468	475					
-2	5	94	90	0	14	97	90	3	6	187	182	0	1	408	422					
2	-5	85	91	0	-14	113	120	3	6	110	108	0	-1	260	258					
2	6	86	64	0	-15	210	206	-3	-6	123	153	0	2	292	317					
-2	-6	431	413	0	-15	206	192	-3	6	127	153	0	-2	1080	1149					
-2	6	73	66	0	-1	80	79	3	-6	127	871	0	3	336	361					
-2	-6	301	308	0	1	80	82	3	7	662	871	0	-3	106	66					
-2	7	272	269	0	-	125	120	-3	7	387	371	0	4	385	408					
2	-8	336	325	0	-2	96	67	-3	-7	615	653	0	-4	466	481					
-2	8	153	130	0	3	76	90	3	8	401	367	0	5	255	273					
-2	-9	83	84	0	-3	125	132	3	8	364	370	0	-5	210	205					
-2	9	117	119	0	-3	83	41	-3	-8	349	372	0	6	249	265					
-2	-9	278	285	0	4	140	134	-1	8	375	378	0	-6	357	372					
2	10	175	163	0	-4	162	163	3	9	367	375	0	8	610	632					
-2	-10	194	213	0	5	140	160	3	-9	134	134	0	9	215	227					
-2	10	75	77	0	-5	86	57	-3	9	1004	977	-2	0	97	112					
-2	-11	207	201	0	-5	108	107	-3	9	166	157	-2	1	135	140					
-2	11	185	192	0	6	83	63	-3	-9	929	906	-2	1	116	128					
-2	-11	179	159	0	6	217	226	3	10	136	134	-2	2	180	183					
-2	12	116	123	0	-6	113	96	-3	-10	156	157	-2	-2	80	88					
2	13	155	165	0	7	142	190	-3	10	131	129	-2	2	126	121					
-2	-13	141	140	0	-7	140	130	3	-10	181	182	2	3	98	124					
-2	14	82	60	0	-7	207	195	-3	11	156	150	-2	-3	96	92					
-2	-14	99	107	0	-8	96	60	3	12	149	128	-2	3	90	64					
2	15	143	94	0	-8	150	193	3	12	237	258	-2	-4	80	62					
-2	15	127	113	0	9	185	205	-3	-12	450	461	-2	4	173	189					
-2	-15	75	12	0	-9	164	145	-3	12	249	232	-2	-4	92	116					
-2	17	78	64	0	10	216	220	-3	-12	426	404	-2	5	204	212					
-4	0	185	170	0	-10	108	160	3	-13	435	426	-2	5	121	104					
-4	-1	162	141	0	-10	108	160	-3	-13	430	414	-2	-6	130	136					
4	1	72	36	0	-11	83	97	3	-14	95	94	-2	6	124	106					
4	2	204	200	0	-11	83	97	-3	-14	85	68	-2	7	151	173					
-4	-2	116	98	0	-12	105	90	3	-15	206	197	-2	7	198	191					
-4	3	140	123	0	-12	173	154	-3	-15	180	166	-2	-7	159	142					
-4	-3	219	213	0	-13	109	113	3	-16	161	152	-2	8	152	167					
-4	3	112	127	-10	0	124	123	5	0	112	117	-2	9	180	185					
4	4	269	252	10	1	83	69	-5	0	149	164	-7	-9	147	156					
4	-4	144	120	10	-1	178	166	5	1	203	260	-7	-12	163	199					
-4	-4	92	99	-10	-1	77	68	5	-1	124	123	-4	0	79	79					
4	5	148	147	-10	2	99	75	-5	1	108	66	4	1	225	237					
4	-5	164	165	-10	3	91	64	5	-2	126	162	4	-1	125	136					
-4	5	292	278	-10	-3	198	193	-5	2	113	89	-4	-1	204	228					
4	6	127	122	-10	4	85	77	-5	-2	146	144	-4	-2	199	217					
-4	6	100	108	-10	-4	159	192	5	3	110	93	-4	-2	181	210					
-4	-6	201	205	-10	4	85	63	-5	3	179	179	-4	-3	263	275					
4	7	276	270	-10	-4	75	51	-5	-3	126	131	4	4	86	91					
-4	-7	224	220	-10	-4	113	98	5	4	175	177	4	-4	209	321					
-4	7	170	168	-10	-5	113	110	5	-4	167	165	-4	-5	160	170					
-4	-7	162	167	-10	-6	113	110	5	5	85	114	4	-5	170	195					
4	8	73	54	-10	-6	124	126	5	-5	155	172	-4	-6	209	213					
-4	-8	176	166	-10	-7	113	142	-5	5	97	102	-4	-9	238	236					
-4	8	218	243	-10	-8	154	131	-5	-5	161	130	-4	-10	105	110					
-4	-8	180	169	-10	5	6	111	105	5	6	146	140	-4	-11	154	147				
4	9	278	294	-10	-5	6	146	140	-5	6	146	140	-4	-12	124	124				
4	-9	215	220	-10	-5	6	126	132	-5	-6	126	132	4	0	218	203				
-4	9	199	194	-10	5	7	118	117	5	7	118	117	-6	0	253	228				
4	10	106	99	-10	-5	7	95	113	5	-7	95	113	6	1	249	268				
4	-10	208	195	-10	5	7	85	107												

TABLE 3(b)-1 Observed and Calculated Structure Amplitudes, Siskiyou Co. Chlorite

K	L	10FO	10FC	K	L	10FO	10FC	K	L	10FO	10FC	K	L	10FO	10FC	K	L	10FO	10FC	K	L	10FO	10FC	K	L	10FO	10FC	K	L	10FO	10FC												
H = 0																																											
	6	17	139	144	-1	17	28	122	5	-10	234	228	-9	6	269	267	7	13	197	184	6	-7	502	531	-10	9	101	106															
	6	-17	99	117	-1	-17	55	37	-5	-10	197	249	-9	-6	556	76	-7	-13	234	250	-6	7	587	396	-10	-9	154	157															
	8	0	115	113	1	18	139	151	-5	-10	210	227	-9	8	163	161	-7	13	156	150	-9	-7	524	577	-10	10	70	72															
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	8	-1	59	16	-1	18	94	64	-5	-11	64	36	9	9	48	66	-2	14	210	221	-6	-8	765	961	-10	10	133	135															
	8	2	48	51	-1	-18	175	173	-5	-11	162	170	9	-9	225	76	-2	-14	326	341	-9	8	1074	1164	-10	-10	107	107															
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	8	3	134	158	1	-19	167	176	5	-12	126	134	-9	-9	911	652	-2	-14	302	217	-6	9	265	260	-10	-11	107	104															
	8	-3	37	37	1	19	145	148	-5	-12	52	63	9	10	593	363	-2	15	272	216	-6	-9	342	349	-10	-11	179	167															
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	8	-4	170	157	3	0	320	343	-5	-13	103	111	-9	-10	519	500	-2	-15	207	216	-6	-9	444	446	-10	-12	61	73															
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	8	6	127	131	3	-1	46	31	5	14	159	164	9	-11	205	219	-2	-16	236	233	-6	-10	292	272	-10	-12	152	152															
	8	-7	211	211	-3	1	982	959	-5	-14	72	68	-9	-11	460	461	-2	-10	183	165	-6	-10	281	297	-10	-12	152	152															
	8	7	269	258	-3	-1	63	58	-5	-14	44	46	-9	-11	134	149	-2	17	192	199	-6	-11	466	471	-10	-12	152	152															
	8	-8	84	61	3	2	1247	1281	5	-15	103	98	9	12	95	95	-2	-17	49	44	-6	-11	37	24	-10	-12	152	152															
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	8	-11	81	79	3	3	797	897	-5	-16	105	100	9	-13	163	157	-2	-18	210	217	-6	-12	239	211	-10	-12	152	152															
	8	11	237	214	-3	3	990	943	5	-17	88	97	-9	-13	244	241	-2	-19	116	115	-6	-13	171	165	-10	-12	152	152															
	8	-12	247	239	3	4	457	393	5	-18	127	132	-9	-13	179	165	-2	-19	204	218	-6	-13	40	28	-10	-12	152	152															
	8	13	127	126	3	-4	269	258	-5	-18	160	178	-9	-14	239	220	-4	0	276	299	-6	-13	197	180	-10	-12	152	152															
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	8	-14	135	137	3	5	1052	1005	-7	0	110	103	-4	-1	333	344	-6	-14	384	380	-6	-14	384	380	-10	-12	152	152															
	8	15	70	70	3	-5	1600	1610	7	1	58	44	-4	-1	453	466	-6	15	219	201	-6	15	219	201	-10	-12	152	152															
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	10	-7	208	166	-3	-8	318	304	7	4	276</																																

