

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

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Abstract

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 IIb-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} ≥ 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	10FO	10FC	K	L	10FO	10FC	K	L	10FO	10FC	K	L	10FO	10FC	K	L	10FO	10FC	K	L	10FO	10FC	
H = 0	8	-9	250	256	7	-12	143	145	-7	-15	118	149	-2	-8	214	239	-6	8	995	1029	-1	3	564	515
0	5	897	978	8	-10	20	72	-3	-12	110	123	7	-17	85	59	2	-9	383	429	6	9	244	253	
6	226	107	8	-11	197	201	7	-12	363	397	-9	0	175	165	-2	-9	404	434	6	-9	354	359		
0	7	666	700	8	-12	153	176	3	-17	291	303	9	-1	766	735	-2	-9	290	265	-1	-4	193	105	
0	8	169	180	8	-12	213	215	-3	-13	403	433	9	-1	80	20	2	-10	283	400	-6	-9	366	379	
0	9	311	321	8	-13	115	94	-3	-13	30	327	-9	-1	659	652	2	-10	108	94	5	10	192	196	
0	10	788	845	8	-13	134	117	3	-14	235	234	9	-2	680	652	-2	-10	167	185	6	-9	271	269	
0	11	166	214	8	-14	166	163	3	-14	374	376	9	-2	455	426	-2	-10	327	369	-6	10	623	225	
0	12	729	790	8	-14	127	115	-3	-14	229	234	-9	-2	685	674	2	-11	388	429	-6	-10	223	245	
0	13	115	145	10	0	99	66	-3	-14	345	349	-9	-2	406	367	-2	-11	299	307	6	-11	448	457	
0	14	623	632	10	1	170	177	3	-15	285	296	9	-3	437	425	2	-12	311	312	-6	-11	381	391	
0	16	696	673	10	-2	177	161	-3	-15	247	262	9	-3	628	594	2	-12	300	215	6	12	193	195	
0	19	251	211	10	3	147	158	7	-16	345	325	-9	-3	499	511	-2	-12	266	270	6	-12	457	462	
2	0	474	416	10	-4	105	102	3	-16	315	305	-9	-3	685	650	-2	-12	351	364	-6	12	193	180	
2	-1	665	571	10	-4	149	158	-3	-16	323	311	9	-4	144	159	2	-13	152	151	-6	-12	414	439	
2	-2	91	59	10	-5	97	96	-3	-16	310	306	9	-4	74	45	2	-13	201	202	6	13	152	149	
2	3	125	131	10	6	182	178	3	-17	518	453	-9	-4	106	117	-2	-13	112	106	-6	13	169	153	
2	-3	589	590	10	-7	193	202	-3	-17	528	466	9	-5	440	430	-2	-13	95	100	6	14	421	237	
2	-4	504	510	10	9	169	160	4	18	218	192	9	-5	695	670	2	-14	141	158	6	-14	322	329	
2	-4	264	282	10	-10	162	165	3	-18	154	136	-9	-5	333	377	2	-14	255	273	-6	-14	256	250	
2	-5	108	137	10	11	118	106	-3	18	248	219	-9	-5	562	522	-2	-14	218	262	-6	-14	265	278	
2	-5	51	264	10	12	111	89	-3	18	115	115	9	6	373	388	-2	-14	229	229	6	15	155	168	
2	-6	459	297	10	-12	124	106	3	-19	459	403	9	-6	381	373	2	-15	155	161	-6	15	162	140	
2	-6	304	313	5	0	500	468	-3	19	458	387	-9	-6	326	348	-2	-15	156	160	-6	-17	155	135	
2	7	205	223	5	0	500	468	-3	19	366	369	9	-7	885	874	-2	-16	206	205	8	0	104	95	
2	-8	221	258	-1	0	361	323	5	1	208	167	-9	-7	390	384	-2	-16	166	156	-8	0	85	99	
2	-9	187	218	-1	1	270	234	-5	1	141	112	-9	-7	389	367	2	-17	155	129	-8	1	213	223	
2	10	124	138	-1	1	459	364	-5	1	355	360	9	8	267	280	-2	-17	89	85	-8	1	225	232	
2	-10	75	63	-1	1	676	575	5	2	228	203	9	-8	79	68	-2	-17	149	136	-8	1	195	203	
2	-11	71	63	-1	-1	171	148	5	-2	561	506	-9	-8	167	167	2	-18	153	147	-8	2	232	222	
2	-12	111	126	1	2	598	585	-5	2	451	433	-9	-8	144	160	-2	-18	116	96	-8	2	66	32	
2	-12	104	120	1	-2	347	306	-5	-2	125	125	-9	-9	797	812	2	-19	81	73	-8	2	181	183	
2	-12	132	141	-1	2	322	334	5	3	361	342	-9	-9	735	748	-2	-19	140	147	-8	3	93	59	
2	-13	111	111	-1	-2	724	709	5	-3	203	189	9	10	367	304	4	-10	363	335	-8	3	271	253	
2	-13	64	46	1	3	224	196	-5	3	55	33	9	-10	393	392	-4	-10	210	209	-8	3	111	93	
2	-15	73	74	1	-3	646	607	-5	-3	526	513	-9	-10	441	459	4	-1	381	327	-8	-3	66	16	
2	-16	100	95	-1	3	531	544	5	-4	221	233	-9	-10	305	309	4	-1	276	247	8	4	77	76	
2	-17	110	103	-1	-3	49	58	-5	4	200	193	9	-11	465	458	-4	-1	357	361	-8	4	195	197	
2	-17	99	68	1	4	369	386	5	5	213	201	9	-11	206	200	-4	-1	483	455	-8	4	190	203	
2	-19	116	108	-1	4	81	74	5	-5	432	453	-9	-11	420	432	4	-2	541	476	-8	4	263	254	
4	0	169	191	-1	-4	424	455	-5	-5	185	192	-9	-11	124	113	-4	-10	304	270	8	5	171	154	
4	1	146	109	1	5	293	332	-5	-5	281	291	9	-10	393	392	-4	-10	210	209	8	7	99	91	
4	-1	259	265	1	-5	413	447	5	6	62	87	9	-12	151	136	4	-3	110	91	-8	5	84	68	
4	-2	233	222	5	-5	342	360	5	-6	102	109	-9	-12	120	112	-3	-3	375	366	-8	10	103	101	
4	-2	55	25	-1	-5	301	321	-5	-6	60	45	9	-13	103	126	4	-4	106	101	-8	6	110	114	
4	3	187	173	1	6	109	129	-5	-6	278	287	9	-13	88	84	4	-4	385	391	-8	6	212	211	
4	-3	360	339	1	-6	179	186	5	-7	285	294	-9	-13	226	197	-4	-4	269	287	-8	6	71	74	
4	4	293	310	-1	6	206	240	-5	7	171	177	-9	-13	161	130	-4	-4	332	343	-8	6	139	167	
4	-6	93	82	-1	-6	176	169	-5	7	195	196	-9	-14	212	207	4	-5	134	119	-8	7	99	91	
4	5	384	368	1	7	265	268	5	8	160	167	-9	-14	168	158	-4	-5	295	289	-8	7	99	87	
4	-5	366	373	1	-7	173	181	5	8	127	127	-9	-14	206	191	-4	-5	102	91	-8	7	122	97	
4	6	282	292	-1	7	139	159	-5	-8	233	262	-9	-14	200	217	-4	-5	308	309	-8	7	133	137	
4	-7	319	307	-1	-7	260	310	5	9	59	208	-9	-14	206	191	-4	-5	311	314	-8	7	133	137	
4	-7	396	394	1	9	117	140	-5	10	173	177	-9	-15	302	296	-4	-5	125	113	-8	7	113	125	
4	-8	299	320	-1	-9	174	204	-5	-10	172	196	-9	-15	302	296	-4	-6	255	260	-8	9	113	125	
4	9	456	484	1	10	169	195	5	11	167	172	-9	-15	102	107	-4	-6	62	63	-8	9	213	218	
4	-9	149	171	1	-10	163	176	-5	-11	134	147	-9	-15	985	973	-4	-6	245	247	-8	9	213	218	
4	-10	440	466	-1	10	90	111	5	-12	120	123	0	-12	359	229	-4	-7	81	165	-8	10	123	129	
4	11	317	351	-1	-10	147	162	5	-13	73	90	0	-13	1309	1339	4	-8	136	135	-8	11	210	210	
4	12	235	243	1	-11	107	147	-5	-13	148	149	0	-14	896	920	4	-8	136	135	-8	12	154	127	
4	-12	336	345	-1	-11	173	176	-5	-13	94	106	0	-15	1031	950	-4	-8	98	94	-8	12	145	144	
4	13	177	167	-1	-11	52	27	5	-14	105	125	0	-15	464	427	-4	-8	292	317	-8	13	107	91	
4	-13	174	170	-1																				

TABLE 3(a)-2

K	L	T	FO	10	FC	K	L	T	FO	10	FC	K	L	T	FO	10	FC	K	L	T	FO	10	FC
8	-7	741	741	-6	3	104	119	1	-4	73	49	-7	-4	145	130	-1	-1	271	222				
8	8	274	277	-6	-3	401	385	-1	-4	90	68	7	5	183	202	1	-2	199	246				
6	-8	661	655	0	4	481	485	-1	-4	162	169	7	-5	90	106	1	3	169	188				
9	9	441	427	6	-4	640	621	1	1	149	152	-7	5	115	120	-1	-1	4	162	171			
0	-9	379	374	-6	4	374	367	1	-12	143	148	7	6	79	65	-1	-4	124	194				
0	10	505	508	-6	-4	632	619	1	11	90	68	-7	6	158	148	1	-5	142	162				
0	-10	1015	1019	6	5	398	424	1	-11	107	95	-7	-9	177	176	3	-3	346	371				
0	-11	276	297	-5	-5	358	380	-1	11	135	124	7	7	421	220	3	-1	109	223				
0	12	313	315	6	6	925	936	-1	-11	121	127	7	-7	153	157	3	-1	5:1	574				
0	-12	226	234	6	-6	709	696	1	-13	96	109	-7	7	93	68	3	-3	365	359				
0	14	98	58	-6	6	921	930	-1	-13	75	65	-7	8	472	205	3	-3	100	65				
0	-14	167	178	-6	-6	635	610	1	-14	103	68	-9	9	304	332	3	-4	348	392				
0	15	192	181	6	7	307	308	1	-15	86	60	-9	-9	376	333	3	-5	366	376				
0	-15	157	146	6	-7	384	383	-1	-15	115	128	-9	1	460	480	3	-6	92	85				
0	-16	265	239	-6	7	209	207	1	-16	108	91	-9	1	350	366								
0	-17	123	135	-6	-7	363	359	3	0	454	795	-9	2	99	58								
2	0	191	182	6	-8	403	396	-3	0	435	374	-9	-2	102	93								
2	-0	249	235	-6	-8	385	369	3	1	759	713	-9	-2	176	80								
2	1	272	262	6	9	396	389	-3	1	700	665	9	3	333	340								
2	-1	395	375	-6	9	422	437	-3	-1	80	76	9	-7	472	499								
-2	1	295	306	-6	-9	138	139	3	-2	210	179	-9	3	377	359								
-2	-1	331	309	6	10	510	500	-3	-2	152	145	-9	-3	484	476								
2	2	247	238	6	-10	821	840	3	3	688	606	-9	-4	375	401								
-2	2	166	143	-6	10	461	464	-3	3	735	699	-9	-4	371	322								
-2	-2	335	335	-6	-10	754	765	-3	3	663	659	-9	-5	259	276								
2	3	74	97	6	-11	409	406	-3	-3	705	701	-9	-5	199	159								
2	-3	525	482	-6	11	101	94	3	4	412	398	-9	-7	296	285								
-2	3	702	190	-6	-11	340	335	3	-4	763	726	-9	-7	323	297								
2	4	149	138	6	12	158	143	-3	4	373	364												
2	-4	204	196	-6	12	188	182	3	-5	447	453	H = 6											
-2	4	112	126	-6	-12	133	137	3	-5	550	564												
-2	-4	485	480	6	-13	129	134	-3	5	408	429	0	0	468	475								
-2	-5	227	222	-6	-13	131	114	-3	-5	511	501	0	1	408	422								
-2	5	94	90	6	-14	97	90	3	6	187	152	0	-1	260	258								
-2	-5	85	91	-6	-14	113	120	3	-6	110	108	0	2	292	317								
2	6	80	64	6	-15	210	206	-3	0	123	153	0	-2	1080	1149								
-2	6	73	66	6	-1	93	79	3	7	602	871	0	3	336	361								
-2	-6	301	308	-6	1	80	82	-3	-7	387	371	0	4	385	408								
-2	-7	272	269	8	2	125	120	-3	-7	613	853	0	-4	466	481								
2	-8	336	325	8	-2	96	67	-3	-7	401	367	0	5	255	273								
-2	8	153	130	8	3	76	90	3	8	364	370	0	-5	210	205								
-2	9	89	84	8	-3	135	132	3	-8	349	372	0	6	249	265								
-2	-9	117	119	-8	-3	83	41	-3	6	375	378	0	-6	357	372								
-2	-9	278	285	-8	4	140	134	-3	-8	367	375	0	8	610	632								
2	10	175	163	-8	-4	162	163	3	9	134	134	0	9	215	227								
2	-10	207	213	8	5	140	160	-3	-9	104	977	-2	0	97	112								
2	10	75	77	8	-5	86	57	-3	9	166	157	2	1	135	140								
-2	-11	207	201	-8	5	108	107	-3	-9	929	906	-2	1	116	128								
-2	-11	185	192	8	6	83	63	3	10	136	134	2	2	180	183								
-2	12	179	159	8	-6	217	226	3	-10	150	157	2	-2	80	88								
-2	-12	116	123	-8	6	113	96	-3	10	131	129	-2	2	126	121								
2	13	155	165	8	7	142	190	-3	-10	181	182	2	3	98	124								
2	-13	141	140	-8	7	140	130	3	11	156	150	2	-3	96	92								
-2	14	82	60	-8	-7	207	195	-3	11	149	148	-2	3	90	84								
-2	-14	99	107	8	-8	96	80	3	12	237	258	2	-4	80	62								
2	15	143	94	8	-9	180	193	3	-12	450	461	-2	4	173	189								
-2	15	127	113	-8	9	125	205	-3	12	249	232	-2	-4	92	116								
-2	-15	75	12	-6	-9	164	145	-3	-12	426	404	-2	5	204	212								
-2	-17	78	64	8	10	216	220	-3	-13	425	426	-2	5	121	104								
-4	-0	195	170	-8	-10	108	100	-3	-13	430	414	-2	-6	130	136								
-4	-1	162	141	-8	-11	200	205	3	-14	95	94	-2	6	124	108								
-4	-1	72	36	-8	-11	83	97	-3	-14	85	88	-2	7	151	173								
-4	2	204	200	-8	-12	105	90	3	-15	206	197	-2	7	188	191								
-4	-2	116	98	-8	-12	173	154	-3	-15	180	166	-2	-7	159	142								
-4	-3	140	123	-8	-13	109	113	3	-16	161	152	-2	8	152	167								
-4	-3	219	213	-10	0	124	123	5	0	112	117	-2	9	180	185								
-4	-3	132	127	-10	0	152	163	-5	0	149	166	-2	9	147	156								
-4	4	269	252	10	1	83	69	5	-1	203	200	-2	-12	163	199								
-4	-4	144	120	10	-1	178	166	5	-1	122	123	-4	0	79	79								
-4	-4	92	99	-10	-1	77	68	-5	-2	146	144	-4	-2	199	217								
-4	-5	164	165	-10	2	91	84	-5	-2	126	162	-4	-1	125	136								
-4	-5	292	278	-10	-3	198	193	-5	-2	146	144	-4	-1	204	228								
-4	-6	100	108	10	-4	159	192	-5	-3	179	179	-4	-3	263	275								
-4	-6	201	205	-10	4	85	63	-5	-3	125	131	-4	4	86	91								
-4	7	276	270	-10	-4	75	51	5	-4	175	177	-4	-4	299	321								
-4	-7	224	220	-10	-5	113	98	5	-4	167	165	-4	-5	160	170								
-4	-7	170	168	-10	-6	113	110	5	5	85	114	-4	-6	170	195								
-4	-7	162	167	-10	-6	124	211	-5	-13	114	127	-4	-6	209	213								
-4	-8	73	54	-10	-7	113	142	-5	-10	231	262	-4	-8	238	236								
-4	-8	176	166	-10	-8	154	131	-5	-7	90	73	-4	-5	105	110								
-4	-8	238	243	-10	-8	154	131	-5	-5	161	150	-4	-11	115	147								
-4	-9	278	294	H = 5	-6	126	133	-5	-7	118	117	-6	0	253	228								
-4	-9	235	220	-5	7	118	117	-5	-9	95	113	-6	1	249	268								
-4	10	106	99	-1	0	148	143	-5	7	85	107	-6	-1	115	109								

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	
H = 0	6	17	139	144	-1	17	28	122	5	-10	234	228	-9	0	489	267	7	13	197	184	0	-7	502	551
0	2	883	845	8	0	115	113	1	18	139	151	-5	-10	210	227	-9	8	183	161	-7	13	156	150	
0	3	1142	1132	8	1	96	83	1	-18	73	73	5	11	237	203	-9	-6	194	190	-7	-13	125	125	
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0	6	271	188	8	-2	170	162	1	19	84	90	5	12	65	68	-9	9	60	56	-2	44	312	302	
0	7	877	776	8	3	134	138	1	-19	167	176	5	-12	128	134	-9	-6	911	852	-2	-14	302	317	
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0	10	994	966	8	-4	170	157	3	0	320	343	5	-13	103	111	-9	16	519	500	-2	-15	207	216	
0	11	225	229	8	5	243	233	-3	0	282	272	-5	13	204	187	-9	-10	376	366	2	16	136	117	
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0	16	1057	976	8	-7	269	258	-3	-1	63	58	-5	-14	44	46	-9	-11	134	149	2	17	192	199	
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4	-6	330	302	1	7	302	296	-3	18	337	355	7	-14	98	95	-2	5	392	364	-4	-13	285	294	
4	-14	262																						

TABLE 3(b)-2

K	L	10FO	10FC	K	L	10FO	10FC	K	L	10FO	10FC	K	L	10FO	10FC	K	L	10FO	10FC	K	L	10FO	10FC								
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-10	87	83	-7	-10	43	21	-2	-5	82	79	5	-7	285	311	-1	5	126	130	5	-8	123	125	2	5	195	178	-3	-1	400	444	
-3	10	448	429	-7	-10	238	227	2	6	49	49	-6	7	273	225	-1	-5	171	162	5	-8	102	92	-2	5	100	96	3	2	46	34
-3	-10	43	39	7	-11	83	79	2	-6	393	366	-6	-7	366	395	1	6	148	139	-5	-8	113	124	-2	-5	43	33	-3	-2	67	63
3	11	565	574	7	-11	185	161	-2	6	62	64	6	8	39	28	1	-6	131	130	-5	-8	99	94	2	6	58	55	-3	-2	60	52
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-3	11	662	649	-7	-11	111	111	2	7	78	60	-6	8	62	51	-1	-6	157	153	5	-9	142	140	-2	5	89	98	3	3	332	293
-3	-11	814	876	7	-12	77	72	2	-7	55	58	-6	-8	422	433	1	7	192	177	-5	-9	53	55	-2	-6	49	31	3	-3	65	55
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-3	-16	201	191	-9	-2	259	226	2	13	171	197	-6	-14	150	161	1	13	67	70	7	2	167	168	-4	-1	48	33	-3	-5	207	203
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