

The crystal structure of hopeite

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Abstract

The crystal structure of hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$, has been solved by the Heavy Atom method from 1421 graphite-monochromatized $MoK\alpha$ data and refined by full matrix least-squares to $R = 0.026$ ($R_w = 0.036$). The structure is orthorhombic, $Pnma$, $a = 10.597(3)$, $b = 18.318(8)$, $c = 5.031(1)$ Å, and $Z = 4$. The Zn atoms occur in two crystallographically distinct sites, one six-coordinated and deficient in Zn, the other four-coordinated. The α and β modifications of this mineral are discussed in relation to its thermal dehydration and infrared absorption properties.

Introduction

Following the discovery of abundant material on a bone breccia in a cave at the Broken Hill mine, Zambia (Spencer, 1908), the mineral hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$, has been the subject of considerable study. Much of this research has centered on the characterization of the α and β modifications first proposed by Spencer (1908) on the basis of differences in optics, density, and thermal behavior. Although most studies of the P_2O_5 -ZnO- H_2O system support the existence of two varieties of hopeite displaying different optical and/or thermal properties, the characterization of these phases remains in a state of disarray: Takahashi *et al.* (1972) suggested that the α form of hopeite occurs in nature, while the β form corresponds to specimens prepared in the laboratory; Goloshechupov and Filatova (1969) seem to have been able to prepare both forms; the material synthesized by Nriagu (1973) has been identified as α -hopeite.

Two-dimensional crystal structure analyses of various natural and synthetic hopeite specimens were completed by Mamedov *et al.* (1961), Gamidov *et al.* (1963), and Liebau (1962, 1965), but the topology of the structure was not confirmed until three-dimensional studies of synthetic hopeite (Kawahara *et al.*, 1972, 1973) and of natural material (Whitaker, 1975) were published: this latter work came to our attention only after the refinement detailed in the present study was completed.

Experimental

Unit-cell dimensions for natural hopeite from Broken Hill, Zambia, (obtained through the courtesy of the South Australian Museum) were determined by a least-squares fitting (Appleman and Evans, 1973) of calculated to observed d -spacings; the data were collected at 21°C by powder diffractometry using LiF monochromatized $CuK\alpha$ radiation ($\lambda = 1.5418$ Å), and Si powder ($a = 5.4305$ Å) as an internal standard. These and other physical constants for hopeite are: $a = 10.597(3)$, $b = 18.318(8)$, $c = 5.031(1)$ Å, $V = 976.60$ Å³, formula weight = 458.1, $F(000) = 896e$, D_m (toluene immersion) = 3.065(9) g.cm⁻³, D_x (for $Z = 4$) = 3.116 g.cm⁻³, $\mu_{MoK\alpha} = 79.49$ cm⁻¹.

Two approximately cubic cleavage fragments, of dimensions 0.20 mm and 0.25 mm, were mounted about a^* and c^* respectively on a Stoe equi-inclination automated diffractometer. A total of 2797 reflections consistent with space group $Pnma$ (suggested from systematic absences) were measured (a axis, $0kl-12kl$; c axis, $kh0-6$) of which 97 percent were within the positive octant of the reflecting sphere. The data set was collected at 21°C with graphite-monochromatized $MoK\alpha$ radiation ($\lambda = 0.7107$ Å), utilizing the ω -scan technique; details of the procedure are described by Snow (1973).

Absorption corrections were applied to the data collected from each crystal using a local modification of the program ABSOR (Busing and Levy, 1957). Lorentz and polarization corrections were then applied, incorporating functions appropriate for use

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Figures in parentheses refer to the last decimal place

APPENDIX VII

HOPEITE (NoKa)

L = 1****		HOPEITE (NoKa)		L = 1****		HOPEITE (NoKa)		L = 1****		HOPEITE (NoKa)		L = 1****		HOPEITE (NoKa)				
N	FORS	FCAL	H	K	FORS	FCAL	H	K	FORS	FCAL	H	K	FORS	FCAL	H	K	FORS	FCAL
2	1535	1487	6	1	194	141	10	16	999	1006	1	25	206	177				
4	2438	2474	6	2	1487	1507	10	17	43	37	2	0	732	710				
6	152	207	6	3	968	985	10	18	627	638	2	1	138	163				
8	1731	1804	6	4	475	401	10	19	156	132	2	2	1741	1701				
10	981	959	6	5	478	514	10	20	279	261	2	3	774	775				
12	3386	3483	6	6	2418	2478	10	21	137	115	2	4	2921	2852				
14	201	115	6	7	267	229	10	22	62	93	2	5	557	572				
16	969	1054	6	8	1104	1146	10	23	406	377	2	6	1103	1138				
18	243	259	6	9	802	829	12	1	154	132	2	7	104	29				
20	1101	1094	6	10	136	110	12	2	385	405	2	8	2147	2150				
22	735	754	6	11	246	236	12	3	504	618	2	9	839	862				
24	1076	1083	6	12	951	970	12	4	139	148	2	10	965	959				
26	58	0	6	13	483	486	12	5	124	111	2	11	901	915				
28	1256	1271	6	14	433	421	12	6	240	242	2	12	1547	1662				
30	1029	1001	6	15	143	189	12	7	32	32	2	13	422	432				
32	661	734	6	16	995	987	12	8	322	335	2	14	1524	1535				
34	1275	1219	6	17	155	122	12	9	221	219	2	15	141	132				
36	1727	1845	6	18	272	271	12	10	435	427	2	16	645	557				
38	763	718	6	19	358	335	12	11	92	57	2	17	578	561				
40	821	674	6	20	149	132	12	12	91	110	2	18	167	159				
42	621	640	6	21	221	243	12	13	178	175	2	19	224	223				
44	1148	1204	8	22	1706	1713	12	14	266	274	2	20	470	471				
46	643	598	8	23	926	949	12	15	37	62	3	21	385	318				
48	898	843	8	24	175	143	12	16	306	286	3	22	560	594				
50	127	121	8	25	522	518	12	17	144	131	3	23	587	575				
52	424	442	8	26	1051	1071	12	18	140	141	3	24	1577	1641				
54	644	646	8	27	758	765	12	19	79	63	3	25	324	333				
56	583	610	8	28	30	65	12	20	85	79	3	26	351	393				
58	58	2	8	29	641	657	12	21	190	187	3	27	1314	1294				
60	675	678	8	30	1142	1163	12	22	313	300	3	28	627	673				
62	295	270	8	31	205	200	12	23	70	79	3	29	153	114				
64	193	114	8	32	562	565	12	24	70	79	3	30	945	987				
66	546	545	8	33	325	343	0	1	1197	1226	3	31	273	280				
68	484	481	8	34	1301	1334	0	2	1067	962	3	32	413	453				
70	224	221	8	35	706	701	0	3	1061	1025	3	33	388	405				
72	355	321	8	36	191	197	0	4	543	559	3	34	583	510				
74	231	221	8	37	143	142	0	5	203	159	3	35	290	40				
76	2715	2495	8	38	674	669	0	6	904	914	3	36	451	458				
78	112	20	8	39	138	137	0	7	422	475	3	37	194	185				
80	1797	1946	8	40	103	119	0	8	225	225	3	38	342	333				
82	345	357	8	41	412	409	0	9	375	367	4	39	167	135				
84	588	453	8	42	595	555	1	10	351	308	4	40	151	88				
86	667	672	8	43	250	264	1	11	1085	1100	4	41	1019	984				
88	1967	2018	8	44	412	366	1	12	485	455	4	42	568	556				
90	266	214	10	45	621	623	1	13	530	615	4	43	352	339				
92	647	784	10	46	415	432	1	14	219	221	4	44	615	609				
94	647	651	10	47	313	297	1	15	503	584	4	45	455	457				
96	2159	2213	10	48	401	412	1	16	845	804	4	46	82	96				
98	134	134	10	49	1274	1270	1	17	959	996	4	47	874	856				
100	1479	1452	10	50	70	48	1	18	198	243	4	48	484	503				
102	241	237	10	51	1320	1337	1	19	192	193	4	49	1228	1230				
104	927	932	10	52	198	192	1	20	734	760	4	50	524	546				
106	383	378	10	53	960	967	1	21	627	657	4	51	391	384				
108	205	201	10	54	264	253	1	22	211	201	4	52	348	345				
110	111	133	10	55	306	313	1	23	196	203	4	53	593	603				
112	1024	1017	10	56	223	218	1	24	169	159	4	54	292	296				
114	554	559	10	57	768	757	1	25	444	453	4	55	406	407				
116	985	995	10	58	361	348	1	26	260	265	4	56	322	321				
118	298	25	10	59	584	592	1	27	229	219	4	57	472	488				
120			10	60	315	308	1	28	231	219	4	58	604	428				

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	
4	23	432	448	7	19	308	286	10	10	337	337	0	0	2742	2655	
5	0	582	523	7	20	169	160	10	11	213	212	0	2	1818	1844	
5	1	687	702	7	21	116	99	10	12	324	326	0	4	766	683	
5	2	562	553	7	23	98	78	10	13	148	141	0	6	1722	1752	
5	3	516	559	7	24	210	195	10	14	439	440	0	8	950	906	
5	4	430	454	8	0	1412	1390	10	15	146	139	0	10	1840	1891	
5	5	785	815	8	1	488	497	10	16	201	212	0	12	1404	1390	
5	6	339	291	8	2	1368	1381	10	17	361	343	0	14	639	660	
5	7	641	686	8	3	96	57	10	18	229	218	0	16	208	193	
5	8	564	574	8	4	737	745	10	19	290	295	0	18	868	888	
5	9	421	450	8	5	68	17	10	20	108	92	0	20	661	676	
5	10	98	97	8	6	127	106	10	21	160	145	0	22	950	939	
5	11	508	525	8	7	301	306	10	22	138	138	0	24	406	413	
5	13	331	342	8	8	924	918	10	23	188	179	1	0	399	468	
5	15	295	295	8	9	132	117	10	24	204	200	U	1	1	31	15
5	16	305	303	8	10	1097	1122	U	11	0	30	6	1	2	110	35
5	17	347	347	8	11	215	210	11	1	216	215	1	3	789	737	
5	23	221	207	8	12	811	826	11	2	492	503	1	4	1195	1212	
6	0	1013	998	8	13	441	441	11	3	322	335	1	5	365	341	
6	1	449	460	8	14	550	567	11	4	132	127	1	6	193	233	
6	2	947	913	8	16	258	256	11	5	197	188	1	7	196	185	
6	3	71	72	8	17	74	62	11	6	356	362	1	8	1457	1493	
6	4	2041	2030	8	18	216	210	U	11	7	31	22	1	9	331	327
6	5	50	15	8	20	725	695	11	8	91	82	1	10	511	460	
6	6	1035	1021	8	21	84	79	11	9	348	56	1	11	130	125	
6	7	541	553	8	22	583	574	11	10	450	457	1	12	839	871	
6	8	1427	1440	8	24	307	299	11	11	126	115	1	13	169	168	
6	9	96	85	9	0	596	628	U	11	12	36	58	1	14	306	301
6	10	242	224	9	1	318	339	11	13	121	113	1	15	207	226	
6	11	98	93	9	2	301	327	11	14	353	345	1	16	679	694	
6	12	500	498	9	3	202	207	11	15	256	253	1	17	180	194	
6	13	473	454	9	4	284	294	U	11	16	37	15	1	20	606	596
6	14	657	661	9	5	408	428	U	11	17	38	26	1	24	204	184
6	15	89	77	9	6	299	302	11	18	229	215	2	0	240	233	
6	16	970	977	9	7	162	171	11	19	83	73	2	1	546	488	
6	17	185	181	9	8	305	318	U	11	20	38	15	2	2	834	838
6	18	468	477	9	9	294	305	11	21	111	99	2	3	358	353	
6	19	348	350	9	10	138	146	11	22	222	199	2	4	143	108	
6	20	560	557	9	11	204	205	12	0	746	758	2	5	135	126	
6	22	171	179	9	12	436	446	12	1	54	61	2	6	1141	1136	
6	24	415	419	9	13	172	173	12	2	1085	1132	2	7	335	310	
6	25	174	169	9	14	209	194	12	3	93	87	2	8	247	259	
7	0	829	841	9	15	179	177	12	4	372	392	2	9	382	381	
7	1	417	433	9	16	147	137	12	5	57	59	2	10	448	461	
7	2	50	37	9	17	160	146	12	6	595	612	2	11	136	104	
7	3	203	242	9	18	150	132	12	7	214	215	2	12	206	181	
7	4	493	507	9	19	175	149	12	8	569	605	2	13	494	496	
7	5	527	570	9	20	148	132	12	10	977	1016	2	14	498	496	
7	6	65	44	9	21	77	62	12	12	417	436	2	17	395	406	
7	7	424	443	9	24	152	139	U	12	13	37	10	2	18	437	440
7	8	461	476	10	0	447	447	12	14	487	489	2	19	366	354	
7	9	318	327	10	1	95	74	U	12	15	39	24	2	22	183	161
7	10	140	128	10	2	543	553	12	16	85	93	2	23	223	220	
7	11	208	216	10	3	592	596	12	18	440	438	3	0	155	204	
7	12	670	691	10	4	358	354	12	19	84	73	3	1	497	479	
7	13	303	298	U	10	5	32	14	12	20	528	554	3	2	1453	1444
7	14	134	123	10	6	426	443	12	21	77	74	3	3	174	184	
7	15	203	199	10	7	132	132	12	22	561	565	3	4	313	363	
7	16	397	391	10	8	251	255	12	24	171	184	3	6	875	908	
7	17	143	143	10	9	370	368	**L =	2***	3	7	441	435			

H	K	FORS	FCAL	H	K	FORS	FCAL	H	K	FORS	FCAL	H	K	FORS	FCAL
3	8	263	274	6	19	259	257	9	17	128	107			***L =	***
3	9	214	196	6	20	152	142 U	9	18	38	53	0	1	228	311
3	10	868	867	6	24	372	380	9	19	205	198	0	3	1516	1538
3	11	392	410	7	0	408	420	9	20	302	282	0	5	889	927
3	12	298	306	7	1	203	211	10	0	261	244	0	7	344	401
3	13	221	229	7	2	326	331	10	1	79	64	0	9	1278	1321
3	14	494	496	7	3	220	233	10	2	754	760	0	11	566	585
3	16	295	285	7	4	297	297	10	3	206	195	0	13	174	173
3	17	157	150	7	5	129	140	10	4	696	681	0	15	764	766
3	18	430	418	7	7	372	322	10	5	259	262	0	17	466	459
3	22	406	402	7	8	314	310	10	6	1280	1280	0	19	164	151
4	0	2692	2651	7	10	251	268	10	7	190	163	0	21	346	321
4	1	350	338	7	11	192	183	10	8	360	354	0	23	449	436
4	2	632	538	7	12	106	99	10	9	222	216	1	0	1052	1001
4	4	1437	1440	7	13	213	216	10	10	464	464	1	1	121	107
4	5	116	123	7	14	469	471	10	11	96	91	1	2	840	825
4	6	681	604	7	17	224	215	10	12	298	306	1	3	228	231
4	7	420	422	7	20	271	260 U	10	13	38	19	1	4	593	586
4	8	1599	1521	7	21	124	112	10	14	757	740	1	5	451	438
4	10	935	893 U	7	22	38	8	10	15	73	46	1	6	894	886
4	12	1600	1617	8	0	755	719	10	16	601	600	1	7	95	73
4	13	374	381	8	1	56	47	10	17	173	160	1	8	211	206
4	14	631	634	8	2	796	796	10	18	636	615	1	9	380	386
4	16	441	434	8	3	554	557	10	19	96	81	1	10	326	378
4	19	206	211	8	4	290	276 U	10	20	41	34	1	11	105	106
4	20	832	852	8	5	70	39	10	21	104	62	1	12	557	564
5	0	309	354	8	6	626	630	10	22	219	198	1	13	103	94
5	2	1408	1411	8	7	187	177	10	23	98	73	1	14	542	535
5	3	506	508	8	8	379	365	11	0	252	250	1	15	255	258
5	4	412	361	8	9	356	358	11	1	158	154	1	16	462	464
5	5	263	239	8	10	819	829 U	11	2	31	26 U	1	17	44	54
5	6	1082	1009	8	11	275	272	11	3	266	256	1	18	378	365
5	7	121	130	8	12	511	515	11	4	356	576	1	19	93	88
5	8	466	431	8	13	260	247	11	5	290	296 U	1	21	44	33
5	10	1028	1034	8	14	414	412 U	11	6	33	21	2	0	310	313
5	11	251	238	8	15	294	282	11	7	161	151	2	1	714	741
5	14	829	831	8	16	185	189	11	8	405	413	2	2	667	646
5	16	176	191	8	17	216	201	11	9	274	260	2	3	401	446
5	17	214	212	8	18	430	406	11	10	152	142	2	4	1840	1827
5	18	562	554	8	19	170	177	11	11	144	156	2	5	714	754
5	20	269	221	8	20	268	269 U	11	13	37	35	2	6	1342	1313
5	22	420	409	8	22	425	407	11	15	174	169	2	7	628	649
5	0	999	982	8	23	278	268	11	16	249	246	2	8	1293	1291
6	1	635	602	9	0	973	986	11	17	164	147	2	9	462	471
6	2	386	342	9	1	255	244	11	19	129	107	2	10	155	150
6	3	85	26	9	2	528	532	11	20	255	240	2	11	385	397
6	4	1155	1143	9	3	283	305	12	0	257	257	2	12	266	254
6	5	114	113	9	4	812	832	12	1	314	304	2	13	470	461
6	6	945	898	9	5	301	311	12	2	64	51	2	14	650	651
6	7	440	432	9	6	97	77	12	3	100	103	2	15	331	330
6	8	673	674	9	7	433	452	12	4	272	276	2	16	1016	1016
6	9	169	163	9	8	545	548	12	5	262	287	2	17	179	172
6	10	74	38	9	9	232	242	12	7	403	408	2	18	546	563
6	11	221	220	9	10	108	110	12	8	196	203	2	19	402	392
6	12	675	670	9	11	97	86	12	12	159	168	2	20	441	437
6	13	476	483	9	12	489	492	12	13	362	359	2	21	173	156
6	14	426	418	9	13	236	237	12	16	197	193	3	0	1274	1223
6	15	116	100	9	14	270	284 U	12	18	40	30	3	1	189	199
6	16	806	791	9	15	141	126	12	19	282	272	3	2	850	823
6	18	378	374	9	16	438	429	12	21	130	115	3	3	361	339

H	K	FORS	FCAL	H	K	FORS	FCAL	H	K	FORS	FCAL	H	K	FORS	FCAL
3	2	328	302	6	8	403	394	9	11	217	197	0	5	136	125
3	3	274	277	6	9	80	53	9	12	227	231	0	7	340	334
3	4	614	628	6	11	41	29	9	14	672	649	0	9	39	9
3	5	134	138	6	12	124	109	9	15	259	241	0	13	502	505
3	6	430	452	6	13	301	291	9	16	321	334	0	15	95	86
3	7	115	121	6	14	245	248	9	17	144	134	1	0	492	497
3	8	692	696	6	15	179	170	9	18	468	452	1	1	232	237
3	9	317	322	6	16	432	424	10	0	102	89	1	2	462	465
3	10	289	281	6	17	179	191	10	1	96	72	1	3	426	444
3	12	853	850	6	18	203	215	10	2	392	383	1	4	691	695
3	14	45	55	6	19	239	233	10	3	114	108	1	5	173	156
3	15	157	154	7	0	41	31	10	4	457	460	1	6	806	812
3	16	276	262	7	1	144	150	10	5	41	40	1	7	101	117
3	18	141	125	7	2	485	494	10	6	605	592	1	8	456	454
3	20	452	441	7	3	316	311	10	7	71	49	1	9	241	237
4	0	1186	1179	7	4	561	549	10	8	163	160	1	10	312	303
4	1	204	198	7	5	229	217	10	9	122	107	1	11	323	323
4	2	540	545	7	6	163	161	10	10	39	43	1	12	435	434
4	3	303	300	7	7	260	191	10	12	39	18	1	13	85	73
4	4	356	369	7	8	369	364	10	13	40	51	1	14	452	455
4	5	383	386	7	9	282	272	10	14	310	303	1	15	226	220
4	6	97	20	7	10	453	439	10	15	40	35	1	16	510	515
4	7	192	185	7	11	145	137	10	16	293	310	1	17	224	204
4	8	463	451	7	12	78	62	10	18	291	278	1	18	378	376
4	10	545	541	7	14	127	117	11	0	97	89	2	1	356	357
4	11	43	39	7	15	210	206	11	1	342	339	2	2	259	275
4	12	711	704	7	16	420	396	11	2	345	334	2	3	355	358
4	13	161	157	7	18	132	119	11	3	38	44	2	4	397	395
4	14	106	122	7	19	188	160	11	4	280	295	2	5	238	244
4	16	158	152	8	0	454	452	11	5	184	172	2	6	483	483
4	18	108	122	8	1	35	30	11	6	426	430	2	7	301	315
4	19	245	236	8	2	428	421	11	7	231	232	2	9	160	154
5	0	1120	1087	8	3	143	133	11	8	161	175	2	11	395	387
5	1	407	416	8	4	133	121	11	9	39	21	2	13	206	201
5	2	626	601	8	5	42	24	11	10	179	169	2	14	263	268
5	3	279	267	8	6	320	312	11	11	194	184	2	15	130	107
5	4	1370	1352	8	7	324	323	11	12	93	79	2	16	263	260
5	5	458	459	8	8	121	118	11	13	310	297	2	17	298	300
5	6	347	328	8	9	115	118	11	14	292	277	2	18	170	174
5	7	476	473	8	10	321	318	11	16	191	199	3	0	951	947
5	8	1310	1292	8	11	161	165	11	17	109	91	3	1	330	334
5	9	127	114	8	12	172	170	11	18	216	213	3	2	668	655
5	10	505	502	8	13	188	194	12	0	38	41	3	3	86	85
5	11	132	140	8	15	132	126	12	1	204	197	3	4	844	851
5	12	812	804	8	17	40	65	12	2	38	54	3	5	271	272
5	13	329	328	8	18	216	195	12	3	152	144	3	6	893	896
5	14	434	442	8	19	155	163	12	4	39	56	3	7	488	487
5	16	762	751	8	20	161	167	12	5	156	163	3	8	679	682
5	17	49	50	9	0	331	335	12	6	125	133	3	9	116	101
5	18	224	245	9	1	125	108	12	7	334	344	3	10	547	550
5	19	308	309	9	2	943	936	12	9	126	130	3	11	45	55
5	20	670	683	9	3	443	430	12	12	120	124	3	12	766	762
6	1	355	360	9	4	556	562	12	13	220	223	3	13	374	367
6	2	96	70	9	5	99	85	12	14	39	28	3	14	540	536
6	3	40	50	9	6	876	853	12	16	95	98	3	15	46	46
6	4	575	561	9	7	47	28	12	19	145	142	3	16	609	604
6	5	160	163	9	8	449	461	**L =		5***		3	18	462	482
6	6	479	472	9	9	335	321	0	1	380	382	4	0	330	315
6	7	117	110	9	10	665	646	0	3	182	193	4	1	133	134

H	K	FORS	FCAL	H	K	FORS	FCAL	H	K	FORS	FCAL	H	K	FORS	FCAL
								**L =		66666					
4	2	343	345	8	9	99	82	0	0	449	474	6	3	214	269
4	3	638	644	8	10	194	190	0	0	238	241	6	4	127	86
4	4	77	85	8	12	305	287	0	2	49	82	6	5	47	5
4	5	334	348	8	13	146	172	0	4	602	587	6	6	325	328
4	6	108	120	8	14	128	109	0	6	228	244	6	8	136	116
4	7	270	274	8	15	100	83	0	8	391	393	12	12	320	316
4	9	498	490	8	8	250	254	0	12	871	894	7	0	276	267
4	10	207	204	9	1	256	242	1	0	40	63	7	1	165	159
4	11	308	293	9	2	240	289	1	1	557	634	7	4	90	111
4	15	289	276	9	4	97	91	1	2	264	276	7	5	49	56
4	16	184	176	9	5	103	96	1	3	650	665	7	6	256	279
4	17	330	292	9	6	143	116	1	4	48	91	7	10	140	157
5	1	132	176	9	7	146	125	1	5	271	266	7	12	225	218
5	2	232	275	9	8	38	31	1	6	220	220	7	0	333	324
5	3	147	181	9	10	312	305	1	7	473	494	7	1	226	216
5	4	255	253	9	11	146	141	1	8	504	506	7	2	124	108
5	5	286	279	9	12	126	132	1	10	193	149	7	4	111	89
5	6	438	446	9	13	170	169	1	12	356	368	7	5	228	219
5	7	256	248	9	14	84	66	2	0	129	142	7	6	206	185
5	9	232	216	9	15	136	111	2	1	290	291	7	7	224	315
5	11	105	96	10	0	284	268	2	2	194	119	7	8	145	89
5	12	147	136	10	1	138	140	2	3	250	250	7	10	122	93
5	14	306	307	10	2	141	153	2	4	183	254	7	11	115	89
5	16	241	252	10	3	271	262	2	5	133	201	7	0	272	370
6	0	83	57	10	4	40	11	2	6	174	119	7	1	157	150
6	1	214	201	10	5	199	186	2	7	250	250	7	2	241	303
6	2	42	52	10	6	237	220	2	8	183	254	7	3	147	153
6	4	328	317	10	7	124	129	2	9	154	220	7	4	525	631
6	5	291	281	10	9	309	307	2	10	117	180	7	5	43	74
6	7	352	341	10	10	156	146	2	12	221	317	7	6	484	489
6	8	259	249	10	11	176	172	2	13	343	322	7	7	140	136
6	12	237	239	10	12	179	160	3	0	43	19	7	8	604	600
6	13	209	197	10	14	169	157	3	1	493	465	7	10	376	375
6	14	208	232	10	15	212	187	3	2	62	74	7	0	41	65
6	15	306	321	11	0	734	749	3	3	95	112	7	1	208	184
7	0	796	802	11	1	154	152	3	5	217	201	7	2	144	134
7	1	83	78	11	2	367	385	3	6	243	306	7	3	117	83
7	2	832	828	11	4	464	496	3	8	595	606	7	4	246	229
7	3	350	350	11	5	97	96	3	10	271	284	7	5	192	183
7	4	574	573	11	6	273	287	3	12	44	31	7	7	170	168
7	5	129	126	11	7	174	153	4	0	359	356	7	8	110	101
7	6	856	849	11	8	514	525	4	2	269	268	7	9	247	230
7	7	46	60	11	9	41	12	4	3	481	402	7	10	87	104
7	8	508	512	11	10	397	420	4	4	111	100	7	2	216	230
7	9	281	273	11	12	555	559	4	5	45	47	7	4	211	198
7	10	707	703	11	13	147	138	4	6	571	582	7	5	217	218
7	11	202	197	11	14	192	207	5	0	49	10	7	3	129	96
7	12	551	564	12	0	109	132	5	1	811	816	7	4	41	35
7	14	498	488	12	1	136	127	5	2	200	200	7	5	133	131
7	15	196	168	12	2	285	278	5	3	137	142	7	6	208	200
7	16	369	372	12	4	155	155	5	4	573	587	7	9	208	200
7	17	199	182	12	5	145	123	5	5	517	551	7	0	313	309
8	0	358	343	12	6	40	47	5	6	635	663	7	1	188	186
8	1	195	182	12	7	40	45	5	8	425	449	7	2	477	500
8	2	36	40	12	10	387	378	5	10	499	512	7	1	142	247
8	4	118	111	12	12	139	150	5	12	48	66	7	2	330	350
8	5	184	162	12	13	82	75	6	0	130	118	7	3	419	434
8	6	38	24	12	14	210	180	6	1			7	2	428	423
8	8	323	305	12	16	93	79	6	2			7	3		