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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; Goloshchapov 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: $a = 10.597(3)^2$, $b = 18.318(8)$, $c = 5.031(1)$ 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 $Pn.a$ (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 (1974).

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

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² e.s.d.'s given in parentheses, refer to the last decimal place.

APPENDIX VII

HOPEITE ($MgAl_2O_4$)

H	K	FORS	FCAL	H	K	FORS	FCAL	H	K	FORS	FCAL	H	K	FORS	FCAL							
$\bullet\bullet L = 18888$																						
2	1545	1467	6	2	1487	1507	0	10	17	43	37	2	0	732	719							
4	2438	2474	6	3	968	985	10	19	627	638	4	1	138	163								
6	152	207	6	4	475	401	10	19	156	132	2	2	1741	1701								
8	1751	1804	6	5	478	514	10	20	279	261	2	3	774	775								
10	981	959	6	6	2418	2478	16	21	137	115	2	4	2921	2852								
12	3386	3483	6	7	257	229	10	22	82	93	2	5	557	572								
14	201	115	6	9	1104	1146	10	24	406	377	2	6	1103	1138								
16	969	1014	6	10	802	829	12	1	154	132	2	7	104	29								
18	243	259	6	12	136	110	12	2	385	405	2	8	2147	2150								
20	1141	1094	6	13	245	236	12	5	504	518	2	9	839	862								
22	735	754	6	14	951	970	12	4	139	148	2	10	965	959								
24	1076	1083	6	15	483	486	12	5	124	111	2	12	901	915								
4	58	0	6	16	433	421	12	6	240	242	2	14	1547	1662								
2	1256	1271	6	17	193	189	0	12	7	32	32	2	15	422	432							
1	1029	1011	6	18	995	987	12	9	322	335	2	16	1524	1535								
2	661	734	6	20	155	122	12	10	221	219	2	17	141	132								
3	1275	1229	6	21	272	271	12	11	435	427	2	18	645	557								
4	1727	1445	6	22	358	335	12	12	92	57	2	20	578	561								
5	743	718	6	23	149	132	12	13	91	110	2	21	167	159								
6	820	674	6	24	221	243	12	14	178	175	2	22	224	223								
7	521	640	6	25	1705	1713	12	15	286	274	2	24	470	471								
8	1148	1204	6	26	926	949	12	16	37	62	3	0	385	318								
9	643	598	6	27	179	143	12	17	306	286	3	1	560	594								
10	898	843	6	28	522	518	12	18	144	131	3	2	587	575								
11	127	121	6	29	1051	1071	12	19	140	141	3	3	1577	1641								
12	424	442	6	30	758	765	12	20	79	63	3	4	384	333								
13	644	646	6	31	30	65	12	21	85	79	3	5	351	393								
14	583	610	6	32	641	657	12	22	190	181	3	6	1314	1294								
15	96	12	6	33	1142	1163	12	23	313	300	3	7	627	673								
16	675	678	6	34	205	200	12	25	70	79	3	8	153	114								
17	245	270	6	35	562	565	$\bullet\bullet L = 18888$															
18	193	114	6	36	11	325	343	0	1	1197	1226	3	10	273	280							
19	586	535	6	37	12	1301	1334	0	3	1057	968	3	11	413	453							
20	484	481	6	38	13	705	701	0	5	1051	1025	3	13	388	405							
21	224	221	6	39	14	191	197	0	7	543	559	3	15	583	510							
22	355	321	6	40	15	143	142	0	9	203	159	3	17	290	190							
23	231	221	6	41	16	574	669	0	13	904	914	3	18	451	158							
24	2715	2495	6	42	17	138	137	0	19	482	475	3	19	194	185							
4	1	12	6	43	18	103	119	0	23	225	225	3	21	342	333							
2	1797	1946	6	44	19	412	409	0	25	575	367	4	0	167	135							
3	345	357	6	45	20	594	555	1	0	351	308	4	1	151	88							
4	588	453	6	46	22	250	264	1	1	1085	1100	4	2	1019	984							
5	667	672	6	47	24	412	366	1	2	485	455	4	3	568	556							
6	1947	2018	6	48	0	621	623	1	3	530	615	4	4	352	339							
7	245	214	6	49	1	416	432	1	4	219	221	4	5	615	609							
8	842	764	6	50	6	313	297	1	5	583	584	4	6	455	457							
9	641	651	6	51	3	411	412	1	5	845	804	4	7	82	96							
10	2159	2213	6	52	1274	1270	1	7	959	996	4	8	874	856								
11	134	134	6	53	79	48	1	9	198	243	4	9	484	503								
12	1479	1452	6	54	1320	1337	1	10	192	193	4	10	1228	1230								
13	241	237	6	55	7	198	192	1	11	734	760	4	11	524	546							
14	927	932	6	56	960	967	1	13	627	657	4	12	391	384								
15	383	378	6	57	9	264	253	1	14	211	201	4	13	348	345							
16	205	201	6	58	10	308	313	1	15	196	203	4	14	593	603							
17	111	133	6	59	11	223	218	1	16	169	159	4	15	292	296							
18	1024	1017	6	60	12	768	757	1	17	444	453	4	17	405	407							
20	554	559	6	61	13	361	348	1	18	260	265	4	18	322	321							
22	985	995	6	62	14	584	592	1	19	229	219	4	20	472	488							
6	298	25	6	63	15	315	308	1	21	231	219	4	22	604	428							

H	K	F0BS	FCAL	H	K	F0BS	FCAL	H	K	F0BS	FCAL	H	K	F0BS	FCAL
4	23	432	448	7	19	308	286	10	10	337	337	9	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
5	16	305	303	8	10	1097	1122	U	11	0	30	6	1	2	110
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
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
6	10	242	224	9	1	318	339	11	13	121	113	1	15	207	
6	11	98	93	9	2	301	327	11	14	353	345	1	16	679	
6	12	500	498	9	3	202	207	11	15	256	253	1	17	180	
6	13	473	454	9	4	284	294	U	11	16	37	15	1	20	606
6	14	657	661	9	5	408	428	U	11	17	38	26	1	24	204
6	15	89	77	9	6	299	302	11	18	229	215	2	0	240	
6	16	970	977	9	7	162	171	11	19	83	73	2	1	546	
6	17	185	181	9	8	305	318	U	11	20	38	15	2	2	834
6	18	468	477	9	9	294	305	11	21	111	99	2	3	358	
6	19	348	350	9	10	138	146	11	22	222	199	2	4	143	
6	20	560	557	9	11	204	205	12	0	746	758	2	5	135	
6	22	171	179	9	12	436	446	12	1	54	61	2	6	1141	
6	24	415	419	9	13	172	173	12	2	1085	1132	2	7	335	
6	25	174	169	9	14	209	194	12	3	93	87	2	8	247	
7	0	829	841	9	15	179	177	12	4	372	392	2	9	382	
7	1	417	433	9	16	147	137	12	5	57	59	2	10	448	
7	2	50	37	9	17	160	146	12	6	595	612	2	11	136	
7	3	203	242	9	18	150	132	12	7	214	215	2	12	206	
7	4	493	507	9	19	175	149	12	8	569	605	2	13	494	
7	5	527	570	9	20	148	132	12	10	977	1016	2	14	498	
7	6	65	44	9	21	77	62	12	12	417	436	2	17	395	
7	7	424	443	9	24	152	139	U	12	13	37	10	2	18	437
7	8	461	476	10	0	447	447	12	14	487	489	2	19	366	
7	9	318	327	10	1	95	74	U	12	15	39	24	2	22	183
7	10	140	128	10	2	543	553	12	16	85	93	2	23	223	
7	11	208	216	10	3	592	596	12	18	440	438	3	0	155	
7	12	670	691	10	4	358	354	12	19	84	73	3	1	497	
7	13	303	298	U	10	5	32	14	12	528	554	3	2	1453	
7	14	134	123	10	6	426	443	12	21	77	74	3	3	174	
7	15	203	199	10	7	132	132	12	22	561	565	3	4	313	
7	16	397	391	10	8	251	255	12	24	171	184	3	6	875	
7	17	143	143	10	9	370	368	*#L =	2***	2***	2***	3	7	441	

H	K	F0BS	FCAL	H	K	F0BS	FCAL	H	K	F0BS	FCAL	H	K	F0BS	FCAL	
3	6	263	274	5	19	259	257	9	17	128	107	4	1	228	311	
3	9	214	196	6	20	152	142	U	9	18	38	53	0	3	1516	1538
3	10	868	867	6	24	372	380	9	19	205	198	0	5	889	927	
3	11	392	410	7	0	408	420	7	20	302	282	0	7	344	401	
3	12	298	306	7	1	203	211	10	0	261	244	0	9	1278	1321	
3	13	221	229	7	2	320	331	10	1	79	64	0	9	1278	1321	
3	14	494	496	7	3	280	233	10	2	754	760	0	11	566	585	
3	15	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	382	10	5	259	262	0	17	466	459	
3	22	406	402	7	8	304	316	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	109	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	504	7	17	224	215	10	12	298	305	1	3	228	231	
4	7	420	422	7	20	271	260	10	13	38	19	1	4	593	586	
4	8	1509	1521	7	21	124	112	10	14	757	740	1	5	451	438	
10	9	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	379	321	8	1	66	47	10	17	173	160	1	8	211	206	
4	15	631	634	8	2	796	796	10	18	636	615	1	9	389	386	
4	18	441	434	8	3	554	557	10	19	96	81	1	10	386	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	194	82	1	12	557	564	
5	0	369	354	8	5	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	
3	3	506	508	8	8	379	365	11	0	252	250	1	15	255	258	
4	4	412	361	8	9	356	358	11	1	158	154	1	16	462	464	
5	5	263	239	8	10	919	829	U	11	2	31	26	U	17	44	54
5	6	1082	1089	8	11	275	272	11	3	266	256	1	18	378	365	
5	7	121	130	8	12	511	515	11	4	356	376	1	19	93	88	
5	8	466	431	8	13	260	247	11	5	290	295	U	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	281	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	248	2	8	1293	1291	
5	1	635	602	9	0	973	986	11	17	164	147	2	9	462	471	
5	2	386	342	9	1	255	244	11	19	129	107	2	10	155	150	
5	3	85	26	9	2	528	532	11	20	255	240	2	11	385	397	
5	4	1155	1143	9	3	283	305	12	0	257	257	2	12	266	254	
5	5	114	113	9	4	812	532	12	1	314	304	2	13	470	461	
5	6	945	898	9	5	301	311	12	2	64	51	2	14	650	651	
5	7	640	632	9	6	97	77	12	3	100	103	2	15	331	330	
5	8	673	674	9	7	433	452	12	4	272	276	2	16	1016	1016	
5	9	169	163	9	8	545	548	12	5	282	287	2	17	179	172	
5	10	74	38	9	9	232	242	12	7	403	408	2	18	546	563	
5	11	221	220	9	10	108	110	12	8	196	203	2	19	402	392	
5	12	675	670	9	11	97	86	12	12	159	168	2	20	441	437	
5	13	476	483	9	12	489	492	12	13	362	359	2	21	173	156	
5	14	426	418	9	13	236	237	12	16	197	193	3	0	1274	1223	
5	15	116	100	9	14	270	284	U	12	18	40	30	3	1	189	199
5	16	806	791	9	15	141	126	12	19	282	272	3	2	850	823	
5	18	378	374	9	16	438	429	12	21	130	115	3	3	361	339	

H	K	F08S	FCAL	H	K	F08S	FCAL	H	K	F08S	FCAL	H	K	F08S	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	0	6	11	41	29	9	14	672	649	0	9	39	9
3	5	134	128	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	592	696	6	15	179	170	9	18	466	452	1	1	232	237	
3	9	317	322	6	16	432	424	10	0	102	89	1	2	462	465	
3	10	289	261	6	17	179	192	10	1	96	72	1	3	425	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	0	7	0	41	31	10	4	457	460	1	6	806	812
3	16	276	262	7	1	144	150	0	10	5	41	40	1	7	101	117
3	18	141	125	7	2	485	494	10	6	605	592	1	8	455	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	228	217	10	9	122	107	1	11	323	323	
4	2	560	545	7	6	163	161	0	10	10	39	1	12	435	434	
4	3	303	300	7	7	200	191	0	10	12	39	1	13	85	73	
4	4	356	369	7	8	369	364	0	10	13	40	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	0	10	15	40	1	16	510	515	
4	7	192	185	7	11	146	137	10	16	293	310	1	17	224	204	
4	8	463	451	7	12	78	62	10	18	291	278	1	18	379	376	
4	10	548	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	0	11	3	38	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	0	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	0	11	9	39	2	13	206	201	
5	2	626	501	0	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	0	12	0	38	3	3	86	85	
5	11	132	140	8	15	132	126	12	1	204	197	3	4	844	851	
5	12	812	804	0	8	17	40	65	0	12	2	38	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	0	12	4	39	3	7	488	487	
5	16	762	751	8	20	161	167	12	5	156	162	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	0	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	0	14	39	28	3	14	540	536	
6	3	40	50	9	6	876	853	12	16	95	98	0	15	46	46	
6	4	575	561	0	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	192	193	4	1	133	134	

H	K	F0BS	FCAL	H	K	F0BS	FCAL	H	K	F0BS	FCAL	H	K	F0BS	FCAL	
4	2	343	345	8	9	99	82	0	0	459	474	6	3	214	209	
4	3	638	644	8	10	194	190	0	2	238	241	5	4	127	86	
4	4	77	85	8	12	305	287	0	4	89	82	5	5	47	5	
4	5	334	348	8	13	186	172	0	6	602	587	6	6	325	328	
4	6	108	120	8	14	128	105	0	8	228	244	8	8	136	116	
4	7	270	274	8	15	100	83	0	12	291	293	12	12	320	316	
4	9	498	490	9	0	259	254	0	1	0	871	894	1	1	276	267
10	207	204	9	1	256	242	1	1	40	63	7	7	155	159		
11	308	293	9	2	280	289	0	1	2	557	634	5	5	49	56	
15	289	276	9	4	97	91	1	1	3	264	276	6	7	245	279	
16	184	176	9	5	103	96	1	3	650	645	7	7	149	157		
17	330	292	9	6	143	115	1	4	88	91	7	7	225	218		
1	182	176	9	7	144	125	1	5	271	256	8	8	333	324		
2	282	275	9	8	138	31	1	5	220	223	9	9	225	216		
3	187	181	9	10	312	305	1	7	473	494	8	8	126	108		
4	255	253	9	11	146	141	1	8	567	676	8	8	111	89		
5	286	279	9	12	126	132	1	9	473	494	8	8	228	219		
6	438	446	9	13	174	169	1	12	564	566	5	5	206	185		
7	255	248	9	14	88	66	1	0	193	149	7	7	324	315		
9	232	216	9	15	136	111	2	1	356	368	8	8	195	89		
11	195	96	10	0	254	268	2	2	322	318	9	9	122	93		
12	147	136	10	1	135	140	2	3	139	142	10	10	115	89		
14	306	307	10	2	190	185	2	4	240	250	11	11	378	370		
16	241	252	10	3	271	262	2	5	124	114	1	1	157	150		
6	83	57	0	10	4	40	11	2	250	250	9	9	281	393		
1	214	201	10	5	199	186	2	7	288	289	8	8	147	153		
2	42	52	10	5	237	226	2	8	153	291	9	9	525	631		
4	328	317	10	7	124	129	2	9	133	280	4	4	484	74		
5	291	281	10	9	309	307	2	10	154	280	5	5	484	489		
7	352	341	10	10	156	146	2	12	117	180	6	6	140	136		
8	259	249	10	11	176	172	2	13	221	317	7	7	608	600		
6	227	239	10	12	179	160	3	0	343	322	8	8	375	375		
12	269	197	10	14	159	157	0	3	1	19	9	9	41	65		
13	208	232	10	15	812	187	3	2	453	465	0	1	208	184		
14	306	321	11	0	734	749	3	3	355	355	1	1	134	134		
15	790	802	11	1	154	152	3	5	195	112	2	2	83	83		
7	1	83	78	11	2	357	385	3	6	207	261	3	3	245	229	
7	2	832	828	11	4	456	496	3	8	283	300	4	4	192	183	
7	3	350	350	11	5	197	96	3	10	595	606	5	5	178	168	
7	4	574	573	11	6	273	287	3	12	671	284	7	7	101	101	
7	5	129	126	11	7	174	153	0	0	44	31	8	8	130	77	
7	6	855	849	11	8	514	525	4	2	359	355	9	9	247	230	
7	7	46	60	11	9	41	12	4	4	269	268	10	10	87	104	
7	8	508	512	11	10	397	420	4	4	481	402	11	11	214	230	
7	9	281	273	11	12	555	559	0	5	161	100	11	11	211	198	
7	10	707	703	11	13	147	138	0	5	45	47	11	11	217	216	
7	11	202	197	11	14	193	207	0	6	571	582	12	12	129	96	
7	12	551	564	12	0	109	132	0	1	49	10	12	12	91	35	
7	14	498	488	12	1	136	127	0	2	801	816	5	5	133	131	
7	15	196	168	12	2	285	278	0	3	200	200	6	6	208	200	
7	16	369	372	12	4	155	155	0	4	548	573	9	9	700000	700000	
7	17	199	182	12	5	145	123	0	5	137	142	1	1	313	309	
8	0	358	343	12	5	40	47	0	6	573	587	2	2	188	186	
8	1	195	182	12	7	40	45	0	8	517	550	1	1	477	500	
8	2	36	40	12	10	387	376	0	10	635	663	2	2	142	247	
8	4	118	111	12	12	139	150	0	12	425	449	3	3	330	350	
8	5	184	162	12	13	82	75	0	1	499	542	0	0	419	434	
8	6	38	24	12	14	210	180	0	1	48	66	2	2	428	423	
8	8	323	305	12	16	93	79	0	2	130	118	3	3	428	423	