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The crystal structure of a third polymorph of $Cu_5(PO_4)_2(OH)_4$

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Abstract

A phase formed in the $CuO-P_2O_5-H_2O$ system is an additional polymorph of pseudomalachite, $Cu_5(PO_4)_2(OH)_4$. This phase crystallizes in the space group $P\bar{1}$ with $a = 4.445(1)$, $b = 5.873(1)$, $c = 8.668(3)$Å, $\alpha = 103.62(2)$, $\beta = 90.35(2)$, $\gamma = 93.02(1)°$. The structure, solved by Patterson methods, was refined by full-matrix least-squares techniques to a residual $R = 0.022$ ($R_w = 0.036$). The four crystallographically unique copper atoms lie in characteristically distorted (four short and two long bonds) six-coordinated sites which link together to form two-dimensional copper-containing sheets. As in the other two polymorphs, these sheets (which are joined together by phosphate tetrahedra and hydrogen bonds) can be derived from a two-dimensional framework of edge-sharing, copper-containing polyhedra.

Introduction

The crystal structure of pseudomalachite (PM) was determined by Ghose (1963) and refined by Shoemaker *et al.* (1977). Recently, we described (Anderson *et al.*, 1977) the crystal structure of a synthetic polymorph of pseudomalachite which, as a convenience, we referred to as PPM.

During the course of a series of hydrothermal experiments designed to establish the conditions for equilibrium between PM and PPM, a careful visual inspection with a high-intensity light source revealed crystals which had a slightly bluer color than the surrounding products. X-ray powder diffraction examination revealed the presence of diffraction lines which could not be explained by the known polymorphs PM and PPM. A powder photograph of the blue-green material alone revealed it to be a third polymorph of $Cu_5(PO_4)_2(OH)_4$, which we shall call QPM.

This paper presents the results of our refinement of the structure of QPM and a description of its structure in terms of polyhedral linkages within a two-dimensional net. The following paper (Shoemaker and Kostiner, 1981) will present a more detailed summary of polymorphism among compounds of the stoichiometry $Cu_5(PO_4)_2(OH)_4$.

Experimental

Once the identity of the new phase had been established, it was found among the products of a number of previous experiments in hydrothermal copper phosphate systems. Additional experiments were carried out in an attempt to determine the effects of temperature and pressure variation on the increasingly complex equilibrium between the polymorphs of $Cu_5(PO_4)_2(OH)_4$.

QPM has never been obtained as the sole product of a hydrothermal reaction. Most commonly, it is found in close conjunction with PM, although in some experiments PPM was the only other polymorph observed. QPM has been grown by hydrothermal technique in sealed gold capsules from nutrient mixtures containing $Cu_3(PO_4)_2$, libethenite, malachite, or copper(II) nitrate with a variety of mineralizing solutions at pressures ranging from 1.2 to 4.0 kbar and bomb temperatures from 205 to 560°C. It has not been observed in mixtures whose pH after reaction was less than 6 or greater than 9.

The crystal used for data collection was obtained from the hydrothermal reaction between 67.4 mg $Cu_3(PO_4)_2$ and 0.5 ml of approximately 1.5 *M* K_3PO_4 solution held at 450°C and 3.8 kbar for four days. In this experiment, QPM formed dendritic crystals which were intimately mixed with PPM crystals and CuO. Significant amounts of QPM can be obtained by the

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H	K	L	FOBS	FCAL
-4	-3	2	410	410
-4	-3	1	25	13
-4	-3	0	203	203
-4	-2	0	488	484
-4	-2	1	46	45
-4	-2	2	240	239
-4	-2	3	365	372
-4	-2	4	378	378
-4	-1	5	205	205
-4	-1	4	214	216
-4	-1	3	308	307
-4	-1	2	182	181
-4	-1	1	331	331
-4	-1	0	165	147
-4	0	0	653	664
-4	0	1	325	328
-4	0	2	45	46
-4	0	3	166	161
-4	0	4	413	416
-4	0	5	84	86
-4	1	4	95	99
-4	1	3	318	327
-4	1	2	441	454
-4	1	1	95	90
-4	1	0	150	152
-4	2	0	405	401
-4	2	1	419	417
-4	2	2	168	168
-4	2	3	91	90
-4	3	2	342	345
-4	3	1	231	230
-4	3	0	152	154
-3	5	0	159	163
-3	4	3	139	133
-3	4	2	202	200
-3	4	1	359	359
-3	4	0	432	439
-3	3	0	155	161
-3	3	1	326	332
-3	3	2	157	153
-3	3	3	296	296
-3	3	4	53	22
-3	2	6	298	298

H	K	L	FOBS	FCAL
-3	2	5	167	172
-3	2	4	742	760
-3	2	3	259	258
-3	2	1	93	94
-3	2	0	717	737
-3	1	0	56	50
-3	1	1	265	274
-3	1	2	502	513
-3	1	3	55	62
-3	1	4	112	107
-3	1	5	36	37
-3	1	6	93	97
-3	0	7	221	220
-3	0	6	528	535
-3	0	5	140	138
-3	0	4	469	430
-3	0	3	641	665
-3	0	2	139	142
-3	0	1	221	218
-3	0	0	702	705
-3	-1	0	84	83
-3	-1	1	116	115
-3	-1	2	559	566
-3	-1	3	527	538
-3	-1	4	88	43
-3	-1	5	76	73
-3	-1	7	120	116
-3	-2	7	85	84
-3	-2	6	569	574
-3	-2	5	65	60
-3	-2	4	310	313
-3	-2	3	129	122
-3	-2	2	202	206
-3	-2	1	250	252
-3	-2	0	992	988
-3	-3	0	189	194
-3	-3	1	23	6
-3	-3	2	94	93
-3	-3	3	403	400
-3	-3	4	432	430
-3	-3	5	223	221
-3	-3	6	306	306
-3	-4	4	407	406

H	K	L	FOBS	FCAL
-3	-4	3	458	442
-3	-4	2	138	130
-3	-4	1	39	36
-3	-4	0	637	631
-2	-5	4	373	374
-2	-5	3	389	385
-2	-5	2	88	86
-2	-5	1	187	188
-2	-5	0	61	53
-2	-4	0	733	729
-2	-4	1	75	61
-2	-4	2	391	388
-2	-4	3	176	171
-2	-4	4	154	155
-2	-4	5	90	88
-2	-4	6	815	819
-2	-4	7	63	64
-2	-3	8	197	196
-2	-3	7	155	153
-2	-3	6	128	126
-2	-3	5	104	104
-2	-3	4	100	99
-2	-3	3	355	363
-2	-3	2	477	474
-2	-3	1	89	84
-2	-3	0	419	420
-2	-2	0	1111	1051
-2	-2	1	186	178
-2	-2	2	401	407
-2	-2	3	982	989
-2	-2	4	321	326
-2	-2	5	202	197
-2	-2	6	521	519
-2	-2	7	101	100
-2	-2	8	157	160
-2	-1	8	385	383
-2	-1	7	76	77
-2	-1	6	108	109
-2	-1	5	59	52
-2	-1	4	325	328
-2	-1	3	452	465
-2	-1	2	498	498
-2	-1	1	147	153

H	K	L	FOBS	FCAL
-2	-1	0	172	165
-2	0	0	859	858
-2	0	1	84	88
-2	0	2	59	54
-2	0	3	573	581
-2	0	4	776	801
-2	0	6	666	709
-2	0	7	105	107
-2	0	8	120	123
-2	1	7	220	221
-2	1	6	28	19
-2	1	5	405	417
-2	1	4	31	28
-2	1	3	597	615
-2	1	2	511	520
-2	1	1	158	153
-2	1	0	329	323
-2	2	0	791	807
-2	2	1	321	335
-2	2	2	571	579
-2	2	3	223	229
-2	2	4	231	236
-2	2	5	202	205
-2	2	6	594	605
-2	2	7	274	277
-2	3	6	124	124
-2	3	5	25	24
-2	3	4	138	145
-2	3	3	196	203
-2	3	2	558	577
-2	3	1	443	448
-2	3	0	66	63
-2	4	0	418	415
-2	4	1	311	311
-2	4	2	157	159
-2	4	3	403	401
-2	4	4	501	503
-2	5	2	300	300
-2	5	1	303	305
-2	5	0	80	80
-1	6	0	410	412
-1	5	0	101	98
-1	5	1	193	190

H	K	L	FOBS	FCAL
-1	5	2	462	456
-1	5	3	222	223
-1	4	5	103	106
-1	4	4	610	608
-1	4	3	68	68
-1	4	1	428	430
-1	4	0	595	609
-1	3	0	166	156
-1	3	1	114	119
-1	3	2	443	443
-1	3	3	501	497
-1	3	4	255	253
-1	3	5	152	149
-1	3	6	47	50
-1	2	7	98	91
-1	2	6	406	406
-1	2	5	117	117
-1	2	4	648	664
-1	2	3	618	621
-1	2	2	149	141
-1	2	1	511	478
-1	2	0	1501	1471
-1	1	0	465	438
-1	1	1	488	482
-1	1	2	523	520
-1	1	3	306	319
-1	1	4	181	188
-1	1	5	132	129
-1	1	6	316	321
-1	1	7	175	173
-1	1	8	407	415
-1	0	8	216	220
-1	0	7	288	300
-1	0	6	908	956
-1	0	5	208	214
-1	0	4	259	262
-1	0	3	250	272
-1	0	2	721	729
-1	0	1	42	21
-1	0	0	1073	1028
-1	-1	0	475	461
-1	-1	1	250	243
-1	-1	2	727	702

H	K	L	FOBS	FCAL
-1	-1	3	1058	1045
-1	-1	4	269	270
-1	-1	5	210	203
-1	-1	6	40	47
-1	-1	8	137	138
-1	-1	9	243	239
-1	-2	9	496	495
-1	-2	8	78	76
-1	-2	7	131	129
-1	-2	6	817	838
-1	-2	5	236	238
-1	-2	4	413	423
-1	-2	3	796	788
-1	-2	2	523	500
-1	-2	1	352	328
-1	-2	0	810	778
-1	-3	0	94	94
-1	-3	1	194	185
-1	-3	2	141	146
-1	-3	3	652	655
-1	-3	4	498	504
-1	-3	5	101	105
-1	-3	6	78	77
-1	-3	7	174	180
-1	-3	8	197	198
-1	-4	8	417	427
-1	-4	7	113	108
-1	-4	6	478	473
-1	-4	5	33	30
-1	-4	4	221	221
-1	-4	3	501	511
-1	-4	2	519	523
-1	-4	1	341	333
-1	-4	0	999	972
-1	-5	0	252	257
-1	-5	1	39	41
-1	-5	2	235	236
-1	-5	3	222	221
-1	-5	4	208	210
-1	-5	5	265	266
-1	-5	6	193	198
-1	-6	3	274	268
-1	-6	2	478	470

H	K	L	FOBS	FCAL
-1	-6	1	152	147
0	-6	0	560	559
0	-6	1	182	180
0	-6	2	378	378
0	-6	3	125	111
0	-6	4	254	254
0	-5	7	126	130
0	-5	6	109	99
0	-5	5	31	39
0	-5	4	388	389
0	-5	3	391	398
0	-5	2	44	47
0	-5	1	343	341
0	-5	0	115	120
0	-4	0	762	758
0	-4	1	184	181
0	-4	2	762	749
0	-4	3	465	472
0	-4	4	39	61
0	-4	5	209	211
0	-4	6	688	699
0	-4	7	107	110
0	-4	8	241	237
0	-3	9	408	413
0	-3	8	128	127
0	-3	7	191	196
0	-3	6	96	49
0	-3	5	217	219
0	-3	4	606	612
0	-3	3	699	695
0	-3	2	190	198
0	-3	1	91	100
0	-3	0	220	229
0	-2	0	829	804
0	-2	1	290	281
0	-2	2	482	483
0	-2	3	650	650
0	-2	4	405	403
0	-2	6	763	803
0	-2	7	184	187
0	-2	8	361	364
0	-2	9	195	188
0	-1	9	274	268

H	K	L	FOBS	FCAL
0	-1	8	426	431
0	-1	7	34	20
0	-1	6	677	691
0	-1	5	98	99
0	-1	4	558	561
0	-1	3	417	433
0	-1	2	272	266
0	-1	1	243	243
0	-1	0	118	112
0	0	1	88	88
0	0	2	231	219
0	0	3	478	481
0	0	4	554	556
0	0	6	744	736
0	0	7	79	132
0	0	8	257	265
0	0	9	406	407
0	1	8	245	[illegible]
0	1	7	209	[illegible]
0	1	5	133	133
0	1	4	406	390
0	1	3	658	634
0	1	2	455	445
0	1	1	190	193
0	1	0	118	112
0	2	0	815	804
0	2	1	323	309
0	2	2	224	230
0	2	3	757	724
0	2	4	602	590
0	2	5	35	26
0	2	6	733	730
0	2	7	174	175
0	3	5	63	55
0	3	4	44	41
0	3	3	480	478
0	3	2	765	754
0	3	1	319	321
0	3	0	217	229
0	4	0	758	758
0	4	1	124	118
0	4	2	168	168
0	4	3	418	423

H	K	L	FOBS	FCAL
0	4	4	473	475
0	4	5	289	289
0	5	3	117	106
0	5	2	197	197
0	5	1	341	343
0	5	0	108	120
0	6	0	558	559
1	5	0	249	257
1	5	1	94	91
1	5	2	416	414
1	5	3	297	294
1	4	5	79	80
1	4	4	291	293
1	4	3	190	189
1	4	2	306	308
1	4	1	404	401
1	4	0	989	972
1	3	0	95	94
1	3	1	114	108
1	3	2	364	370
1	3	3	517	521
1	3	4	137	130
1	3	5	236	236
1	3	6	251	249
1	2	7	110	96
1	2	6	508	503
1	2	5	85	78
1	2	4	498	495
1	2	3	675	670
1	2	2	251	247
1	2	1	309	281
1	2	0	793	778
1	1	0	471	461
1	1	1	314	300
1	1	2	606	569
1	1	3	845	789
1	1	4	375	370
1	1	5	153	149
1	1	7	152	154
1	1	8	303	304
1	0	8	106	100
1	0	7	93	89
1	0	6	873	897

H	K	L	FOBS	FCAL
1	0	5	166	163
1	0	4	301	288
1	0	3	1042	1012
1	0	2	888	871
1	0	1	105	113
1	0	0	1063	1028
1	-1	0	466	438
1	-1	1	493	479
1	-1	2	610	594
1	-1	3	316	328
1	-1	4	177	181
1	-1	5	82	76
1	-1	6	22	33
1	-1	8	37	28
1	-1	9	438	433
1	-2	9	298	298
1	-2	8	258	260
1	-2	7	307	304
1	-2	6	864	876
1	-2	5	307	313
1	-2	4	212	218
1	-2	3	271	294
1	-2	2	545	548
1	-2	1	309	285
1	-2	0	1490	1471
1	-3	0	161	156
1	-3	1	41	36
1	-3	2	58	56
1	-3	3	583	604
1	-3	4	531	554
1	-3	5	303	302
1	-3	6	315	311
1	-3	7	126	127
1	-3	8	221	223
1	-4	8	404	402
1	-4	7	37	40
1	-4	6	440	443
1	-4	5	161	161
1	-4	4	277	280
1	-4	3	517	525
1	-4	2	462	471
1	-4	1	218	220
1	-4	0	590	609

H	K	L	FOBS	FCAL
1	-5	0	100	98
1	-5	1	57	66
1	-5	2	57	59
1	-5	3	35	35
1	-5	4	509	515
1	-5	5	368	372
1	-5	6	30	39
1	-5	7	166	163
1	-6	3	211	212
1	-6	2	637	639
1	-6	1	72	69
1	-6	0	413	412
2	-5	6	98	102
2	-5	5	202	201
2	-5	4	346	355
2	-5	3	408	415
2	-5	2	54	50
2	-5	1	85	88
2	-5	0	86	80
2	-4	0	411	415
2	-4	1	55	50
2	-4	2	662	681
2	-4	3	140	150
2	-4	5	401	408
2	-4	6	524	526
2	-4	7	230	227
2	-3	8	67	66
2	-3	7	130	131
2	-3	6	27	11
2	-3	5	313	316
2	-3	4	86	82
2	-3	3	276	283
2	-3	2	372	377
2	-3	1	334	332
2	-3	0	72	63
2	-2	0	778	807
2	-2	1	327	342
2	-2	2	792	809
2	-2	3	586	592
2	-2	4	233	237
2	-2	5	21	16
2	-2	6	702	716
2	-2	7	91	88

H	K	L	FOBS	FCAL
2	-2	8	431	424
2	-1	8	158	157
2	-1	7	40	46
2	-1	6	115	111
2	-1	5	94	96
2	-1	4	721	736
2	-1	3	527	529
2	0	0	819	858
2	0	1	19	8
2	0	2	464	476
2	0	3	455	475
2	0	4	353	352
2	0	5	190	193
2	0	6	464	462
2	0	7	94	86
2	0	8	308	313
2	1	7	168	164
2	1	6	204	197
2	1	5	117	119
2	1	4	312	315
2	1	3	993	989
2	1	2	289	292
2	1	1	140	143
2	1	0	169	165
2	2	0	1066	1051
2	2	1	216	209
2	2	2	458	459
2	2	3	308	315
2	2	4	120	123
2	2	5	29	21
2	2	6	782	784
2	3	5	28	16
2	3	4	175	175
2	3	3	209	189
2	3	2	433	431
2	3	1	32	29
2	3	0	415	420
2	4	0	733	729
2	4	1	68	71
2	4	2	198	196
2	4	3	412	408
2	4	4	409	407
2	5	1	261	256

H	K	L	FOBS	FCAL
2	5	0	56	53
3	4	2	156	159
3	4	1	52	50
3	4	0	638	631
3	3	0	138	194
3	3	1	22	5
3	3	2	92	92
3	3	3	400	402
3	3	4	348	355
3	2	5	76	75
3	2	4	425	426
3	2	3	441	438
3	2	2	169	171
3	2	1	205	202
3	2	0	978	988
3	1	0	82	83
3	1	2	287	283
3	1	3	117	115
3	1	4	298	301
3	1	5	317	320
3	1	6	252	252
3	0	6	575	583
3	0	5	76	80
3	0	4	25	26
3	0	3	483	497
3	0	2	598	608
3	0	1	85	92
3	0	0	691	705
3	-1	0	54	50
3	-1	1	87	84
3	-1	2	51	46
3	-1	3	648	666
3	-1	4	397	408
3	-1	5	151	143
3	-1	7	49	40
3	-2	7	97	91
3	-2	6	492	489
3	-2	5	246	249
3	-2	4	197	202
3	-2	3	71	74
3	-2	2	513	526
3	-2	1	35	34
3	-2	0	710	737

H	K	L	FOBS	FCAL
3	-3	0	158	161
3	-3	1	219	230
3	-3	2	264	266
3	-3	3	183	185
3	-3	4	556	563
3	-3	5	143	146
3	-3	6	131	133
3	-4	5	175	177
3	-4	4	294	300
3	-4	3	322	322
3	-4	2	460	462
3	-4	1	213	219
3	-4	0	427	439
3	-5	0	162	163
3	-5	2	50	52
3	-5	3	149	150
4	-3	4	219	228
4	-3	3	113	113
4	-3	2	26	26
4	-3	0	155	154
4	-2	0	403	401
4	-2	1	196	196
4	-2	2	580	589
4	-2	3	285	293
4	-2	4	34	25
4	-1	5	356	359
4	-1	4	331	327
4	-1	3	165	158
4	-1	2	45	43
4	-1	1	98	92
4	-1	0	149	152
4	0	0	646	664
4	0	1	168	171
4	0	2	261	263
4	0	3	321	325
4	0	4	284	288
4	1	4	265	270
4	1	3	364	364
4	1	2	86	80
4	1	1	289	295
4	1	0	164	147
4	2	0	478	484
4	2	2	440	445

H	K	L	FOBS	FCAL
4	3	0	204	203
-6	-2	0	292	292
-6	-2	1	27	29
-6	-2	3	197	203
-6	-1	4	28	23
-6	-1	2	146	148
-6	-1	1	155	157
-6	-1	0	96	97
-6	0	0	414	416
-6	0	1	229	225
-6	0	3	76	73
-6	0	4	407	405
-6	1	3	172	164
-6	1	2	148	139
-6	1	1	77	76
-6	1	0	65	67
-6	2	0	59	54
-6	2	1	178	180
-6	2	2	157	160
-6	2	3	82	87
-6	3	1	253	254
-6	3	0	101	102
-5	5	1	143	133
-5	5	2	199	204
-5	4	4	281	279
-5	4	3	77	80
-5	4	2	203	202
-5	4	1	332	330
-5	4	0	232	234
-5	3	0	165	162
-5	3	1	150	151
-5	3	2	175	173
-5	3	4	24	18
-5	3	5	110	108
-5	2	6	152	149
-5	2	4	371	365
-5	2	3	133	132
-5	2	2	39	24
-5	2	1	170	168
-5	2	0	346	346
-5	1	0	54	45
-5	1	1	420	418
-5	1	2	254	258

H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL
-5	1	3	108	102	-5	-4	0	419	422	-4	1	7	296	303	-3	3	5	243	248	-3	-6	6	359	363
-5	1	4	34	23	-5	-5	2	147	149	-4	1	6	43	32	-3	3	6	65	50	-3	-6	5	36	24
-5	1	6	40	37	-4	-6	0	452	453	-4	1	5	153	149	-3	3	7	230	230	-3	-6	3	372	370
-5	1	7	91	89	-4	-6	1	58	57	-4	2	4	393	395	-3	3	8	213	213	-3	-6	2	418	420
-5	0	7	347	349	-4	-6	2	122	119	-4	2	6	436	438	-3	3	9	47	49	-3	-6	0	338	335
-5	0	6	298	301	-4	-6	3	189	195	-4	2	7	189	187	-3	2	9	181	183	-3	-7	0	113	114
-5	0	5	176	183	-4	-6	4	198	193	-4	3	7	56	56	-3	2	8	231	234	-3	-7	1	149	145
-5	0	4	295	294	-4	-6	5	83	78	-4	3	6	93	96	-3	2	7	281	280	-3	-7	2	94	88
-5	0	3	279	275	-4	-5	7	52	53	-4	3	5	47	44	-3	1	7	44	38	-3	-7	3	331	336
-5	0	2	275	272	-4	-5	5	102	104	-4	3	4	57	56	-3	1	8	299	303	-3	-7	4	135	133
-5	0	1	143	143	-4	-5	4	84	84	-4	3	3	30	23	-3	1	9	184	184	-3	-7	5	31	23
-5	0	0	194	200	-4	-5	3	470	470	-4	4	0	278	278	-3	1	10	160	156	-2	-7	7	37	30
-5	-1	0	165	163	-4	-5	2	186	187	-4	4	1	119	120	-3	0	10	256	258	-2	-7	6	120	128
-5	-1	1	66	69	-4	-5	1	69	72	-4	4	2	134	139	-3	0	9	97	94	-2	-7	5	143	148
-5	-1	2	317	318	-4	-5	0	28	9	-4	4	3	131	129	-3	0	8	34	15	-2	-7	4	370	368
-5	-1	3	144	141	-4	-4	0	389	387	-4	4	4	472	473	-3	-1	8	293	296	-2	-7	3	132	133
-5	-1	4	68	63	-4	-4	1	89	95	-4	4	5	74	74	-3	-1	9	312	309	-2	-7	2	56	56
-5	-1	5	170	171	-4	-4	2	277	276	-4	4	6	63	64	-3	-1	10	76	75	-2	-7	1	50	49
-5	-1	6	134	131	-4	-4	3	374	375	-4	5	4	36	15	-3	-1	11	141	137	-2	-7	0	100	93
-5	-1	7	102	102	-4	-4	4	100	98	-4	5	3	104	103	-3	-2	11	29	18	-2	-6	0	567	559
-5	-1	8	38	33	-4	-4	5	33	26	-4	5	2	74	69	-3	-2	10	340	341	-2	-6	1	28	11
-5	-2	7	61	56	-4	-4	6	501	502	-4	5	1	259	256	-3	-2	9	376	379	-2	-6	2	216	209
-5	-2	6	416	416	-4	-4	7	24	9	-4	5	0	285	290	-3	-2	8	75	76	-2	-6	3	369	378
-5	-2	5	36	22	-4	-3	9	221	218	-4	6	0	251	250	-3	-3	7	93	92	-2	-6	4	233	236
-5	-2	4	316	305	-4	-3	8	100	101	-4	6	1	241	236	-3	-3	8	260	259	-2	-6	5	203	207
-5	-2	3	184	193	-4	-3	6	41	36	-4	6	2	45	40	-3	-3	9	87	86	-2	-6	6	394	394
-5	-2	2	81	80	-4	-3	5	60	58	-3	7	1	297	299	-3	-3	10	95	89	-2	-6	7	119	121
-5	-2	1	192	191	-4	-3	4	31	31	-3	7	2	126	126	-3	-4	9	241	245	-2	-6	8	230	226
-5	-2	0	492	494	-4	-3	3	181	181	-3	6	4	298	298	-3	-4	8	255	251	-2	-6	9	268	272
-5	-3	0	136	134	-4	-2	5	221	221	-3	6	3	126	124	-3	-4	7	58	55	-2	-5	10	204	201
-5	-3	1	57	59	-4	-2	6	494	498	-3	6	2	216	213	-3	-4	6	527	534	-2	-5	9	102	101
-5	-3	2	219	216	-4	-2	7	287	287	-3	6	1	200	196	-3	-5	0	32	22	-2	-5	8	87	82
-5	-3	3	288	290	-4	-2	8	178	177	-3	6	0	121	128	-3	-5	1	27	20	-2	-5	7	57	59
-5	-3	4	51	40	-4	-2	9	194	190	-3	5	1	214	217	-3	-5	2	192	194	-2	-5	6	135	134
-5	-3	5	86	94	-4	-1	9	92	95	-3	5	2	358	359	-3	-5	3	251	234	-2	-4	8	127	130
-5	-3	6	115	121	-4	-1	8	353	352	-3	5	3	61	60	-3	-5	4	263	258	-2	-4	9	252	261
-5	-3	7	126	130	-4	-1	7	152	148	-3	5	4	144	140	-3	-5	5	101	101	-2	-4	10	283	278
-5	-4	6	191	192	-4	-1	6	141	137	-3	5	5	41	33	-3	-5	6	131	137	-2	-4	11	48	44
-5	-4	5	27	16	-4	0	6	276	276	-3	5	6	187	189	-3	-5	7	54	50	-2	-3	11	155	157
-5	-4	4	293	300	-4	0	7	104	99	-3	4	8	39	21	-3	-5	8	198	200	-2	-3	10	181	179
-5	-4	3	311	315	-4	0	8	51	54	-3	4	7	165	167	-3	-5	9	265	268	-2	-3	9	474	473
-5	-4	2	27	12	-4	0	9	275	275	-3	4	6	228	228	-3	-6	8	151	155	-2	-2	9	316	311
-5	-4	1	46	48	-4	1	8	212	214	-3	4	4	333	337	-3	-6	7	28	23	-2	-2	10	163	164

H	K	L	FOBS	FCAL
-2	-2	11	85	84
-2	-1	11	26	29
-2	-1	10	78	69
-2	-1	9	294	288
-2	0	9	355	355
-2	0	10	272	267
-2	0	11	248	246
-2	1	11	107	105
-2	1	10	149	155
-2	1	9	115	110
-2	1	8	131	131
-2	2	8	40	42
-2	2	9	182	179
-2	2	10	381	389
-2	3	9	209	206
-2	3	8	248	248
-2	3	7	209	202
-2	4	5	111	110
-2	4	6	300	300
-2	4	7	248	245
-2	4	8	52	53
-2	5	7	200	203
-2	5	5	67	60
-2	5	4	94	95
-2	5	3	69	60
-2	6	0	406	408
-2	6	1	287	285
-2	6	2	70	78
-2	6	3	118	115
-2	6	4	429	434
-2	6	5	78	79
-2	6	6	213	212
-2	7	3	134	130
-2	7	2	171	180
-2	7	1	127	124
-2	7	0	64	69
-2	8	0	136	133
-1	8	1	177	179
-1	8	0	224	225
-1	7	0	177	171
-1	7	1	276	273
-1	7	2	145	144
-1	6	6	203	199

H	K	L	FOBS	FCAL
-1	6	5	188	181
-1	6	4	333	335
-1	6	3	171	168
-1	6	2	225	226
-1	6	1	162	162
-1	5	4	158	156
-1	5	5	124	123
-1	5	6	60	64
-1	5	7	116	115
-1	5	8	138	139
-1	4	9	139	140
-1	4	7	154	149
-1	4	6	470	468
-1	3	7	290	287
-1	3	8	353	356
-1	3	9	75	70
-1	3	10	86	86
-1	2	11	65	48
-1	2	10	164	170
-1	2	9	301	297
-1	2	8	134	137
-1	1	9	320	321
-1	1	11	127	130
-1	0	12	380	379
-1	0	11	29	25
-1	0	10	262	269
-1	0	9	174	174
-1	-1	10	242	238
-1	-1	11	91	86
-1	-1	12	235	233
-1	-2	12	320	316
-1	-2	11	110	104
-1	-2	10	210	205
-1	-3	9	322	324
-1	-3	10	137	129
-1	-3	11	99	95
-1	-3	12	90	89
-1	-4	12	338	341
-1	-4	10	53	54
-1	-4	9	389	394
-1	-5	7	260	263
-1	-5	8	103	102
-1	-5	9	296	294

H	K	L	FOBS	FCAL
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-1	-5	11	33	28
-1	-6	10	155	156
-1	-6	9	144	147
-1	-6	8	189	193
-1	-6	6	608	616
-1	-6	5	172	173
-1	-6	4	87	83
-1	-6	0	254	253
-1	-7	0	29	18
-1	-7	1	130	130
-1	-7	2	82	81
-1	-7	3	235	239
-1	-7	4	221	220
-1	-7	5	163	170
-1	-7	6	144	143
-1	-7	7	98	96
-1	-7	8	55	54
-1	-7	9	153	159
-1	-8	6	290	290
-1	-8	5	255	257
-1	-8	4	55	52
-1	-8	3	133	132
-1	-8	2	332	333
-1	-8	1	52	50
-1	-8	0	382	383
0	-8	0	109	111
0	-8	1	66	64
0	-8	2	371	372
0	-8	3	210	213
0	-8	4	117	116
0	-8	5	167	166
0	-8	6	244	245
0	-7	9	103	96
0	-7	8	73	76
0	-7	7	156	175
0	-7	6	89	76
0	-7	5	256	263
0	-7	4	279	283
0	-7	3	198	196
0	-7	2	41	42
0	-7	1	40	34
0	-7	0	61	78

H	K	L	FOBS	FCAL
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0	-6	6	309	313
0	-6	7	201	198
0	-6	8	458	464
0	-6	9	248	253
0	-6	10	58	58
0	-5	11	96	90
0	-5	10	276	278
0	-5	9	211	213
0	-5	8	53	53
0	-4	9	342	347
0	-4	10	75	73
0	-4	11	118	118
0	-4	12	261	255
0	-3	12	139	141
0	-3	11	35	29
0	-3	10	207	205
0	-2	10	99	98
0	-2	11	55	54
0	0	11	62	69
0	0	12	295	305
0	1	11	30	14
0	1	10	72	69
0	1	9	339	341
0	2	8	94	92
0	2	9	244	247
0	2	10	343	340
0	3	10	28	28
0	3	9	295	298
0	3	8	263	264
0	3	7	66	67
0	4	6	390	391
0	4	7	265	265
0	4	8	219	221
0	4	9	78	79
0	5	8	213	216
0	5	7	240	237
0	5	6	79	81
0	5	5	116	116
0	5	4	58	57
0	6	1	330	325
0	6	2	116	118
0	6	3	207	200

H	K	L	FOBS	FCAL
0	6	4	425	425
0	6	5	74	71
0	6	6	223	223
0	7	3	213	207
0	7	2	263	261
0	7	1	144	149
0	7	0	70	78
0	8	0	109	111
0	8	1	209	209
1	8	0	385	383
1	7	1	303	300
1	7	2	303	308
1	7	3	118	117
1	6	6	320	325
1	6	5	72	75
1	6	4	302	300
1	6	3	235	235
1	6	2	205	209
1	6	1	217	221
1	6	0	255	253
1	5	4	29	16
1	5	5	134	136
1	5	6	110	110
1	5	7	185	188
1	4	9	210	215
1	4	8	51	40
1	4	7	28	13
1	4	6	579	577
1	3	7	301	297
1	3	8	228	231
1	3	9	103	102
1	3	10	83	84
1	2	10	180	183
1	2	9	276	279
1	2	8	250	251
1	1	9	431	438
1	1	10	65	61
1	0	12	278	280
1	0	11	39	40
1	0	10	167	168
1	0	9	327	328
1	-1	10	241	240
1	-1	11	59	57

H	K	L	FOBS	FCAL
1	-1	12	144	147
1	-2	12	289	287
1	-2	11	44	14
1	-2	10	258	258
1	-3	9	173	169
1	-3	10	234	233
1	-3	11	188	188
1	-3	12	172	167
1	-4	12	389	386
1	-4	11	114	113
1	-4	10	30	23
1	-4	9	267	271
1	-5	9	334	335
1	-5	10	147	148
1	-5	11	128	124
1	-6	9	34	33
1	-6	8	335	335
1	-6	6	495	498
1	-6	5	127	124
1	-7	0	174	171
1	-7	1	183	176
1	-7	3	165	167
1	-7	4	144	139
1	-7	5	151	148
1	-7	8	138	135
1	-7	9	105	104
1	-8	6	150	153
1	-8	5	256	260
1	-8	4	183	183
1	-8	2	292	294
1	-8	0	222	225
2	-8	0	139	133
2	-8	1	83	87
2	-8	2	419	424
2	-8	3	121	122
2	-8	4	86	90
2	-8	5	97	102
2	-7	6	25	9
2	-7	5	272	270
2	-7	4	263	260
2	-7	3	143	139
2	-7	2	72	72
2	-7	1	60	56

H	K	L	FOBS	FCAL
2	-7	0	70	69
2	-6	0	403	408
2	-6	1	51	52
2	-6	2	367	369
2	-6	3	89	81
2	-6	4	204	207
2	-6	5	259	258
2	-6	6	288	287
2	-6	7	66	64
2	-6	8	351	355
2	-6	9	225	228
2	-5	10	262	260
2	-5	9	114	109
2	-5	8	37	29
2	-4	8	232	232
2	-4	9	179	179
2	-4	10	252	252
2	-4	11	152	156
2	-3	10	218	216
2	-3	9	331	324
2	-2	9	218	212
2	-2	10	53	44
2	-2	11	52	48
2	-1	11	148	149
2	-1	10	107	110
2	-1	9	337	340
2	0	9	448	456
2	0	10	120	115
2	0	11	95	94
2	1	11	31	41
2	1	10	239	241
2	1	9	188	194
2	1	8	189	195
2	2	7	59	63
2	2	8	93	94
2	2	9	131	137
2	2	10	193	197
2	3	9	294	298
2	3	8	141	144
2	3	7	51	62
2	3	6	126	131
2	4	5	182	180
2	4	6	408	413

H	K	L	FOBS	FCAL
2	4	7	174	175
2	4	8	106	108
2	5	7	64	63
2	5	6	127	124
2	5	5	27	13
2	5	4	196	203
2	5	3	329	334
2	5	2	221	218
2	6	0	568	559
2	6	1	112	110
2	6	2	71	69
2	6	3	163	165
2	6	4	368	373
2	6	5	46	39
2	7	2	242	246
2	7	1	30	27
2	7	0	94	93
3	7	0	113	114
3	6	3	312	314
3	6	2	186	183
3	6	1	52	39
3	6	0	338	335
3	5	0	27	22
3	5	2	361	364
3	5	3	392	394
3	5	4	69	73
3	5	5	26	11
3	4	7	28	19
3	4	6	342	353
3	4	5	72	53
3	4	4	221	221
3	4	3	242	242
3	3	5	51	45
3	3	6	134	142
3	3	7	36	38
3	3	8	174	178
3	2	9	202	203
3	2	8	233	233
3	2	7	32	26
3	2	6	518	524
3	1	7	96	95
3	1	8	186	186
3	1	9	308	306

H	K	L	FOBS	FCAL
3	1	10	30	36
3	0	10	129	132
3	0	9	73	68
3	0	8	187	189
3	0	7	36	32
3	-1	9	317	317
3	-1	10	321	321
3	-1	11	115	111
3	-2	11	28	11
3	-2	10	78	76
3	-2	9	313	314
3	-2	8	337	339
3	-3	7	51	39
3	-3	9	106	101
3	-3	10	141	141
3	-4	10	62	60
3	-4	9	72	68
3	-4	8	501	491
3	-4	7	155	155
3	-4	6	278	279
3	-5	4	166	169
3	-5	5	342	346
3	-5	6	56	49
3	-5	7	115	118
3	-5	8	39	16
3	-5	9	233	231
3	-6	8	272	264
3	-6	6	204	201
3	-6	5	212	212
3	-6	4	46	36
3	-6	3	41	34
3	-6	2	499	502
3	-6	1	43	38
3	-6	0	129	128
3	-7	1	114	104
3	-7	2	26	20
3	-7	3	133	135
3	-7	4	140	141
3	-7	5	139	138
3	-7	6	172	167
3	-7	7	29	33
4	-6	0	254	250
4	-6	2	280	277

H	K	L	FOBS	FCAL
4	-6	3	133	131
4	-6	4	206	210
4	-6	5	179	177
4	-6	6	46	42
4	-5	8	85	90
4	-5	7	66	66
4	-5	6	61	64
4	-5	5	152	155
4	-5	4	235	225
4	-5	3	99	98
4	-5	2	149	140
4	-5	1	95	94
4	-5	0	287	290
4	-4	0	278	278
4	-4	2	464	469
4	-4	3	36	30
4	-4	4	106	113
4	-4	5	202	202
4	-4	6	455	453
4	-4	7	43	41
4	-4	8	247	243
4	-4	9	44	40
4	-3	9	234	228
4	-3	8	106	108
4	-3	7	121	116
4	-3	6	80	79
4	-3	5	302	298
4	-2	5	99	81
4	-2	6	298	295
4	-2	7	36	32
4	-2	8	298	301
4	-2	9	79	66
4	-1	9	234	236
4	-1	8	146	145
4	-1	7	66	61
4	-1	6	108	108
4	0	5	208	209
4	0	6	437	440
4	0	7	256	252
4	0	8	242	245
4	0	9	200	202
4	1	8	39	44
4	1	6	39	50

H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL
4	1	5	32	32	4	4	3	443	444	5	3	1	38	39	5	1	5	154	155	5	-1	3	287	283
4	2	3	149	150	4	4	4	101	100	5	3	3	290	290	5	1	6	98	98	5	-1	4	145	140
4	2	4	45	54	4	4	5	91	94	5	3	4	288	289	5	0	7	36	23	5	-1	5	151	151
4	2	5	54	56	4	5	4	190	190	5	2	6	170	175	5	0	6	425	424	5	-1	6	119	115
4	2	6	484	493	4	5	3	174	183	5	2	4	90	82	5	0	5	74	74	5	-2	7	256	249
4	2	8	116	116	4	5	2	132	127	5	2	3	280	285	5	0	4	75	77	5	-2	6	223	222
4	3	5	63	66	4	5	1	45	44	5	2	2	283	284	5	0	3	114	111	5	-2	5	310	309
4	3	4	65	67	4	6	0	452	453	5	2	1	124	123	5	0	2	461	463	5	-2	4	122	117
4	3	3	402	400	4	6	1	98	96	5	2	0	493	494	5	0	1	123	124					
4	3	2	260	263	5	4	2	112	117	5	1	0	169	163	5	0	0	196	200					
4	4	0	386	387	5	4	1	90	96	5	1	2	41	27	5	-1	0	56	45					
4	4	1	82	85	5	4	0	424	422	5	1	3	192	195	5	-1	1	263	269					
4	4	2	258	257	5	3	0	136	134	5	1	4	233	227	5	-1	2	65	54					