

## Crystal structure and optical spectroscopy (300 to 2200 nm) of $\text{CaCrSi}_4\text{O}_{10}$

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### Abstract

Crystals of  $\text{CaCr}^{2+}\text{Si}_4\text{O}_{10}$  were synthesized at 1 atm and 1400–1350°C in a closed system with  $f_{\text{O}_2} = 10^{-16}$  bar.  $\text{CaCrSi}_4\text{O}_{10}$  crystallizes in the space group  $P4/ncc$  with  $a = 7.378(5)\text{\AA}$  and  $c = 15.119(2)\text{\AA}$ . The structure was refined to  $R = 0.026$  ( $R_w = 0.031$ ) based on 546 reflections.  $\text{CaCrSi}_4\text{O}_{10}$  is a structural analog of gillespite and other  $\text{ABSi}_4\text{O}_{10}$  compounds, and although not itself a mineral, has been shown to exhibit structural and compression properties nearly identical to those of gillespite. The most interesting aspects of the structure are the square-planar coordination of  $\text{Cr}^{2+}$ , and the Si–O–Si bond angle of 176.8°. Apparently,  $\text{Cr}^{2+}$  is stable in the gillespite structure because it is readily accepted into the square-planar site, in contrast to other  $\text{Cr}^{2+}$  compounds that are distorted from type-structures as a result of the Jahn–Teller effect in  $\text{Cr}^{2+}$ . The optical absorption spectrum of  $\text{CaCrSi}_4\text{O}_{10}$  has bands at 511 and 670 nm polarized  $\perp c$  and at 453 nm  $\parallel c$ , with all absorption occurring only through vibronic coupling. Diamond cell experiments indicate that  $\text{CaCrSi}_4\text{O}_{10}$  remains tetragonal to at least 50 kbar, with compression behavior identical to that of gillespite.

### Introduction

Until recently, minerals containing divalent chromium were virtually unknown.  $\text{Cr}^{2+}$  was first observed by Haggerty et al. (1970) in lunar minerals, and by Meyer and Boyd (1972) in terrestrial olivines included in diamonds from kimberlites. The presence of  $\text{Cr}^{2+}$  in meteorites was established by Keil and Brett (1973) in the mineral later named heideite  $[(\text{Fe},\text{Cr})_1 + x(\text{Ti},\text{Fe})_2\text{S}_4]$ , and is implied by the formula for brezninaite,  $\text{Cr}_3\text{S}_4$  (Bunch and Fuchs, 1969). No known terrestrial mineral contains divalent chromium as an essential element. Nevertheless, the presence of small amounts of  $\text{Cr}^{2+}$  in lunar, and possibly mantle phases, suggests that the mineral chemistry of divalent chromium is a topic worthy of investigation. Furthermore, the electronic configuration of diva-

lent chromium and the resulting Jahn–Teller effect make  $\text{Cr}^{2+}$  interesting from a purely crystal-chemical viewpoint.

Gasparik (1981) synthesized several  $\text{Cr}^{2+}$ -bearing phases in the system  $\text{CaO–MgO–Cr}^0\text{–Cr}_2\text{O}_3\text{–SiO}_2$ , including the new compound  $\text{CaCrSi}_4\text{O}_{10}$ . The crystals of  $\text{CaCrSi}_4\text{O}_{10}$  used in this study were synthesized at 1 atm in an evacuated and closed silica glass tube by cooling from 1400°C to 1350°C in 24 hours. The starting material was a mechanical mix of 3.1 moles of  $\text{SiO}_2$ , 1.0  $\text{CaSiO}_3$ , 0.33  $\text{Cr}_2\text{O}_3$ , and 0.4  $\text{Cr}^0$ . An excess of chromium metal kept the oxygen fugacity below the  $\text{Cr}^0\text{–Cr}_2\text{O}_3$  buffer, approximately  $10^{-16}$  bar at 1300°C. The run produced compact aggregates of subhedral plates separated by small amounts of blue interstitial glass. The crystals are pink to

h	k	l	F(obs)	F(cal)	A(cal)	B(cal)	Delta(F)
2	0	0	89.936	83.269	-83.224	2.727	6.668
4	0	0	218.334	223.302	223.265	4.026	-4.967
6	0	0	23.701	23.324	23.087	3.317	.377
8	0	0	91.725	93.412	93.349	3.441	-1.688
9	1	0	9.536	9.514	-9.432	-1.248	.022
7	1	0	10.384	9.345	-9.265	-1.217	1.040
5	1	0	12.275	12.772	-12.708	-1.282	-.497
3	1	0	18.375	18.478	-18.436	-1.247	-.104
1	1	0	15.986	14.904	-14.849	-1.279	1.082
2	2	0	149.462	142.092	142.029	4.213	7.370
4	2	0	128.968	127.493	127.445	3.518	1.475
6	2	0	51.847	50.454	50.353	3.180	1.394
8	2	0	85.667	84.673	84.607	3.351	.994
10	2	0	58.877	56.949	56.855	3.277	1.927
11	3	0	11.062	9.770	-9.690	-1.248	1.292
5	3	0	17.855	17.125	-17.082	-1.206	.730
3	3	0	5.804	5.988	-5.844	-1.304	-.184
4	4	0	27.185	24.915	24.729	3.035	2.270
6	4	0	126.099	127.914	127.851	4.015	-1.815
10	4	0	56.618	57.544	57.465	3.020	-.926
7	5	0	13.208	13.613	-13.559	-1.216	-.405
8	6	0	94.665	93.253	93.177	3.769	1.412
10	6	0	28.831	28.950	28.844	2.468	-.119
9	7	0	14.114	14.209	-14.153	-1.266	-.095
4	11	1	14.467	14.827	.298	-14.824	-.360
2	11	1	16.078	15.911	-.284	15.908	.168
1	11	1	11.614	10.204	10.204	-.014	1.410
1	10	1	26.355	26.213	-.427	26.210	.142
3	10	1	22.907	22.308	.369	-22.305	.600
5	10	1	17.165	16.718	-.298	16.716	.447
7	9	1	14.788	11.624	11.623	.180	3.163
5	9	1	11.926	10.487	-10.486	-.136	1.439
4	9	1	24.461	23.795	-.357	23.793	.666
3	9	1	24.270	24.072	-24.071	-.169	.198
2	9	1	22.868	23.129	.323	-23.127	-.260
1	9	1	18.443	18.720	18.718	.321	-.277
4	7	1	36.209	35.424	.407	-35.421	.786
3	7	1	50.036	50.337	50.335	.383	-.301
2	7	1	32.879	32.634	-.357	32.632	.246
1	7	1	43.711	43.417	-43.414	-.545	.294
7	6	1	8.626	6.032	-.073	-6.032	2.594
4	5	1	51.996	52.763	-.439	52.762	-.767
3	5	1	68.594	68.346	-68.345	-.355	.248
2	5	1	46.234	46.564	.380	-46.563	-.331
1	5	1	52.923	53.966	53.964	.523	-1.044
1	4	1	87.492	86.793	-.432	86.792	.699
3	4	1	71.115	70.570	.440	-70.569	.545
6	4	1	7.279	3.084	-3.084	-.029	4.195

2	3	1	64.956	63.024	-.386	63.023	1.932
1	3	1	56.766	58.795	58.795	-.164	-2.030
1	2	1	82.586	80.654	.535	-80.653	1.932
8	1	1	9.365	5.913	.274	-5.907	3.452
0	0	2	62.798	68.283	68.247	2.238	-5.485
1	0	2	11.618	13.780	-1.806	13.661	-2.162
2	0	2	170.713	165.408	165.384	2.810	5.305
3	0	2	91.523	86.073	-2.572	86.034	5.450
4	0	2	54.893	53.112	53.060	2.351	1.782
5	0	2	25.339	25.503	-1.574	-25.454	-.164
6	0	2	43.775	42.728	42.665	2.323	1.047
7	0	2	34.560	33.944	-1.867	33.892	.616
8	0	2	60.232	58.449	58.407	2.215	1.782
9	0	2	74.587	72.258	-2.245	72.223	2.329
10	0	2	41.574	40.794	40.736	2.169	.780
11	0	2	21.526	21.890	-1.510	21.838	-.364
10	1	2	37.275	37.166	1.969	-37.114	.109
8	1	2	9.301	9.722	1.648	-9.582	-.422
7	1	2	11.356	10.938	10.936	-.188	.418
6	1	2	65.647	64.884	2.196	-64.846	.764
5	1	2	6.596	6.334	6.332	-.160	.263
4	1	2	13.660	13.299	1.774	-13.180	.361
3	1	2	23.307	23.339	23.338	-.137	-.031
2	1	2	116.657	113.938	2.342	-113.914	2.719
1	1	2	18.908	17.792	17.791	-.127	1.117
2	2	2	32.450	30.694	30.608	2.298	1.756
3	2	2	27.345	27.834	-1.547	27.791	-.490
4	2	2	108.469	106.717	106.688	2.515	1.752
5	2	2	103.890	103.451	-2.386	103.423	.440
6	2	2	68.229	67.529	67.486	2.408	.700
7	2	2	36.378	36.333	-1.995	36.278	.045
8	2	2	34.211	34.246	34.179	2.141	-.034
9	2	2	23.889	23.821	-1.345	-23.783	.068
10	2	2	26.672	26.910	26.842	1.907	-.238
11	2	2	22.435	23.451	-1.920	23.372	-1.016
9	3	2	10.107	8.966	8.963	-.231	1.141
8	3	2	49.649	49.632	2.251	-49.581	.017
6	3	2	9.686	8.280	1.511	-8.141	1.406
5	3	2	19.637	19.915	19.915	-.165	-.279
4	3	2	73.833	75.450	2.461	-75.410	-1.616
4	4	2	49.797	48.792	48.731	2.443	1.005
5	4	2	13.227	13.584	-1.599	-13.489	-.357
6	4	2	34.086	34.023	33.959	2.076	.063
7	4	2	22.840	22.215	-1.730	22.147	.625
8	4	2	51.716	52.134	52.084	2.279	-.418
9	4	2	70.002	70.891	-2.285	70.854	-.889
10	4	2	38.693	38.616	38.566	1.959	.077
11	4	2	13.626	14.668	-1.350	14.606	-1.043
10	5	2	43.801	45.510	1.996	-45.466	-1.709
7	5	2	13.243	13.934	13.932	-.199	-.691

6	5	2	65.465	65.952	2.183	-65.916	-.486	
6	6	2	72.632	73.038	72.996	2.469	-.406	
7	6	2	35.074	35.367	35.385	35.985	35.311	-.293
	8	5	2	13.288	13.387	13.269	1.779	-.099
	9	6	2	22.130	23.643	-1.165	-23.615	-1.513
	10	6	2	33.762	33.582	33.524	1.960	.180
	9	7	2	9.598	8.498	8.495	-.226	1.100
	8	7	2	14.366	14.191	1.564	-14.104	.176
	8	8	2	44.516	46.536	46.489	2.103	-2.021
	4	11	3	11.058	9.944	.142	-9.943	1.114
	2	11	3	15.625	15.856	-.156	15.856	-.232
	1	10	3	13.966	13.313	-.190	13.312	.652
	5	9	3	16.243	15.121	15.120	.210	1.121
	4	9	3	12.965	14.236	-.167	14.235	-1.271
	3	9	3	21.154	21.660	21.659	.210	-.505
	2	9	3	21.023	20.486	.173	-20.485	.538
	1	9	3	41.875	41.549	-41.546	-.541	.326
	2	8	3	9.020	5.434	-5.434	-.071	3.586
	5	8	3	8.735	8.156	.046	8.156	.578
	6	7	3	9.606	11.038	-.004	-11.038	-1.432
	5	7	3	12.223	10.851	-10.851	.033	1.372
	4	7	3	16.138	15.987	.177	-15.986	.151
	3	7	3	38.870	39.047	-39.044	-.491	-.177
	2	7	3	24.334	24.670	-.181	24.669	-.336
	1	7	3	65.374	65.068	65.062	.845	.306
	1	6	3	42.345	42.338	-.076	42.338	.006
	3	6	3	30.012	31.452	.049	-31.452	-1.440
	5	6	3	16.664	17.086	-.010	17.086	-.421
	4	5	3	15.586	16.595	-.175	16.594	-1.009
	3	5	3	70.062	71.004	71.002	.486	-.942
	2	5	3	28.755	29.588	.181	-29.587	-.833
	1	5	3	105.406	105.872	-105.868	-.856	-.466
	3	4	3	9.683	8.095	.151	-8.093	1.589
	2	3	3	28.937	29.554	-.169	29.554	-.617
	1	3	3	22.399	20.675	20.671	.371	1.724
	1	2	3	29.238	27.660	.160	-27.660	1.578
	0	0	4	215.432	215.405	-215.404	-.837	.026
	1	0	4	131.834	135.694	-2.408	135.673	-3.860
	2	0	4	111.076	105.918	105.914	.894	5.159
	3	0	4	7.890	7.788	-1.860	7.563	.102
	4	0	4	44.627	43.926	-43.926	-.166	.701
	5	0	4	48.884	48.475	-2.310	48.420	.409
	6	0	4	52.951	51.489	51.488	.212	1.462
	7	0	4	37.843	37.410	-2.086	37.352	.433
	8	0	4	13.873	14.354	-14.353	-.082	-.481
	9	0	4	22.186	21.750	-1.764	21.678	.436
	10	0	4	62.285	62.376	62.373	.570	-.091
	11	0	4	32.017	32.530	-1.957	32.471	-.513
	11	1	4	26.314	24.950	24.897	1.617	1.364
	10	1	4	10.785	9.039	1.728	-8.872	1.746

9	1	4	38.784	39.268	39.225	1.852	-.484
8	1	4	51.373	50.594	2.145	-50.548	.780
7	1	4	38.978	38.162	38.114	1.930	.815
6	1	4	13.909	12.216	1.929	-12.063	1.693
5	1	4	68.470	67.814	67.781	2.121	.656
4	1	4	91.109	91.021	2.333	-90.991	.088
3	1	4	66.771	67.034	67.000	2.136	-.263
2	1	4	10.115	9.682	2.025	-9.468	.432
1	1	4	97.788	98.755	98.730	2.222	-.967
2	2	4	66.723	68.248	68.247	-.219	-1.525
3	2	4	104.384	103.904	-2.499	103.874	.480
4	2	4	8.219	7.557	-7.555	.179	.662
5	2	4	41.259	41.224	-1.954	41.177	.035
6	2	4	40.011	39.837	39.836	.322	.173
7	2	4	30.459	29.816	-1.979	29.751	.642
9	2	4	32.324	33.060	-2.117	32.992	-.736
10	2	4	10.582	11.073	-11.070	-.262	-.491
11	3	4	30.678	31.064	31.019	1.684	-.386
10	3	4	40.881	41.672	2.106	-41.619	-.791
9	3	4	26.842	27.324	27.270	1.728	-.483
7	3	4	50.762	51.933	51.895	1.996	-1.171
6	3	4	65.975	65.671	2.336	-65.629	.304
5	3	4	35.657	35.552	35.498	1.961	.105
4	3	4	9.029	7.951	1.836	-7.73	1.079
3	3	4	84.509	83.888	83.259	2.194	.621
4	4	4	53.903	53.717	53.715	.473	.185
5	4	4	36.804	37.930	-2.208	37.865	-1.126
6	4	4	30.331	30.771	-30.768	-.456	-.440
7	4	4	37.512	37.452	-2.082	37.394	.059
8	4	4	45.723	45.402	45.400	.508	.321
9	4	4	15.503	15.654	-1.654	15.567	-.152
11	4	4	33.678	34.489	-1.975	34.433	-.811
10	5	4	19.691	21.376	1.675	-21.310	-1.685
9	5	4	34.493	35.592	35.549	1.744	-1.099
8	5	4	26.791	26.591	2.024	-26.514	.200
7	5	4	26.695	26.939	26.879	1.802	-.244
6	5	4	31.414	31.716	1.895	-31.659	-.302
5	5	4	60.071	61.668	61.633	2.053	-1.596
6	6	4	59.909	60.337	60.331	.831	-.428
7	6	4	18.784	19.119	-1.817	19.032	-.334
8	6	4	30.619	31.418	-31.412	-.616	-.799
9	6	4	30.603	31.725	-2.073	31.657	-1.122
10	6	4	13.542	14.047	14.045	.244	-.505
9	7	4	26.914	28.004	27.954	1.673	-1.090
8	7	4	26.843	27.800	1.929	-27.733	-.957
7	7	4	33.944	34.977	34.933	1.744	-1.033
8	8	4	41.616	42.765	42.762	.545	-1.149
4	10	4	9.536	10.636	10.636	-.035	-1.099
2	11	5	14.806	13.558	.326	-13.555	1.247
1	11	5	11.809	12.015	-12.015	-.038	-.206

1	10	5	41.261	40.924	.556	-40.920	.338
3	10	5	33.886	34.015	-.479	34.012	-.129
5	10	5	23.875	24.646	.383	-24.643	-.771
4	9	5	40.211	40.667	.480	-40.665	-.456
3	9	5	15.809	15.116	15.116	.063	.693
2	9	5	18.827	20.335	-.371	20.332	-1.508
1	8	5	37.195	37.011	-.425	37.008	.184
3	8	5	27.889	28.628	.356	-28.626	-.738
5	8	5	18.308	17.694	-.270	17.692	.615
7	8	5	12.736	11.975	.235	-11.973	.761
6	7	5	9.349	8.823	.143	-8.822	.526
4	7	5	51.764	51.312	-.527	51.310	.451
3	7	5	24.229	23.182	-23.182	-.093	1.047
2	7	5	26.290	25.080	.399	-25.077	1.210
1	6	5	14.984	15.884	-.003	-15.884	-.899
3	6	5	7.879	6.135	.058	6.134	1.744
9	6	5	9.767	8.556	-.117	8.555	1.211
4	5	5	59.101	59.705	.533	-59.703	-.604
3	5	5	36.548	35.680	35.680	.100	.868
2	5	5	23.796	24.562	-.405	24.558	-.766
1	4	5	58.052	58.155	.469	-58.153	-.103
3	4	5	60.578	60.554	-.500	60.552	.023
2	3	5	12.637	12.493	.389	-12.487	.143
1	3	5	64.624	64.098	-64.098	-.060	.525
0	0	6	24.729	31.023	-31.020	-.458	-6.295
1	0	6	75.350	77.852	-.562	77.850	-2.502
2	0	6	32.167	32.094	-32.047	-1.752	.072
3	0	6	16.623	17.184	.006	-17.184	-.561
5	0	6	36.873	36.910	-.587	36.905	-.037
6	0	6	17.747	16.882	16.845	-1.102	.865
8	0	6	13.736	14.178	-14.136	-1.086	-.442
9	0	6	21.599	20.932	-.032	-20.932	.666
10	0	6	36.890	37.440	-37.408	-1.548	-.550
11	1	6	42.148	42.039	41.948	2.758	.109
10	1	6	13.646	12.473	.124	12.472	1.173
9	1	6	48.592	47.672	47.580	2.947	.920
8	1	6	27.352	26.305	.482	-26.301	1.047
7	1	6	67.762	67.005	66.928	3.211	.758
6	1	6	24.191	24.260	.135	24.260	-.069
5	1	6	75.441	74.334	74.259	3.319	1.107
4	1	6	50.754	50.685	.535	-50.682	.069
3	1	6	110.245	110.176	110.120	3.494	.069
2	1	6	49.176	49.230	.126	49.230	-.054
1	1	6	113.584	117.761	117.708	3.518	-4.177
2	2	6	28.056	28.260	28.251	-.731	-.204
3	2	6	30.970	31.255	-.665	31.248	-.286
4	2	6	34.984	35.281	-35.258	-1.267	-.297
5	2	6	19.427	19.008	-.088	-19.008	.419
6	2	6	32.174	31.861	-31.833	-1.341	.313
9	2	6	31.923	31.465	-.588	31.459	.458

10	2	6	26.128	25.462	25.449	-.805	.666
11	3	6	35.643	35.875	35.778	2.629	-.232
10	3	6	16.333	16.516	.556	-16.506	-.183
9	3	6	52.129	53.833	53.751	2.976	-1.705
8	3	6	12.451	11.521	.029	11.521	.930
7	3	6	48.687	48.354	48.256	3.062	.334
6	3	6	24.723	24.236	.601	-24.229	.487
5	3	6	90.193	88.829	88.765	3.371	1.364
4	3	6	15.632	16.355	.021	16.355	-.723
3	3	6	73.984	73.964	73.889	3.342	.020
4	4	6	8.105	7.618	-7.490	-1.391	.487
5	4	6	26.745	26.954	-.527	26.949	-.209
6	4	6	31.577	31.369	31.363	-.647	.208
8	4	6	29.100	28.696	-28.656	-1.507	.404
9	4	6	21.357	22.426	.034	-22.426	-1.070
10	4	6	21.774	22.322	-22.294	-1.119	-.548
9	5	6	39.224	39.595	39.496	2.801	-.372
8	5	6	16.282	16.497	.468	-16.490	-.215
7	5	6	62.151	62.111	62.035	3.074	.040
6	5	6	9.609	10.468	.131	10.468	-.859
5	5	6	47.673	47.866	47.765	3.103	-.194
6	6	6	73.688	73.705	-73.680	-1.898	-.017
8	6	6	43.380	43.001	42.998	-.491	.379
9	6	6	27.927	28.445	-.624	28.438	-.518
9	7	6	38.110	39.189	39.099	2.641	-1.078
7	7	6	39.510	41.304	41.204	2.874	-1.794
4	7	6	7.814	7.234	.392	-7.223	.580
8	8	6	41.524	42.684	-42.654	-1.607	-1.161
3	11	7	10.484	8.004	-8.001	-.204	2.480
1	11	7	15.840	15.851	-15.850	-.142	-.011
1	10	7	9.895	8.722	-.123	8.721	1.174
5	9	7	13.241	13.516	-13.514	-.206	-.274
3	9	7	14.967	15.580	-15.578	-.194	-.613
1	9	7	48.722	48.186	48.183	.574	.536
1	8	7	25.413	24.836	.149	-24.835	.578
3	8	7	19.755	19.395	-.124	19.395	.359
5	8	7	15.845	14.699	.098	-14.699	1.146
6	7	7	13.794	13.500	-.071	13.500	.294
5	7	7	20.767	21.659	21.659	.003	-.892
3	7	7	17.694	16.333	16.327	.433	1.361
1	7	7	58.255	57.804	-57.798	-.839	.451
3	6	7	7.684	7.485	-.034	7.485	.199
5	6	7	10.924	10.118	.054	-10.118	.806
9	6	7	12.473	11.025	.059	-11.025	1.448
3	5	7	52.525	54.514	-54.512	-.464	-1.989
1	5	7	109.821	111.760	111.757	.890	-1.940
1	4	7	16.139	14.732	-.054	-14.732	1.408
4	3	7	7.310	5.474	.072	5.474	1.835
1	3	7	62.479	62.645	-62.644	-.429	-.166
1	2	7	8.923	7.607	.071	7.606	1.317

7	2	7	10.145	7.374	-.094	7.374	2.770
0	0	8	129.069	126.448	126.448	.158	2.621
1	0	8	97.686	101.151	2.009	-101.131	-3.465
2	0	8	49.274	48.300	-48.294	-.718	.975
3	0	8	25.651	25.007	1.189	24.978	.645
4	0	8	59.241	59.161	59.161	-.165	.080
5	0	8	50.979	51.275	1.977	-51.237	-.296
7	0	8	30.092	29.003	1.658	-28.956	1.089
8	0	8	9.585	5.201	-5.186	-.396	4.383
10	0	8	21.679	20.482	-20.471	-.670	1.197
11	0	8	31.702	31.606	1.644	-31.563	.096
11	1	8	33.572	32.451	32.387	2.035	1.121
9	1	8	38.982	38.383	38.320	2.201	.599
8	1	8	46.702	46.343	-1.781	46.309	.359
7	1	8	45.851	46.744	46.684	2.383	-.894
5	1	8	61.330	61.165	61.114	2.505	.165
4	1	8	74.145	75.757	-1.941	75.732	-1.612
3	1	8	69.202	70.893	70.845	2.607	-1.691
2	1	8	10.404	10.186	-1.451	-10.083	.217
1	1	8	82.607	85.576	85.535	2.650	-2.969
2	2	8	16.019	14.972	14.971	-.154	1.047
3	2	8	95.995	97.386	2.203	-97.361	-1.390
4	2	8	10.749	11.034	-11.025	-.439	-.285
5	2	8	12.311	11.912	1.359	-11.835	.398
6	2	8	16.471	15.519	-15.511	-.507	.952
7	2	8	18.728	19.223	1.501	-19.164	-.495
8	2	8	27.790	27.923	27.921	-.305	-.133
9	2	8	36.683	37.092	1.838	-37.047	-.410
10	2	8	16.377	15.150	15.147	-.281	1.227
10	3	8	43.633	42.543	-1.845	42.503	1.090
9	3	8	34.403	33.894	33.824	2.176	.509
8	3	8	11.698	10.693	-1.118	-10.635	1.004
7	3	8	49.615	50.144	50.090	2.333	-.529
6	3	8	65.978	65.461	-2.039	65.430	.517
5	3	8	46.863	47.632	47.568	2.468	-.769
4	3	8	17.758	18.429	-1.197	-18.390	-.671
3	3	8	74.037	74.167	74.123	2.555	-.130
4	4	8	25.042	23.996	23.992	-.453	1.046
5	4	8	38.408	39.476	1.862	-39.432	-1.058
6	4	8	18.235	17.227	17.226	-.159	1.008
7	4	8	31.261	31.578	1.694	-31.532	-.316
8	4	8	15.024	13.719	-13.704	-.630	1.306
10	4	8	11.478	13.162	-13.154	-.462	-1.684
9	5	8	34.896	36.695	36.635	2.100	-1.799
8	5	8	26.854	27.341	-1.698	27.289	-.488
7	5	8	35.086	35.343	35.271	2.244	-.256
6	5	8	14.369	14.095	-1.357	14.030	.274
5	5	8	52.690	53.447	53.394	2.375	-.758
6	6	8	27.931	27.618	-27.606	-.795	.313
7	6	8	11.737	9.934	1.332	-9.845	1.803



8	6	8	32.879	32.789	32.789	-.078	.090
9	6	8	35.022	36.278	1.845	-36.231	-1.256
8	7	8	23.043	23.867	-1.578	23.815	-.824
7	7	8	40.485	40.805	40.748	2.159	-.320
1	10	9	27.738	28.746	-.451	28.742	-1.008
3	10	9	24.418	25.335	.394	-25.332	-.917
4	9	9	29.777	29.054	-.390	29.052	.723
1	9	9	14.091	15.177	-15.175	-.253	-1.086
1	8	9	20.392	19.523	.323	-19.520	.869
3	8	9	17.655	17.478	-.280	17.476	.177
5	8	9	15.178	15.062	.230	-15.060	.115
7	8	9	14.204	14.415	-.215	14.414	-.211
5	7	9	15.156	14.971	14.971	.083	.185
4	7	9	40.106	40.167	.441	-40.164	-.061
3	7	9	23.268	22.724	-22.722	-.259	.545
2	7	9	10.230	10.711	-.306	10.706	-.430
1	7	9	45.549	44.415	44.413	.464	1.133
1	6	9	14.231	13.815	.071	-13.815	.416
2	6	9	7.000	1.618	1.618	.021	5.382
3	6	9	12.779	12.536	-.098	12.535	.243
5	6	9	10.005	10.188	.123	-10.187	-.183
4	5	9	53.371	54.173	-.470	54.171	-.802
2	5	9	14.674	14.777	.324	-14.773	-.103
1	5	9	30.890	31.073	-31.070	-.392	-.182
1	4	9	76.963	77.903	-.463	77.901	-.940
3	4	9	66.960	67.992	.471	-67.990	-1.031
2	3	9	16.030	16.823	-.327	16.819	-.793
1	3	9	32.461	32.682	32.682	.221	-.221
1	2	9	16.635	17.389	.325	-17.386	-.754
0	0	10	75.117	77.891	-77.888	.671	-2.774
1	0	10	89.688	92.137	2.204	-92.110	-2.449
2	0	10	148.982	152.913	152.892	2.536	-3.931
3	0	10	39.756	40.827	2.022	-40.777	-1.071
5	0	10	30.367	29.839	2.044	-29.769	.528
6	0	10	29.096	30.174	30.133	1.566	-1.078
7	0	10	23.574	23.313	1.929	-23.233	.261
8	0	10	30.659	30.344	30.313	1.373	.315
9	0	10	22.311	22.745	1.800	-22.673	-.433
10	0	10	51.678	52.234	52.202	1.837	-.557
9	1	10	11.636	13.089	13.084	.356	-1.453
8	1	10	44.021	43.506	-1.967	43.462	.515
7	1	10	15.979	16.458	16.454	.375	-.479
5	1	10	17.699	18.037	18.031	.463	-.338
4	1	10	69.930	69.595	-2.141	69.562	.335
3	1	10	23.845	24.150	24.145	.463	-.305
2	1	10	7.547	6.079	-1.997	5.741	1.468
1	1	10	24.617	24.986	24.981	.504	-.369
2	2	10	24.869	24.259	-24.234	1.103	.609
3	2	10	40.388	41.031	2.116	-40.977	-.644
4	2	10	63.104	63.177	63.153	1.761	-.073

5	2	10	41.642	41.616	1.994	-41.568	.026
6	2	10	55.412	56.249	56.221	1.777	-.837
7	2	10	31.380	31.328	1.931	-31.269	.052
8	2	10	17.979	17.079	17.026	1.357	.900
9	2	10	26.906	26.656	1.873	-26.590	.250
10	3	10	23.289	23.209	-1.802	23.139	.080
9	3	10	10.749	11.628	11.624	.277	-.879
8	3	10	21.722	23.041	-1.815	22.970	-1.319
7	3	10	13.065	13.900	13.894	.418	-.835
6	3	10	30.474	31.016	-2.001	30.951	-.542
5	3	10	19.375	19.506	19.503	.380	-.132
4	3	10	34.766	33.945	-1.971	33.887	.822
3	3	10	18.849	19.225	19.218	.503	-.376
4	4	10	55.178	55.397	55.364	1.923	-.219
5	4	10	24.560	24.687	1.980	-24.608	-.127
6	4	10	15.733	15.344	-15.319	.882	.389
7	4	10	23.425	22.936	1.889	-22.858	.489
8	4	10	58.922	59.101	59.070	1.897	-.179
9	4	10	19.088	19.826	1.739	-19.749	-.738
10	4	10	23.331	24.641	24.610	1.232	-1.310
9	5	10	12.236	8.854	8.849	.294	3.382
8	5	10	17.069	18.222	-1.822	18.131	-1.153
7	5	10	17.142	17.578	17.575	.338	-.436
6	5	10	33.305	33.030	-1.896	32.976	.275
5	5	10	11.596	12.516	12.509	.431	-.921
1	6	10	8.824	9.166	1.897	-8.968	-.342
6	6	10	93.169	93.800	93.771	2.340	-.631
7	6	10	24.516	24.886	1.817	-24.820	-.371
8	6	10	22.259	22.745	-22.737	.598	-.486
9	6	10	24.469	23.389	1.784	-23.321	1.080
8	7	10	16.581	18.825	-1.746	18.744	-2.244
1	10	11	12.447	13.777	.331	-13.773	-1.330
3	9	11	11.760	11.644	11.643	.141	.115
2	9	11	21.763	20.829	-.281	20.827	.934
1	9	11	31.625	31.364	-31.361	-.394	.261
1	8	11	13.770	14.054	-.261	14.051	-.283
3	8	11	10.056	11.031	.219	-11.029	-.975
7	8	11	12.646	8.793	.164	-8.792	3.853
5	7	11	18.521	18.999	-18.999	-.019	-.477
4	7	11	15.123	15.004	-.301	15.001	.119
2	7	11	29.996	29.458	.315	-29.456	.539
1	7	11	30.170	29.433	29.428	.547	.737
1	6	11	13.396	12.513	-.060	12.513	.883
3	6	11	12.044	12.311	.084	-12.310	-.267
5	6	11	9.496	8.057	-.098	8.057	1.438
8	5	11	11.362	10.560	-.182	10.558	.802
4	5	11	20.798	20.520	.317	-20.518	.278
3	5	11	33.029	34.536	34.535	.319	-1.507
2	5	11	38.862	38.588	-.334	38.586	.275
1	5	11	64.987	66.055	-66.053	-.600	-1.068

1	4	11	28.421	29.471	.306	-29.469	-1.050
3	4	11	27.327	27.179	-.317	27.177	.147
9	4	11	12.212	8.002	.258	-7.998	4.210
2	3	11	49.526	49.351	.343	-49.350	.175
1	3	11	33.280	32.725	32.724	.283	.555
1	2	11	54.950	55.885	-.342	55.884	-.935
0	0	12	110.094	110.276	110.228	3.265	-.182
1	0	12	14.728	15.907	.342	15.903	-1.149
2	0	12	32.846	33.513	33.391	2.859	-.667
3	0	12	55.306	55.725	1.085	-55.714	-.418
4	0	12	55.237	55.292	55.212	2.977	-.055
5	0	12	21.696	21.437	.216	21.436	.259
6	0	12	46.192	46.045	45.959	2.813	.146
8	0	12	56.390	55.394	55.327	2.724	.995
9	0	12	29.575	29.742	.859	-29.729	-.167
10	0	12	49.345	48.895	48.834	2.448	.451
10	1	12	17.089	17.075	-.691	17.061	.014
6	1	12	26.606	26.173	-.767	26.161	.433
4	1	12	11.968	12.363	-.347	-12.358	-.395
3	1	12	8.849	7.492	-7.435	-.921	1.358
2	1	12	36.318	37.569	-.828	37.560	-1.250
2	2	12	104.916	107.406	107.359	3.169	-2.490
3	2	12	32.362	32.706	.090	32.706	-.344
4	2	12	64.041	64.118	64.051	2.936	-.077
5	2	12	38.162	37.652	.893	-37.641	.510
6	2	12	60.371	60.143	60.077	2.810	.228
7	2	12	11.085	11.252	.622	-11.235	-.167
8	2	12	32.194	31.564	31.456	2.610	.629
9	2	12	17.468	17.119	.143	17.118	.349
10	2	12	22.814	24.677	24.556	2.446	-1.863
8	3	12	30.035	30.202	-.921	30.188	-.166
6	3	12	22.370	20.887	-.132	-20.887	1.482
5	3	12	10.895	8.783	-8.734	-.919	2.113
4	3	12	45.542	45.068	-1.017	45.057	.473
4	4	12	21.069	21.237	21.063	2.713	-.167
5	4	12	14.403	13.935	.271	13.933	.467
6	4	12	63.318	62.745	62.679	2.867	.573
8	4	12	34.735	34.156	34.065	2.494	.579
9	4	12	32.470	31.987	.929	-31.973	.483
6	5	12	24.132	23.771	-.774	23.758	.360
6	6	12	44.189	42.425	42.350	2.513	1.764
7	6	12	15.097	15.450	.681	-15.435	-.352
8	6	12	30.014	30.309	30.203	2.531	-.295
5	7	12	12.329	9.036	-8.989	-.918	3.293
1	7	12	8.277	5.741	-5.668	-.913	2.536
5	8	12	9.493	8.020	.270	8.016	1.472
1	10	13	14.681	15.375	.230	-15.373	-.694
4	9	13	20.395	19.103	.216	-19.102	1.292
1	9	13	17.705	17.035	17.030	.406	.669
1	8	13	13.016	12.415	-.169	12.414	.601

3	8	13	9.686	9.014	.140	-9.012	.672
5	7	13	22.738	20.542	-20.542	-.131	2.196
4	7	13	22.865	21.929	-.232	21.928	.936
3	7	13	44.285	43.771	43.768	.470	.514
2	7	13	8.607	5.218	.152	-5.216	3.389
1	7	13	59.725	59.009	-59.004	-.757	.716
1	6	13	13.155	13.062	.021	-13.062	.093
3	6	13	8.464	8.595	.004	8.595	-.131
4	5	13	22.964	23.310	.231	-23.309	-.346
3	5	13	24.175	24.747	-24.744	-.348	-.572
1	5	13	41.341	42.262	42.257	.647	-.921
1	4	13	19.244	20.221	.200	-20.220	-.978
3	4	13	21.712	22.071	-.215	22.070	-.359
1	3	13	17.716	18.324	-18.322	-.304	-.608
0	0	14	148.846	149.252	149.214	3.390	-.406
1	0	14	36.628	35.079	-1.217	35.058	1.549
3	0	14	43.201	43.574	-1.478	43.549	-.373
4	0	14	68.639	70.406	70.355	2.669	-1.767
6	0	14	30.068	29.330	29.243	2.255	.738
7	0	14	9.855	8.609	-1.119	8.536	1.246
8	0	14	54.868	53.770	53.720	2.308	1.098
9	0	14	20.541	20.678	-1.243	20.641	-.137
8	1	14	21.912	20.943	1.094	-20.915	.969
6	1	14	9.988	8.901	1.233	-8.815	1.088
4	1	14	30.424	29.354	1.189	-29.330	1.070
3	1	14	8.277	6.808	6.794	-.433	1.470
2	1	14	9.172	10.165	1.306	-10.081	-.993
2	2	14	75.442	76.276	76.222	2.881	-.835
4	2	14	55.236	53.766	53.715	2.348	1.470
5	2	14	35.353	34.769	-1.365	34.742	.584
6	2	14	30.556	29.528	29.452	2.114	1.028
7	2	14	22.324	21.628	-1.214	21.594	.695
8	2	14	37.724	37.430	37.365	2.200	.295
8	3	14	25.225	25.500	1.298	-25.467	-.275
5	3	14	14.415	12.665	12.659	-.397	1.750
4	3	14	36.423	36.253	1.419	-36.225	.170
3	3	14	9.210	6.499	-6.478	-.526	2.711
6	4	14	76.211	73.564	73.512	2.751	2.647
8	4	14	11.272	9.805	9.660	1.679	1.467
6	5	14	26.666	25.801	1.259	-25.770	.865
5	5	14	11.036	6.993	-6.971	-.548	4.043
7	6	14	22.012	21.145	-1.191	21.112	.867
2	9	14	9.227	6.808	.952	-6.741	2.419
2	9	15	27.236	26.519	.363	-26.517	.717
1	9	15	10.357	8.025	8.024	.106	2.332
1	8	15	22.937	22.065	.350	-22.062	.872
3	8	15	15.907	15.630	-.287	15.627	.277