

The crystal structure of CaGeO_3 perovskite and the crystal chemistry of the GdFeO_3 -type perovskites

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Abstract

A single-crystal X-ray study indicates that the perovskite form of CaGeO_3 is orthorhombic ($Pbnm$), and isotypic with GdFeO_3 , although it was previously reported as a cubic form; the cell dimensions are $a = 5.2607(6)\text{\AA}$, $b = 5.2688(10)$, $c = 7.4452(15)$ and $V = 206.36(6)\text{\AA}^3$ ($Z = 4$; $D_{\text{calc}} = 5.17 \text{ g/cm}^3$). The crystal structure is close to that of SmAlO_3 . Although the unit cell of CaGeO_3 is pseudocubic, the structure itself is very distorted through the tilting and distortion of polyhedra. The oxygen polyhedra are less tilted and less distorted than those of other GdFeO_3 -type perovskites. The structural deformation of the GdFeO_3 -type perovskite is determined primarily by the size-ratio of two kinds of cation occupying A and B sites. Some structural characteristics such as O(2)-O(2)-O(2) and A-O(1)-B angles and bond-length distortions exhibit systematic relationships as a function of the observed tolerance factor which is newly defined here. A strong correlation between the Goldschmidt tolerance factor and the observed tolerance factor has made possible some predictions for GdFeO_3 -type perovskites.

Introduction

The perovskite structure, with general formula ABO_3 , consists of a framework of B octahedra that share corners with each other and triangular faces with cubooctahedra containing A cations in twelve coordination. For compositions in which their constituent atoms are not of the ideal relative size, many distorted types of perovskite may replace the ideal structure. Some metasilicates and metagermanates are known to crystallize as perovskites in cubic (SrGeO_3 ; above 50 kbar), hexagonal (BaGeO_3 ; above 95 kbar), and orthorhombic phases (MgSiO_3 ; above 300 kbar) (Shimizu *et al.*, 1970; Liu, 1976a; Yagi *et al.*, 1978; Ito and Matsui, 1978). The high-pressure transformation of a metasilicate to a perovskite form is geophysically important for interpreting seismic wave velocities in the Earth's lower mantle. Also, germanates are useful as structural analogs of common silicate minerals at high pressures because new dense phases frequently exist at much lower pressures than the corresponding isotypic silicates.

CaGeO_3 is a typical example of such germanates and is known to transform from the wollastonite through a garnet-like structure to the perovskite structure at more than 65 kbar and 900°C (Susaki and Akimoto, private comm.). CaGeO_3 has previously been indexed as cubic perovskite with $a = 3.723\text{\AA}$ (Ringwood and Major, 1967), although Prewitt and Sleight (1969) reported a doubling of the unit cell ($a = 7.448\text{\AA}$). In order to confirm the cell dimension and the space group of CaGeO_3 perovskite, we

examined a single crystal using X-ray diffraction techniques, to refine its crystal structure, and to make a systematic study of crystallographic correlations among the GdFeO_3 -type perovskites. A preliminary communication on this result has been reported (Sasaki *et al.*, 1981).

Experimental

Sample

A polycrystalline specimen of CaGeO_3 perovskite was synthesized by hot-pressing CaGeO_3 wollastonite powder in squeezer solid-media apparatus for two hours at $P = 100$ kbar and at $T = 1000^\circ\text{C}$ (see details in Liebermann *et al.*, 1977). After sintering at elevated pressure and temperature, the run was slowly cooled (20–60 minutes) to room temperature after which the pressure was released. Examination of the recovered specimen using a polarizing microscope and X-ray powder diffraction analyses confirmed that it was a single phase with the perovskite structure. A single crystal of parallelepiped shape and dimensions, $0.14 \times 0.10 \times 0.07 \text{ mm}$ was extracted from the polycrystalline aggregate and prepared for single-crystal X-ray diffraction study.

Space group determination

The unit cell and space group of CaGeO_3 perovskite were determined with the aid of precession and Weissenberg photographs and intensity data collected with a Picker four-circle diffractometer. The space group deter-

Table 5

$2\theta_{\text{calc}}$	$2\theta_{\text{peak}}$	d	<u>h</u> <u>k</u> <u>l</u>	I_c	I_p	Mark
23.90	23.90	3.7231	1 1 0	19	28	
23.90		3.7231	0 0 2	9		
34.04	34.04	2.6337	0 2 0	17	100	
34.06		2.6322	1 1 2	67		
34.08		2.6307	2 0 0	16		
40.18	40.18	2.2443	1 0 3	1	2	***
40.18		2.2443	2 1 1	1		***
48.94	48.94	1.8611	2 2 0	25	38	
48.94		1.8611	0 0 4	13		
55.14	55.16	1.6656	1 3 0	3	13	
55.16		1.6651	2 2 2	4		
55.16		1.6651	1 1 4	4		
55.20		1.6639	3 1 0	2		
56.62	56.62	1.6255	1 3 1	1	1	***
60.92	60.96	1.5207	1 3 2	11	39	
60.94		1.5203	0 2 4	7		
60.98		1.5194	2 0 4	7		
61.00		1.5189	3 1 2	14		
71.64	71.70	1.3172	0 4 0	3	18	
71.70		1.3163	2 2 4	12		
71.76		1.3153	4 0 0	3		
76.76	76.81	1.2416	0 4 2	1	5	
76.78		1.2414	1 3 4	2		
76.84		1.2405	3 1 4	1		
76.88		1.2400	4 0 2	1		
81.76	81.82	1.1779	2 4 0	2	13	
81.82		1.1772	3 3 2	4		
81.82		1.1772	1 1 6	5		
81.86		1.1767	4 2 0	2		
91.62	91.68	1.0751	0 4 4	3	6	
91.74		1.0740	4 0 4	3		
96.60	96.60	1.0325	3 3 4	1	2	
96.60		1.0325	2 2 6	1		
101.48	101.59	0.9956	1 5 2	3	20	
101.54		0.9952	2 4 4	3		
101.54		0.9952	1 3 6	3		
101.62		0.9946	3 1 6	4		
101.62		0.9946	4 2 4	3		
101.68		0.9942	5 1 2	4		
111.86	111.86	0.9306	4 4 0	2	3	
111.86		0.9306	0 0 8	1		

Table 5 (Continued)

117.16	117.22	0.9034	1 5 4	1	4
117.18		0.9033	3 5 0	1	
117.26		0.9029	4 4 2	1	
117.26		0.9029	1 1 8	1	
122.78	122.95	0.8781	0 6 0	1	16
122.86		0.8778	3 5 2	3	
122.92		0.8775	0 2 8	2	
122.94		0.8775	3 3 6	3	
122.96		0.8774	2 0 8	2	
123.02		0.8771	5 3 2	4	
123.10		0.8768	6 0 0	1	
135.50	135.67	0.8329	2 6 0	2	13
135.66		0.8324	4 4 4	4	
135.68		0.8324	2 2 8	5	
135.84		0.8319	6 2 0	2	
143.02	143.21	0.8129	2 6 2	1	7
143.12		0.8126	3 5 4	2	
143.18		0.8125	1 3 8	1	
143.28		0.8122	3 1 8	1	
143.34		0.8121	5 3 4	1	
143.44		0.8119	6 2 2	1	
152.18	152.52	0.7942	0 6 4	3	17
152.28		0.7940	1 5 6	4	
152.68		0.7933	5 1 6	7	
152.78		0.7932	6 0 4	3	
155.16	155.21	0.7894	2 4 7	1	2 ***
155.26		0.7892	4 4 5	1	***
173.20	173.76	0.7726	3 5 5	2	4 ***
174.32		0.7718	5 3 5	2	***

*** CAGEO3 PEROVSKITE; STRUCTURE FACTOR TABLES: 412 REFLECTIONS

* * < 1 >

H	K	L	F(OBS)	F(CALC)	SIGF	H	K	L	F(OBS)	F(CALC)	SIGF	H	K	L	F(OBS)	F(CALC)	SIGF		
2	0	0	152.79	143.33	2.67	5	5	0	18.44	20.48	.44	2	3	1	8.90	9.45	.24		
4	0	0	135.74	129.83	2.54	7	5	0	26.18	27.22	.62	3	3	1	16.45	16.60	.31		
6	0	0	74.30	72.48	1.50	8	5	0	6.83	7.66	.43	4	3	1	13.59	13.11	.33		
8	0	0	52.02	51.58	.97	9	6	0	61.61	67.31	1.32	5	3	1	14.53	15.11	.31		
1	1	0	77.12	78.48	1.40	1	6	0	11.07	11.12	.31	6	3	1	6.94	6.51	.36		
2	1	1	18.75	16.81	.31	2	6	0	71.70	70.24	1.48	7	3	1	7.93	8.08	.32		
3	1	0	56.49	52.17	1.07	3	6	0	13.17	12.78	.32	9	3	1	8.64	8.10	.37		
4	1	0	17.15	17.16	.32	4	6	0	50.09	50.93	1.06	0	4	1	25.33	25.06	.43		
5	1	0	27.57	27.69	.59	6	6	0	41.79	42.59	.91	1	4	1	3.90	.52	.24		
6	1	0	11.86	11.87	.29	4	7	0	45.75	44.20	.89	2	4	1	16.36	17.37	.31		
7	1	0	20.61	19.99	.51	3	7	0	28.52	29.57	.60	3	4	1	6.22	7.48	.30		
8	1	0	10.51	10.38	.33	5	7	0	33.42	35.15	.73	4	4	1	18.66	18.93	.36		
9	1	0	12.48	10.95	.36	0	8	0	41.39	43.07	.78	5	4	1	4.17	2.44	.44		
0	2	0	149.26	145.17	2.83	1	8	0	11.40	10.57	.37	6	4	1	14.03	14.31	.33		
1	2	0	16.51	14.58	.28	2	8	0	44.46	41.78	.98	8	4	1	10.52	11.25	.36		
2	2	0	180.10	179.96	3.34	3	8	0	5.24	4.06	.48	1	5	1	22.51	24.37	.40		
3	2	0	11.72	11.26	.24	4	8	0	33.65	34.93	.81	2	5	1	7.37	6.87	.30		
4	2	0	92.88	90.96	1.79	5	8	0	7.51	7.52	.43	3	5	1	21.12	21.63	.41		
5	2	0	73.38	73.99	1.50	1	9	0	33.31	33.23	.68	4	5	1	5.47	5.24	.40		
6	2	0	50.24	50.82	1.07	3	9	0	35.21	35.32	.78	5	5	1	14.89	15.75	.34		
7	2	0	65.17	65.83	1.26	4	9	0	1.26	2.86	.75	1	9	6	5	1	6.96	6.79	.40
8	2	0	8.79	9.03	.21	3	0	1	16.81	15.56	.32	7	5	1	12.87	13.09	.36		
9	2	0	39.00	39.19	.76	9	0	1	6.20	5.64	.44	0	6	1	17.82	17.28	.35		
0	3	0	9.08	9.29	.25	1	1	1	9.54	10.58	.17	2	6	1	20.60	21.83	.40		
1	3	0	36.94	38.02	.77	2	1	1	20.71	19.49	.39	3	6	1	4.72	3.87	.48		
2	3	0	11.17	11.59	.30	3	1	1	12.01	11.84	.24	4	6	1	17.02	16.84	.37		
3	3	0	10.87	12.94	.39	4	1	1	14.88	14.94	.33	6	6	1	16.12	16.33	.38		
4	3	0	4.64	4.22	.49	5	1	1	4.04	2.33	.33	1	7	1	20.40	21.59	.41		
5	3	0	17.18	17.25	.50	6	1	1	10.12	10.64	.32	3	7	1	18.74	19.27	.41		
6	3	0	123.77	130.79	2.49	7	1	1	6.18	5.85	.34	5	7	1	15.15	15.29	.38		
7	3	0	18.78	17.95	.34	8	1	1	16.14	15.02	.45	0	8	1	19.20	17.91	.41		
8	3	0	92.52	90.15	1.80	9	1	1	13.76	14.73	.23	2	8	1	14.08	14.13	.37		
9	3	0	6.07	6.12	.27	1	2	1	10.87	13.46	.27	4	8	1	16.83	16.22	.40		
0	4	0	83.27	85.40	1.68	2	2	1	16.33	18.32	.29	1	9	1	16.52	16.42	.41		
1	4	0	8.19	8.44	.28	3	2	1	7.66	4.74	.25	3	9	1	14.58	13.89	.42		
2	4	0	52.69	54.13	1.10	4	2	1	10.66	10.56	.25	0	0	2	70.46	69.93	.29		
3	4	0	39.70	41.15	.89	5	2	1	3.58	4.62	.39	2	0	2	8.83	9.06	.20		
4	4	0	50.28	48.45	.93	6	2	1	9.51	9.26	.48	4	0	2	52.24	50.01	.99		
5	4	0	48.69	49.37	.95	7	1	1	7.08	7.14	.37	6	0	2	29.19	28.14	.60		
6	4	0	5.42	5.94	.36	8	0	2	26.02	26.02	.40	0	2	22.10	21.94	.45			

** CAGE03 PEROVSKITE; STRUCTURE FACTOR TABLES: 412 REFLECTIONS

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< 2 >

H	K	L	F(OBS)	F(CALC)	SIGF	H	K	L	F(OBS)	F(CALC)	SIGF	H	K	L	F(OBS)	F(CALC)	SIGF
2	1	2	15.19	13.71	2.23	3	6	2	3.97	4.25	.45	2	4	3	23.68	25.67	.42
3	1	2	118.33	122.47	2.24	4	6	2	29.34	29.47	.63	3	4	3	4.69	.47	.33
4	1	2	13.46	13.80	.27	5	6	2	8.42	8.38	.36	4	4	3	12.40	12.80	.29
5	1	2	92.92	90.46	1.79	6	6	2	29.44	30.20	.66	5	4	3	5.64	5.52	.40
6	1	2	12.17	12.24	.29	7	2	47.16	47.69	1.10	6	4	3	15.06	15.09	.35	
7	1	2	72.39	72.76	1.49	3	7	2	36.75	38.20	.88	8	4	3	11.37	11.91	.37
8	1	2	7.60	7.23	.37	5	7	2	48.37	47.21	1.10	1	5	3	23.69	23.77	.43
9	1	2	49.76	50.80	.97	0	8	2	31.75	29.90	.61	3	5	3	16.71	18.15	.34
0	1	2	12.08	10.84	.24	1	8	2	6.79	7.28	.38	4	5	3	11.88	11.47	.34
1	1	2	14.86	14.43	.25	2	8	8	29.84	30.57	.65	5	5	3	17.95	17.93	.39
2	1	2	55.62	55.82	1.07	3	8	8	10.10	9.54	.36	7	5	3	8.43	9.75	.39
3	1	2	4.16	3.98	.25	4	8	8	30.07	29.54	.67	0	6	6	26.82	26.17	.49
4	1	2	27.13	26.65	.54	5	9	2	28.54	26.34	.58	2	6	6	12.34	12.60	.30
5	1	2	5.17	5.13	.31	3	10	0	30.77	28.54	.54	3	6	6	3.80	5.65	.39
6	1	2	34.14	33.93	.70	4	10	0	3.86	3.36	.26	4	6	6	20.77	21.17	.43
7	1	2	24.01	24.47	.56	5	10	0	7.23	7.19	.31	6	6	6	14.45	14.08	.37
8	1	2	116.91	109.69	2.28	6	11	0	7.80	7.53	.39	7	7	3	21.14	20.78	.42
9	1	2	6.75	7.11	.20	1	11	1	14.59	15.01	.25	2	7	3	6.12	5.42	.48
0	1	2	86.82	88.77	1.76	2	12	1	12.08	12.65	.28	3	7	3	17.73	18.10	.39
1	1	2	9.81	10.51	.25	3	13	1	16.17	15.87	.35	5	7	3	14.58	14.98	.38
2	1	2	86.50	85.60	1.76	4	14	1	12.55	12.35	.29	6	7	3	7.13	6.69	.64
3	1	2	5.87	6.21	.36	5	15	1	8.72	8.02	.33	7	8	3	10.74	10.11	.35
4	1	2	56.01	56.57	1.17	6	16	1	5.10	6.35	.45	8	9	3	19.74	19.76	.43
5	1	2	8.99	9.34	.37	7	17	1	7.26	6.60	.41	4	8	3	11.81	11.48	.39
6	1	2	54.45	49.94	1.03	8	18	1	22.75	23.33	.37	1	9	3	16.52	15.08	.41
7	1	2	11.69	12.05	.24	9	19	1	11.41	10.95	.27	0	0	4	176.20	183.97	.3.25
8	1	2	24.20	26.25	.50	10	20	1	7.41	7.53	.18	2	0	4	114.93	118.97	.2.18
9	1	2	12.10	12.58	.27	11	21	1	15.32	16.13	.32	4	4	4	102.86	105.85	.2.03
0	1	2	41.43	41.51	.82	12	22	1	12.77	13.34	.27	6	0	4	68.03	66.38	1.43
1	1	2	26.50	27.53	.59	13	23	1	7.91	8.04	.30	8	0	4	49.42	47.92	.94
2	1	2	4.54	3.96	.47	14	24	1	5.86	6.13	.45	1	1	4	57.49	56.00	1.08
3	1	2	22.67	23.67	.55	15	25	1	19.08	19.30	.33	2	1	4	7.17	7.39	.18
4	1	2	69.91	69.29	1.46	16	26	1	13.52	12.68	.30	3	1	4	42.13	45.01	.86
5	1	2	71.98	74.20	1.54	17	27	1	20.30	21.84	.37	4	1	4	8.56	9.55	.24
6	1	2	51.40	51.01	1.08	18	28	1	1.8	1.63	.45	1	1	4	26.35	25.58	.55
7	1	2	6.44	6.84	.39	19	29	2	7.20	7.43	.29	6	1	4	7.59	7.05	.32
8	1	2	55.37	55.21	1.21	20	30	3	11.40	11.56	.36	7	1	4	17.50	17.42	.47
9	1	2	32.87	30.56	.64	21	31	4	13.39	13.61	.35	8	1	4	7.25	6.99	.41
0	1	2	12.42	12.67	.29	22	32	5	10.80	10.80	.24	9	1	4	13.25	10.99	.38
1	1	2	37.80	37.72	.72	23	33	6	8.31	9.60	.00	1	4	118.22	119.34	2.22	

** CAGE03 PEROVSKITE; STRUCTURE FACTOR TABLES; 412 REFLECTIONS

** < 3 >

H	K	L	F(OBS)	F(CALC)	SIGF	H	K	L	F(OBS)	F(CALC)	SIGF	H	K	L	F(OBS)	F(CALC)	SIGF	
2	2	2	4	131.15	133.54	2.56	2	1	5	12.78	11.79	.29	4	7	5	9.11	9.12	.56
3	3	2	4	6.35	6.31	.23	3	1	5	14.32	15.20	.28	5	7	5	14.34	13.52	.38
4	4	2	4	78.41	82.53	1.63	4	1	5	9.45	9.21	.29	0	8	5	22.30	21.35	.47
6	6	2	4	67.08	65.90	1.41	5	1	5	5.28	5.22	.35	2	8	5	8.67	7.55	.37
8	8	2	4	47.91	46.79	1.08	6	1	5	10.44	10.69	.36	0	0	6	35.82	35.12	.71
1	1	3	4	56.44	54.89	1.09	7	1	5	11.62	11.29	.34	2	0	6	24.12	23.15	.50
3	3	3	4	4.38	5.04	.25	0	2	5	4.31	3.38	.23	4	0	6	31.56	32.44	.62
4	3	3	4	35.45	37.10	.68	1	2	5	20.59	19.64	.39	6	0	6	24.82	24.40	.56
5	5	3	4	5.17	5.18	.29	2	2	5	16.21	17.25	.30	8	0	6	20.08	20.15	.49
6	6	3	4	30.31	31.31	.68	3	2	5	6.38	5.43	.36	1	1	6	95.25	94.36	1.84
7	7	3	4	7.28	8.10	.38	4	2	5	6.63	6.16	.26	3	1	6	84.66	87.58	1.71
0	0	4	4	14.08	13.70	.40	5	2	5	8.20	7.21	.32	4	1	6	3.42	3.43	.39
1	1	4	4	109.36	106.30	2.14	6	2	5	9.22	8.64	.32	5	1	6	73.09	73.60	1.49
2	2	4	4	10.27	9.74	.24	8	2	5	6.05	6.92	.47	6	1	6	4.54	4.34	.46
4	4	4	4	79.44	81.20	1.66	1	3	5	20.58	20.20	.37	7	1	6	61.30	60.22	1.32
5	5	4	4	73.49	74.42	1.51	2	3	5	4.13	3.39	.41	0	0	6	22.80	22.42	.48
6	6	4	4	6.37	6.35	.34	3	3	5	8.39	8.69	.25	1	2	6	3.61	2.78	.30
7	7	4	4	51.23	50.15	1.11	4	3	5	15.05	14.61	.35	2	2	6	34.90	34.96	.67
8	8	4	4	38.76	38.29	.88	5	3	5	17.42	18.25	.36	4	2	6	24.97	26.06	.55
9	9	4	4	44.29	43.46	.82	6	3	5	6.89	7.54	.51	6	2	6	26.04	26.22	.56
0	0	4	4	39.62	41.54	.80	0	0	4	27.12	27.41	.48	8	2	2	21.10	21.43	.54
1	1	4	4	20.27	21.16	.46	1	4	5	7.02	6.19	.28	1	3	6	80.28	79.60	1.65
2	2	4	4	22.81	23.19	.56	2	4	5	7.62	7.74	.25	3	3	6	70.08	72.27	1.46
3	3	4	4	62.77	60.98	1.35	3	4	5	10.53	10.46	.31	4	3	6	3.81	4.05	.42
4	4	4	4	5.86	6.19	.33	4	4	5	18.83	19.95	.37	5	3	6	65.38	66.03	1.42
5	5	4	4	61.19	62.88	1.31	6	4	5	11.29	11.59	.36	7	3	6	52.87	51.60	1.14
6	6	4	4	8.68	8.90	.32	1	1	5	20.11	19.68	.38	0	0	4	35.01	33.69	.67
7	7	4	4	45.88	47.01	1.03	2	2	5	9.52	8.75	.31	2	2	6	25.48	25.81	.55
8	8	4	4	41.11	39.21	.92	3	5	5	20.26	20.60	.40	3	4	6	5.43	5.03	.32
9	9	4	4	43.41	40.87	.82	5	5	5	10.58	11.40	.33	4	6	6	29.68	30.34	.61
0	0	4	4	27.88	28.95	.58	5	5	5	12.24	11.04	.41	6	4	6	24.02	24.62	.56
1	1	4	4	30.59	30.68	.68	5	5	5	14.37	13.96	.38	3	1	6	56.98	56.86	1.25
2	2	4	4	41.33	39.67	.83	6	6	5	9.02	7.91	.28	3	3	6	54.76	56.75	1.25
3	3	4	4	7.31	7.23	.38	6	4	5	3.67	4.23	.41	5	5	6	46.80	47.32	1.04
4	4	4	4	35.92	38.09	.90	7	6	5	24.46	25.16	.47	0	0	6	27.62	25.68	.59
5	5	4	4	32.72	33.06	.80	8	7	5	11.25	10.96	.33	1	1	6	5.30	4.39	.38
6	6	4	4	32.23	31.60	.68	9	6	5	5.91	4.87	.51	2	2	6	30.16	30.00	.62
7	7	4	4	18.16	17.59	.33	0	0	5	16.56	15.75	.41	4	4	6	25.21	25.78	.58
8	8	4	4	18.84	.38	2.4	1	1	5	18.93	.43	4.48	5	5	6	5.61	4.98	.48
9	9	4	4	1.67	.38	2.4	2	1	5	16.64	.38	2.38	5	5	6	25.73	26.10	.60

** CAGEO3 PEROVSKITE; STRUCTURE FACTOR TABLES; 412 REFLECTIONS

**

	H	K	L	F(OBS)	F(CALC)	SIGF	H	K	L	F(OBS)	F(CALC)	SIGF	H	K	L	F(OBS)	F(CALC)	SIGF
1	3	7	6	34.36	35.53	.86	2	7	7	6.36	6.14	.55						
2	0	8	6	28.93	27.33	.62	3	7	7	15.77	14.99	.39						
3	2	8	6	27.71	25.45	.63	0	8	7	5.58	4.66	.50						
4	3	8	6	4.90	4.93	.58	0	0	8	94.14	92.44	1.86						
5	3	8	6	19.54	19.06	.39	2	0	8	88.44	86.17	1.78						
6	0	0	0	7.23	7.19	.35	4	0	8	68.33	68.98	1.42						
7	0	0	0	6.81	7.37	.36	6	0	8	53.96	52.50	1.20						
8	1	1	1	9.43	9.15	.23	5	1	8	20.19	19.93	.48						
9	1	1	1	6.64	5.88	.32	7	1	7	11.76	11.69	.33						
10	1	1	1	12.69	13.29	.32	5	1	7	12.69	13.29	.32						
11	1	1	1	5.94	5.75	.63	7	1	7	11.76	11.69	.33						
12	1	1	1	6.70	5.56	.44	6	0	6	6.70	5.89	.54						
13	1	1	1	6.06	5.89	.54	15	56	15.68	.30								
14	1	1	1	4.06	3.45	.33	11	80	11.74	.30								
15	1	1	1	14.32	13.86	.34	2	2	7	4.06	3.45	.33						
16	1	1	1	10.81	11.09	.29	14	32	12.36	11.97	.28							
17	1	1	1	7.13	6.19	.37	10	56	10.56	9.38	.31							
18	1	1	1	11.15	11.65	.41	17	46	17.46	18.36	.35							
19	1	1	1	14.06	13.97	.39	11	15	11.15	11.65	.41							
20	1	1	1	10.29	10.01	.32	21	89	10.29	10.01	.32							
21	1	1	1	21.89	22.27	.42	22	27	21.89	22.27	.42							
22	1	1	1	6.54	6.11	.48	6	37	6.54	6.11	.48							
23	1	1	1	12.84	12.81	.37	12	27	12.84	12.81	.37							
24	1	1	1	19.41	18.94	.39	16	44	19.41	18.94	.39							
25	1	1	1	13.35	13.21	.33	24	77	13.35	13.21	.33							
26	1	1	1	7.58	8.36	.32	7	26	7.58	8.36	.32							
27	1	1	1	16.44	16.25	.39	19	85	16.44	16.25	.39							
28	1	1	1	6.07	4.77	.42	19	38	6.07	4.77	.42							
29	1	1	1	17.61	19.38	.44	40	40	17.61	19.38	.44							