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Braunite: its structure and relationship to bixbyite, and some insights on the genealogy of fluorite derivative structures

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Abstract

Braunite, $Mn^{2+}Mn_6^{3+}SiO_{12}$, a = 9.408(16), c = 18.668 (32)Å, tetragonal holosymmetric, space group $I4_1/acd$, Z = 8, is a derivative structure of fluorite with ordered anion vacancies. R = 0.036 (Rw = 0.050) for 511 non-zero reflections.

The structures of cubic and orthorhombic bixbyite (α–Mn_2O_3), braunite, and probably braunite-II ($Mn^{2+}Mn_{14}^{3+}SiO_{24}$), are related according to the space group *Ibca*. The regions in common include sheets of edge- and corner-linked octahedra (the *A* and *A'* sheets of bixbyite). Braunites differ in having *B* sheets in place of the *A'* sheets in bixbyite. The *B* sheets consist of Mn^{2+} in cubic coordination, Mn^{3+} in octahedral coordination, and Si^{4+} in tetrahedral coordination with respect to oxygen.

Average polyhedral distances are $^{8}Mn(1)^{2+}$–O 2.33, $^{6}Mn(2)^{3+}$–O 2.04, $^{6}Mn(3)^{3+}$–O 2.05, $^{6}Mn(4)^{3+}$–O 2.04, and ^{4}Si–O 1.61Å. The $Mn^{3+}O_6$ groups are distorted as a result of Jahn-Teller effects, forming elongate tetragonal bipyramids which are further distorted by shared polyhedral edges.

With help from an enumeration theorem, a cooperative lattice game is proposed which conveniently classifies all structures derived from fluorite.

Introduction

Braunite has been a crystal-chemical enigma since it was first characterized by Haidinger in 1831. Variously interpreted as $(Mn,Si)_2O_3$, $3Mn^{2+}Mn^{4+}O_3 \cdot MnSiO_3$ or $3Mn_2O_3 \cdot MnSiO_3$, the problematical compound has been a center of controversy concerning the role of silica and the oxidation states of the transition metal. Dispute also centered around its crystal class and space group: Aminoff (1931) proposed the space group $I4_1/acd$ and Byström and Mason (1943) proposed $I\bar{4}c2$, the latter study including a crystal structure analysis. In addition, they concluded that the correct formula was $3Mn_2O_3 \cdot MnSiO_3$. Those authors also presented an account of earlier studies on the species.

There the matter stood until de Villiers and Herbstein (1967) investigated braunites from several localities and concluded from single crystal study that the space group was in fact $I4_1/acd$, the group originally proposed by Aminoff. A variant of braunite (braunite-II) was also characterized, which required a doubling of the c axis, a halving of the amount of SiO_2, but a space group which was the same as ordinary braunite. The question then arose as regards the correct crystal structure, the relationship between the two braunites, and their relationship with bixbyite, α–Mn_2O_3. With these facts at hand, we concluded that the braunite problem required further study.

We have also explored more deeply the subtle relation between braunite and bixbyite with the large family of anion-deficient fluorite derivative structures. Perhaps the most intriguing part of this study is not the braunite structure *per se*, but its relationship with other equally complex compounds.

Experimental

A single crystal of braunite was selected from a specimen from St. Marcel, Piedmont, Italy, originally from the collection of George L. English (University of Chicago number 1663). Gorgeu (1893) reported MnO 74.40; O 7.50; Fe_2O_3, Al_2O_3 3.80; CaO 0.50; MgO, K_2O, Na_2O 1.00; PbO, CuO 0.15; CoO 0.30; BaO trace; H_2O 0.20; SiO_2 9.80; P_2O_5 0.05, gangue 2.60 percent for Piedmont material. Accepting the sum of cations = 8 and the sum of O^{2-} = 12, the

BRAUNITE

SHEET NO. 1 PART 1

(1)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FC	FC	H	K	L	FO	FC
14	0	0	39.8	41.9	10	1	7	10.7	15.9	14	2	8	32.2	33.5	3	2	17	23.5	17.9
14	0	2	161.1	165.7	10	1	9	10.9	22.6	14	2	10	73.8	70.5	3	2	19	57.3	61.3
14	0	4	146.1	146.3	10	1	11	170.5	169.4	13	2	1	22.0	21.7	3	2	21	77.7	82.7
14	0	6	28.6	34.9	10	1	13	129.5	123.5	13	2	3	25.5	14.3	3	2	23	20.1	2.6
14	0	8	22.2	32.3	10	1	15	11.3	32.3	13	2	5	25.6	21.8	3	2	25	10.4	0.4
14	0	10	24.4	29.4	10	1	17	31.2	33.4	13	2	7	11.2	20.3	3	2	27	10.8	15.7
12	0	0	228.3	238.1	10	1	19	72.3	74.6	13	2	9	11.1	19.3	3	2	29	11.0	23.7
12	0	2	124.3	120.8	10	1	21	83.8	79.4	13	2	11	22.1	25.2	2	2	0	67.0	65.9
12	0	4	11.1	31.0	9	1	2	23.5	6.7	13	2	13	11.3	13.6	2	2	4	1144.5	1074.9
12	0	6	81.7	79.5	9	1	4	29.5	13.8	12	2	0	134.7	134.5	2	2	8	88.1	96.8
12	0	8	179.6	177.1	9	1	6	39.2	45.2	12	2	2	104.5	100.6	2	2	12	725.6	764.4
12	0	10	107.1	110.3	9	1	8	27.3	26.9	12	2	4	49.6	53.1	2	2	16	45.4	41.1
12	0	12	32.5	21.4	9	1	10	43.5	47.4	12	2	6	123.3	121.1	2	2	20	474.3	487.5
12	0	14	119.9	112.5	9	1	12	10.7	7.5	12	2	8	142.8	142.8	2	2	24	41.9	34.8
12	0	16	186.0	179.9	9	1	14	31.2	15.2	12	2	10	103.9	105.7	2	2	28	331.8	321.9
12	0	18	60.8	57.1	9	1	16	28.6	29.2	12	2	12	33.1	43.2	14	3	1	41.5	40.2
10	0	0	79.3	80.3	9	1	18	10.9	5.4	12	2	14	84.9	81.9	14	3	3	57.5	59.4
10	0	2	37.4	39.8	9	1	20	27.0	5.5	12	2	16	117.9	107.2	14	3	5	73.8	75.9
10	0	4	143.3	148.1	9	1	22	11.3	19.8	11	2	1	50.4	47.1	14	3	7	71.7	70.0
10	0	6	153.3	156.5	9	1	24	23.0	27.9	11	2	3	10.6	8.0	14	3	9	66.9	67.0
10	0	8	72.9	67.3	8	1	1	237.7	240.0	11	2	5	57.7	64.1	13	3	2	23.5	26.2
10	0	10	174.8	169.8	8	1	3	34.1	17.4	11	2	7	25.1	9.8	13	3	4	36.0	29.7
10	0	12	95.0	93.9	8	1	5	11.1	6.3	11	2	9	20.4	6.2	13	3	6	25.9	29.3
10	0	14	70.3	72.6	8	1	7	162.4	156.8	11	2	11	67.9	73.9	13	3	8	25.0	18.5
10	0	16	76.8	72.0	8	1	9	123.0	120.1	11	2	13	11.3	22.5	13	3	10	43.3	36.3
10	0	18	39.2	24.9	8	1	11	10.6	17.1	11	2	15	29.4	28.8	13	3	12	25.6	22.8
10	0	20	110.8	107.9	8	1	13	20.0	29.5	11	2	17	11.3	18.3	12	3	1	72.7	75.4
10	0	22	60.0	62.9	8	1	15	144.3	145.0	11	2	19	11.5	2.8	12	3	3	10.9	15.8
8	0	0	520.8	520.5	8	1	17	158.4	161.7	10	2	0	31.1	8.2	12	3	5	56.9	55.7
8	0	2	105.9	107.6	8	1	19	22.0	11.0	10	2	2	91.0	94.9	12	3	7	115.9	121.9
8	0	4	32.4	28.6	8	1	21	10.9	4.8	10	2	4	300.2	307.0	12	3	9	101.2	96.5
8	0	6	126.2	128.3	8	1	23	107.8	103.4	10	2	6	100.8	102.0	12	3	11	58.3	55.9
8	0	8	420.0	418.5	8	1	25	63.3	70.8	10	2	8	21.2	26.0	12	3	13	39.4	30.4
8	0	10	55.4	55.2	7	1	2	56.7	52.7	10	2	10	108.0	106.1	12	3	15	56.2	61.3
8	0	12	25.0	20.7	7	1	4	99.4	96.6	10	2	12	252.3	249.6	12	3	17	81.0	76.9
8	0	14	49.8	48.5	7	1	6	41.4	44.4	10	2	14	83.8	85.6	11	3	2	48.2	44.1
8	0	16	336.4	339.9	7	1	8	11.0	3.6	10	2	16	20.4	12.4	11	3	4	63.7	67.6
8	0	18	116.0	112.6	7	1	10	20.0	25.7	10	2	18	59.6	57.5	11	3	6	50.5	49.2
8	0	20	11.0	23.2	7	1	12	51.4	49.5	10	2	20	212.1	206.0	11	3	8	10.9	14.6
8	0	22	76.2	73.0	7	1	14	36.2	29.3	9	2	1	23.9	10.8	11	3	10	43.2	35.3
8	0	24	246.7	239.4	7	1	16	10.3	4.8	9	2	3	44.2	46.1	11	3	12	42.1	46.6
6	0	0	90.7	90.0	7	1	18	22.7	12.2	9	2	5	48.4	50.1	11	3	14	11.4	25.7
6	0	2	121.3	118.7	7	1	20	10.8	18.0	9	2	7	40.8	47.4	11	3	16	11.4	19.0

6	0	4	11.7	19.1	7	1	22	27.2	14.9	9	2	9	32.4	36.0	11	3	18	38.7	41.6
6	0	6	77.8	79.1	7	1	24	26.1	6.0	9	2	11	28.6	20.5	10	3	1	42.7	45.4
6	0	8	116.0	119.9	7	1	26	11.1	8.2	9	2	13	24.2	18.8	10	3	3	162.7	166.9
6	0	10	10.8	19.1	6	1	1	11.8	24.3	9	2	15	20.0	6.8	10	3	5	144.0	144.4
6	0	12	104.5	104.2	6	1	3	255.9	249.3	9	2	17	20.5	14.0	10	3	7	20.8	19.6
6	0	14	42.7	41.9	6	1	5	192.2	192.3	9	2	19	41.6	44.0	10	3	9	20.4	12.5
6	0	16	39.5	39.1	6	1	7	22.1	7.1	9	2	21	31.7	32.6	10	3	11	98.0	97.9
6	0	18	82.6	88.3	6	1	9	22.8	14.1	9	2	23	11.2	9.6	10	3	13	100.0	102.6
6	0	20	27.4	26.1	6	1	11	110.8	120.6	8	2	0	115.7	113.8	10	3	15	26.3	14.4
6	0	22	57.2	56.9	6	1	13	137.1	139.3	8	2	2	127.3	131.1	10	3	17	34.5	26.3
6	0	24	76.7	77.5	6	1	15	23.0	8.0	8	2	4	76.6	75.3	10	3	19	135.8	127.6
6	0	26	11.2	7.7	6	1	17	26.5	21.5	8	2	6	81.5	79.4	10	3	21	116.9	113.9
4	0	0	652.1	624.6	6	1	19	151.0	152.7	8	2	8	84.8	84.8	9	3	2	24.4	29.4
4	0	2	46.3	43.4	6	1	21	114.2	114.7	8	2	10	88.6	86.2	9	3	4	10.6	15.6
4	0	4	66.3	70.6	6	1	23	10.7	8.5	8	2	12	73.6	76.2	9	3	6	39.0	41.1
4	0	6	24.4	28.1	6	1	25	11.1	13.2	8	2	14	97.6	98.5	9	3	8	10.7	8.2
4	0	8	1068.5	1053.5	6	1	27	56.6	59.3	8	2	16	72.6	68.6	9	3	10	48.3	33.0
4	0	10	64.5	65.0	5	1	2	121.9	116.1	8	2	18	66.8	70.7	9	3	12	10.7	12.1
4	0	12	61.6	63.8	5	1	4	11.4	11.0	8	2	20	44.4	42.7	9	3	14	20.6	13.4
4	0	14	44.6	47.2	5	1	6	42.9	34.4	8	2	22	51.4	53.4	9	3	16	30.7	14.8
4	0	16	458.4	471.9	5	1	8	23.8	7.6	8	2	24	49.5	49.8	9	3	18	23.2	21.6
4	0	18	10.0	2.1	5	1	10	20.6	24.7	7	2	1	11.4	11.3	9	3	20	20.4	1.5
4	0	20	19.8	14.3	5	1	12	20.3	3.8	7	2	3	178.4	179.2	9	3	22	23.0	26.6
4	0	22	10.5	12.0	5	1	14	19.2	8.5	7	2	5	43.4	45.9	8	3	1	165.2	171.0
4	0	24	384.4	384.1	5	1	16	30.9	10.3	7	2	7	39.0	41.5	8	3	3	10.9	16.4
4	0	26	34.6	35.5	5	1	18	46.8	53.6	7	2	9	27.9	30.1	8	3	5	24.5	8.9
4	0	28	47.6	51.1	5	1	20	10.2	3.9	7	2	11	10.5	7.5	8	3	7	130.5	131.9
2	0	0	151.2	149.0	5	1	22	45.7	48.3	7	2	13	116.5	117.9	8	3	9	171.6	172.8
2	0	2	23.0	25.2	5	1	24	10.8	4.2	7	2	15	21.8	11.4	8	3	11	26.7	20.3
2	0	4	51.3	51.4	5	1	26	22.4	8.1	7	2	17	10.3	7.2	8	3	13	10.5	14.4
2	0	6	21.9	16.1	5	1	28	23.8	0.5	7	2	19	56.7	59.2	8	3	15	154.2	158.5
2	0	8	67.0	74.5	4	1	1	89.1	90.8	7	2	21	21.0	8.0	8	3	17	77.6	78.5
2	0	10	28.4	25.2	4	1	3	24.5	29.7	7	2	23	39.4	28.2	8	3	19	21.4	15.3
2	0	12	100.6	105.4	4	1	5	11.2	11.5	7	2	25	11.0	1.4	8	3	21	10.9	3.4
2	0	14	32.6	29.0	4	1	7	219.8	224.1	6	2	0	68.0	71.8	8	3	23	62.0	69.1
2	0	16	80.8	79.6	4	1	9	242.9	254.7	6	2	2	78.9	76.8	7	3	2	11.5	10.6
2	0	18	10.1	5.7	4	1	11	32.0	28.2	6	2	4	656.5	649.2	7	3	4	77.3	73.9
2	0	20	10.0	5.6	4	1	13	23.0	30.6	6	2	6	63.1	65.0	7	3	6	107.6	105.3
2	0	22	10.1	2.4	4	1	15	113.5	113.9	6	2	8	10.9	12.4	7	3	8	10.8	5.4
2	0	24	34.2	26.5	4	1	17	55.9	53.6	6	2	10	47.0	50.9	7	3	10	87.2	88.4
2	0	26	24.7	15.9	4	1	19	10.1	10.5	6	2	12	496.6	512.2	7	3	12	44.0	46.2
2	0	28	51.5	49.4	4	1	21	29.4	5.5	6	2	14	43.8	48.2	7	3	14	10.2	16.4
0	0	4	110.2	121.9	4	1	23	84.7	74.9	6	2	16	25.0	34.9	7	3	16	19.3	12.1
0	0	8	570.8	610.0	4	1	25	94.1	97.3	6	2	18	42.0	46.3	7	3	18	27.2	25.4
0	0	12	54.7	56.0	4	1	27	10.9	27.0	6	2	20	356.6	347.6	7	3	20	10.8	16.8
0	0	16	786.8	816.6	3	1	2	45.7	47.8	6	2	22	10.9	35.9	7	3	22	47.0	49.6
0	0	20	72.0	73.8	3	1	4	73.6	77.0	6	2	24	20.6	16.9	7	3	24	23.3	10.9
0	0	24	392.8	391.4	3	1	6	158.5	159.6	6	2	26	24.9	24.2	6	3	1	25.4	25.0
0	0	28	10.7	5.8	3	1	8	10.6	13.2	5	2	1	62.1	64.1	6	3	3	219.8	218.5
15	1	2	21.5	18.4	3	1	10	40.8	42.0	5	2	3	100.8	100.4	6	3	5	133.3	136.7
14	1	1	69.9	69.9	3	1	12	34.5	30.4	5	2	5	29.1	39.7	6	3	7	22.2	1.7

14	1	3	73.7	76.1	3	1	14	64.1	67.3	5	2	7	18.8	3.7	6	3	9	10.7	1.3
14	1	5	65.0	67.2	3	1	16	19.9	7.0	5	2	9	10.8	17.5	6	3	11	170.6	173.7
14	1	7	47.9	50.5	3	1	18	19.6	21.4	5	2	11	57.6	62.0	6	3	13	189.8	195.9
14	1	9	44.0	48.1	3	1	20	9.9	2.8	5	2	13	88.6	88.0	6	3	15	10.2	0.8
14	1	11	58.2	61.5	3	1	22	66.6	62.6	5	2	15	10.1	4.3	6	3	17	10.1	3.1
13	1	2	27.2	24.1	3	1	24	10.4	4.9	5	2	17	31.0	22.5	6	3	19	89.6	88.7
13	1	4	11.0	1.2	3	1	26	10.7	2.9	5	2	19	38.2	41.2	6	3	21	61.6	70.1
13	1	6	11.0	5.7	3	1	28	10.8	3.1	5	2	21	10.4	17.1	6	3	23	10.6	18.3
13	1	8	28.0	26.7	2	1	1	32.0	33.4	5	2	23	39.5	28.6	6	3	25	10.9	5.8
13	1	10	11.3	5.5	2	1	3	141.1	146.3	5	2	25	10.7	6.6	5	3	2	11.7	16.4
13	1	12	11.4	8.4	2	1	5	63.8	66.2	5	2	27	30.6	32.0	5	3	4	36.0	32.5
13	1	14	36.7	21.5	2	1	7	35.8	35.1	4	2	0	37.4	22.2	5	3	6	11.2	25.9
12	1	1	113.2	113.5	2	1	9	30.8	35.3	4	2	2	38.9	39.4	5	3	8	10.6	7.2
12	1	3	51.6	46.8	2	1	11	89.7	97.1	4	2	4	106.6	109.5	5	3	10	10.6	2.3
12	1	5	51.2	58.0	2	1	13	93.6	94.6	4	2	6	83.5	86.0	5	3	12	10.2	9.7
12	1	7	110.2	108.8	2	1	15	39.7	47.0	4	2	8	42.3	27.2	5	3	14	10.1	5.8
12	1	9	102.4	102.4	2	1	17	24.2	13.4	4	2	10	44.1	46.5	5	3	16	19.4	10.2
12	1	11	32.4	37.9	2	1	19	10.1	36.1	4	2	12	33.7	34.4	5	3	18	23.7	20.3
12	1	13	34.1	30.1	2	1	21	50.5	45.6	4	2	14	20.3	20.1	5	3	20	10.3	0.3
12	1	15	93.1	90.0	2	1	23	10.2	15.1	4	2	16	10.1	3.6	5	3	22	19.6	19.6
12	1	17	89.2	83.9	2	1	25	24.2	16.1	4	2	18	31.6	40.0	5	3	24	10.7	2.3
11	1	2	19.9	14.7	2	1	27	47.1	52.9	4	2	20	71.2	67.4	5	3	26	10.6	1.9
11	1	4	53.2	57.2	2	1	29	44.4	26.4	4	2	22	37.5	35.2	4	3	1	202.6	201.5
11	1	6	10.9	9.2	1	1	2	53.7	58.4	4	2	24	26.6	22.6	4	3	3	32.0	26.4
11	1	8	11.0	4.3	1	1	6	26.9	25.0	4	2	26	10.8	15.7	4	3	5	21.2	22.2
11	1	10	13.1	1.9	1	1	10	97.5	96.8	4	2	28	21.0	19.4	4	3	7	162.4	171.4
11	1	12	46.5	41.5	1	1	14	115.9	114.1	3	2	1	13.2	3.0	4	3	9	80.8	84.7
11	1	14	26.9	2.8	1	1	18	9.9	11.3	3	2	3	41.9	42.2	4	3	11	23.1	12.2
11	1	16	30.2	13.5	1	1	22	30.7	39.2	3	2	5	278.1	281.8	4	3	13	10.3	21.2
11	1	18	25.3	6.8	1	1	26	29.0	33.3	3	2	7	35.7	39.8	4	3	15	72.8	77.8
11	1	20	24.4	15.4	14	2	0	39.1	40.7	3	2	9	18.6	4.3	4	3	17	136.5	137.4
10	1	1	32.5	36.6	14	2	2	101.8	99.3	3	2	11	115.5	119.3	4	3	19	21.4	27.5
10	1	3	109.5	115.7	14	2	4	126.9	129.9	3	2	13	19.4	20.0	4	3	21	20.3	0.8
10	1	5	160.3	160.2	14	2	6	85.9	89.3	3	2	15	10.1	0.6	4	3	23	94.0	97.8

BRAUNITE

SHEET NO. 1 PART 2

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FC	FC	H	K	L	FO	FC
4	3	25	37.6	35.5	12	5	3	27.7	40.2	8	6	18	96.3	96.5					
4	3	27	31.1	2.1	12	5	5	39.7	33.6	8	6	20	21.1	16.6					
3	3	2	219.4	212.5	12	5	7	76.3	76.1	8	6	22	100.9	94.9					
3	3	6	79.9	81.2	12	5	9	86.1	83.3	7	6	1	10.8	16.8					
3	3	10	21.7	5.1	12	5	11	34.7	28.8	7	6	3	100.8	98.2					
3	3	14	125.4	130.8	12	5	13	44.2	37.5	7	6	5	174.7	175.6					
3	3	18	41.3	42.7	12	5	15	94.8	95.9	7	6	7	10.6	7.6					
3	3	22	10.4	26.6	11	5	2	47.1	48.1	7	6	9	32.1	30.1					
3	3	26	31.9	34.6	11	5	4	10.9	17.2	7	6	11	132.9	134.1					
14	4	0	11.1	14.5	11	5	6	53.0	53.2	7	6	13	68.6	72.3					
14	4	2	65.3	61.0	11	5	8	10.9	5.5	7	6	15	33.3	35.7					
14	4	4	118.6	119.9	11	5	10	59.7	54.0	7	6	17	10.6	1.9					
14	4	6	143.0	142.7	11	5	12	11.1	7.6	7	6	19	83.2	81.1					
13	4	1	65.1	61.9	11	5	14	50.9	49.8	7	6	21	102.9	104.0					
13	4	3	39.4	38.4	11	5	16	11.4	8.2	7	6	23	11.0	11.6					
13	4	5	20.7	24.0	10	5	1	23.4	23.5	6	6	0	31.5	30.0					
13	4	7	25.5	33.1	10	5	3	140.7	145.2	6	6	4	424.1	433.0					
13	4	9	37.0	30.4	10	5	5	84.8	81.7	6	6	8	37.1	30.5					
13	4	11	27.2	15.9	10	5	7	54.4	41.4	6	6	12	318.4	330.6					
12	4	0	151.6	147.7	10	5	9	41.8	36.2	6	6	16	20.8	9.0					
12	4	2	74.7	78.2	10	5	11	73.7	76.1	6	6	20	264.7	271.0					
12	4	4	10.8	13.7	10	5	13	105.5	104.7	6	6	24	20.5	11.7					
12	4	6	95.2	96.1	10	5	15	34.5	19.1	13	7	2	85.7	87.5					
12	4	8	185.9	191.4	10	5	17	11.1	1.6	13	7	4	11.2	23.0					
12	4	10	64.4	66.8	10	5	19	99.4	100.3	12	7	1	78.0	82.3					
12	4	12	11.0	10.9	9	5	2	88.0	88.8	12	7	3	46.5	49.0					
12	4	14	56.2	55.6	9	5	4	24.5	23.6	12	7	5	23.5	19.0					
12	4	16	129.3	124.5	9	5	6	58.1	57.8	12	7	7	37.6	34.6					
11	4	1	34.4	37.4	9	5	8	30.5	15.1	12	7	9	48.6	47.2					
11	4	3	21.7	16.9	9	5	10	45.3	48.6	12	7	11	11.2	15.3					
11	4	5	42.5	37.6	9	5	12	10.8	11.1	11	7	2	93.5	89.5					
11	4	7	70.6	71.5	9	5	14	56.0	59.5	11	7	4	21.3	32.2					
11	4	9	52.2	46.4	9	5	16	22.2	22.0	11	7	6	43.5	48.4					
11	4	11	58.1	57.2	9	5	18	59.3	60.0	11	7	8	10.9	7.2					
11	4	13	36.9	43.1	9	5	20	23.0	2.7	11	7	10	62.4	65.3					
11	4	15	11.3	14.2	8	5	1	101.5	101.1	11	7	12	21.7	26.2					
11	4	17	30.8	39.3	8	5	3	10.6	1.1	11	7	14	94.9	95.1					
10	4	0	42.8	50.4	8	5	5	10.6	8.8	10	7	1	10.9	5.9					
10	4	2	161.6	164.9	8	5	7	190.6	193.5	10	7	3	98.5	100.2					
10	4	4	104.8	106.4	8	5	9	188.0	192.5	10	7	5	108.5	109.1					
10	4	6	97.3	97.4	8	5	11	25.2	6.0	10	7	7	11.0	10.1					
10	4	8	38.4	38.2	8	5	13	23.5	7.8	10	7	9	20.7	30.2					
10	4	10	74.3	68.5	8	5	15	95.7	96.0	10	7	11	109.0	108.2					

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10	4	12	100.4	101.6	8	5	17	81.0	79.8	10	7	13	99.9	101.3
10	4	14	103.8	106.4	8	5	19	10.9	12.4	10	7	15	11.3	18.2
10	4	16	11.4	32.9	8	5	21	22.8	13.7	10	7	17	11.4	9.1
10	4	18	129.8	124.7	8	5	23	100.4	98.4	9	7	2	56.0	49.6
10	4	20	72.0	63.7	7	5	2	65.9	71.7	9	7	4	26.1	16.7
9	4	1	34.9	43.0	7	5	4	33.8	41.0	9	7	6	80.0	75.4
9	4	3	10.6	10.6	7	5	6	24.5	37.4	9	7	8	11.0	8.8
9	4	5	30.4	34.5	7	5	8	10.6	16.5	9	7	10	78.9	79.8
9	4	7	114.5	114.1	7	5	10	26.4	29.0	9	7	12	11.1	6.6
9	4	9	120.7	120.4	7	5	12	29.8	20.7	9	7	14	57.8	58.0
9	4	11	39.2	40.7	7	5	14	44.0	41.2	9	7	16	31.3	11.7
9	4	13	10.9	18.4	7	5	16	33.7	15.9	9	7	18	45.5	39.8
9	4	15	52.6	52.3	7	5	18	43.5	38.2	8	7	1	91.3	90.9
9	4	17	23.2	34.0	7	5	20	10.8	2.4	8	7	3	35.4	39.5
9	4	19	11.1	1.6	7	5	22	25.3	31.3	8	7	5	10.7	11.4
9	4	21	11.2	12.5	7	5	24	33.8	12.9	8	7	7	139.4	143.4
8	4	0	397.2	406.8	6	5	1	23.9	29.5	8	7	9	89.9	90.2
8	4	2	64.9	65.3	6	5	3	111.2	108.3	8	7	11	10.9	9.6
8	4	4	10.7	5.4	6	5	5	182.1	184.9	8	7	13	42.5	45.6
8	4	6	46.7	47.1	6	5	7	67.4	64.5	8	7	15	41.7	44.2
8	4	8	352.3	354.2	6	5	9	55.4	58.4	8	7	17	95.3	95.4
8	4	10	75.7	77.7	6	5	11	151.4	156.8	8	7	19	36.7	21.8
8	4	12	10.5	16.0	6	5	13	88.7	91.4	8	7	21	11.2	22.0
8	4	14	59.7	66.7	6	5	15	20.1	4.3	7	7	2	96.4	96.9
8	4	16	281.5	283.2	6	5	17	10.3	8.0	7	7	6	75.4	77.7
8	4	18	24.1	16.6	6	5	19	68.3	76.4	7	7	10	60.0	54.8
8	4	20	10.9	2.7	6	5	21	86.5	87.3	7	7	14	55.9	59.1
8	4	22	21.6	27.7	6	5	23	10.8	13.9	7	7	18	71.3	73.2
8	4	24	209.9	204.8	6	5	25	11.0	14.4	7	7	22	63.3	64.5
7	4	1	107.1	111.7	5	5	2	11.7	25.3	12	8	0	134.1	138.2
7	4	3	31.4	36.0	5	5	6	97.3	94.8	12	8	2	20.3	31.5
7	4	5	46.7	42.6	5	5	10	111.0	114.4	12	8	4	11.2	22.6
7	4	7	61.3	57.6	5	5	14	64.9	65.6	12	8	6	29.9	31.7
7	4	9	100.9	101.9	5	5	18	10.2	21.2	12	8	8	69.1	72.4
7	4	11	10.4	21.9	5	5	22	24.6	24.1	11	8	1	66.5	65.8
7	4	13	10.3	1.7	5	5	26	46.8	43.0	11	8	3	40.1	41.1
7	4	15	106.3	114.1	13	6	1	25.4	32.4	11	8	5	47.8	44.4
7	4	17	40.3	42.9	13	6	3	41.0	38.5	11	8	7	35.3	33.7
7	4	19	23.7	25.9	13	6	5	38.0	37.2	11	8	9	42.4	47.9
7	4	21	44.5	40.8	13	6	7	52.3	51.7	11	8	11	26.4	21.9
7	4	23	32.3	22.6	13	6	9	50.0	49.0	10	8	0	45.4	30.9
7	4	25	64.8	64.1	12	6	0	111.9	116.7	10	8	2	148.4	150.3
6	4	0	49.3	44.4	12	6	2	146.6	151.1	10	8	4	59.6	56.1
6	4	2	105.8	106.7	12	6	4	21.7	9.4	10	8	6	126.1	126.1
6	4	4	54.8	49.8	12	6	6	106.3	98.9	10	8	8	11.1	5.8
6	4	6	80.7	79.9	12	6	8	84.6	81.4	10	8	10	136.0	131.1
6	4	8	37.6	32.9	12	6	10	111.7	108.5	10	8	12	63.0	60.2
6	4	10	108.2	110.6	12	6	12	26.6	14.9	10	8	14	135.7	132.9
6	4	12	22.9	16.8	11	6	1	24.9	29.0	9	8	1	138.5	138.6
6	4	14	96.5	99.8	11	6	3	90.4	93.8	9	8	3	29.4	30.6
6	4	16	45.2	45.5	11	6	5	74.3	71.6	9	8	5	10.9	3.4

6	4	18	42.6	40.7
6	4	20	50.2	49.3
6	4	22	43.5	40.3
6	4	24	10.8	7.3
6	4	26	65.7	65.9
5	4	1	243.9	245.7
5	4	3	33.1	25.8
5	4	5	33.7	28.2
5	4	7	74.4	75.4
5	4	9	50.5	49.3
5	4	11	10.2	1.0
5	4	13	10.1	2.3
5	4	15	119.4	122.0
5	4	17	128.6	135.8
5	4	19	19.1	32.0
5	4	21	19.9	21.8
5	4	23	70.2	65.3
5	4	25	25.8	41.9
5	4	27	21.4	11.3
4	4	0	929.3	922.6
4	4	4	51.3	48.6
4	4	8	522.2	542.3
4	4	12	21.7	20.6
4	4	16	484.6	507.6
4	4	20	42.3	38.7
4	4	24	305.9	302.5
14	5	1	50.9	46.1
14	5	3	46.3	48.1
13	5	2	53.1	52.3
13	5	4	32.7	23.9
13	5	6	61.5	55.5
13	5	8	11.1	20.1
13	5	10	58.9	51.3
12	5	1	111.2	113.5
11	6	7	47.1	40.8
11	6	9	24.6	17.6
11	6	11	47.1	47.7
11	6	13	67.5	64.6
11	6	15	23.4	11.4
10	6	0	10.7	7.7
10	6	2	63.3	63.2
10	6	4	196.0	200.7
10	6	6	44.8	46.5
10	6	8	22.3	8.8
10	6	10	29.7	25.4
10	6	12	204.8	202.5
10	6	14	42.3	38.2
10	6	16	11.3	5.4
10	6	18	53.1	58.9
9	6	1	78.2	79.8
9	6	3	94.1	97.5
9	6	5	62.2	63.8
9	6	7	10.7	3.7
9	6	9	10.8	3.6
9	6	11	68.8	68.9
9	6	13	83.9	78.7
9	6	15	61.0	53.2
9	6	17	39.2	35.5
9	6	19	64.0	61.7
8	6	0	35.1	36.8
8	6	2	106.7	105.5
8	6	4	10.7	10.3
8	6	6	164.8	165.0
8	6	8	59.3	64.0
8	6	10	125.6	128.4
8	6	12	10.8	6.2
8	6	14	78.9	78.1
8	6	16	29.3	35.2
9	8	7	67.4	71.1
9	8	9	60.2	63.2
9	8	11	11.1	2.0
9	8	13	19.7	20.9
9	8	15	100.5	96.1
9	8	17	101.4	100.1
8	8	0	183.7	184.6
8	8	4	10.8	10.6
8	8	8	243.7	245.6
8	8	12	33.6	32.7
8	8	16	154.2	155.9
12	9	1	53.3	56.6
12	9	3	20.0	21.2
11	9	2	86.7	86.4
11	9	4	11.1	5.3
11	9	6	55.9	57.6
11	9	8	29.5	9.0
11	9	10	53.3	53.4
10	9	1	29.3	18.7
10	9	3	48.8	48.1
10	9	5	79.4	78.4
10	9	7	46.5	48.0
10	9	9	30.7	34.2
10	9	11	70.3	70.3
10	9	13	49.2	42.6
9	9	2	88.8	87.5
9	9	6	81.9	82.0
9	9	10	71.1	69.4
9	9	14	66.8	64.0
11	10	1	11.0	2.4
11	10	3	71.0	75.0
10	10	0	10.9	5.0
10	10	4	112.3	117.1
10	10	8	59.5	53.7