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The crystal structure of thadeuite, $\text{Mg}(\text{Ca},\text{Mn})(\text{Mg},\text{Fe},\text{Mn})_2(\text{PO}_4)_2(\text{OH},\text{F})_2$ ¹

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Abstract

Thadeuite, $\text{Mg}(\text{Ca},\text{Mn})(\text{Mg},\text{Fe},\text{Mn})_2(\text{PO}_4)_2(\text{OH},\text{F})_2$, is orthorhombic, space group $C222_1$, $a = 6.412(3)$, $b = 13.563(8)$, $c = 8.545(5)\text{\AA}$, with $Z = 4$. The crystal structure has been determined with direct methods and refined to a conventional R-value of 3.2% for all reflections. There are three cation coordination polyhedra, $[\text{MO}_4(\text{OH})_2]^{-8}$, with the cation compositions: $\text{M}(1) = \text{Mg}$; $\text{M}(2) = \text{Ca}_{0.95}\text{Mn}_{0.05}$; $\text{M}(3) = \text{Mg}_{0.59}\text{Fe}_{0.29}\text{Mn}_{0.12}$. The structure is comprised of three basic features: helical chains of $\text{M}(3)$ octahedra parallel to c ; slightly distorted chains composed of alternating $\text{M}(1)$ and $\text{M}(2)$ octahedra parallel to a ; and insular phosphate tetrahedra, which crosslink the $\text{M}(3)$ chains to form a network of channels parallel to a into which the $\text{M}(1)$ - $\text{M}(2)$ chains fit. Thadeuite shows only limited structural similarity to other phosphates of related composition, or to those with which it is associated.

Introduction

Thadeuite, $\text{Mg}(\text{Ca},\text{Mn})(\text{Mg},\text{Fe},\text{Mn})_2(\text{PO}_4)_2(\text{OH},\text{F})_2$, was originally described by Isaacs *et al.* (1979) as occurring in phosphate-rich zones in selvages of hydrothermal tin-tungsten veins in the Panasqueira mining district of central Portugal. As originally reported, thadeuite is intergrown with a previously unreported phase, the OH-equivalent of isokite. This material has subsequently been determined to be a new mineral, panasqueiraite, $[\text{CaMgPO}_4(\text{OH},\text{F})]$, described by Isaacs and Peacor (1981). In addition to panasqueiraite, thadeuite is associated with the phosphates fluorapatite, wolfeite and althausite. Thadeuite, wolfeite, panasqueiraite and althausite all have the same general formula type, $\text{M}_2\text{PO}_4(\text{F},\text{OH})$, where the M sites are filled by divalent cations which commonly have octahedral coordination. The structures of each of these minerals associated with thadeuite, discussed in a later section, show only limited similarity to each other. It is unusual for so many compounds to coexist which have the same formula type based on similar cations and yet have diverse structures. We there-

fore initiated an analysis of the thadeuite crystal structure, in order to define its chemical and structural relations to the associated phases.

Experimental procedure

As reported by Isaacs *et al.* (1979), thadeuite is orthorhombic with space group $C222_1$, as determined by a combination of precession and Weissenberg methods. Unit cell parameters, determined by least-squares refinement of 30 reflections obtained by powder diffraction, are $a = 6.412(3)$, $b = 13.563(8)$, $c = 8.545(5)\text{\AA}$, with $Z = 4$. Powder diffraction data are tabulated in Isaacs *et al.* (1979).

Intensity data were obtained using a cleavage fragment measuring approximately $0.3\text{C} \times 0.34 \times 0.38$ mm, mounted for rotation about the b -axis of a Weissenberg-geometry diffractometer. $\text{MoK}\alpha$ radiation, monochromated with a flat graphite crystal and detected with a scintillation counter, was used with a Supper-Pace automated diffractometer system, employing a scan across each reflection with background measured on each side. The intensities of 591 reflections were measured, of which only four had intensities below minimum observable values, up to a $\sin\theta$ limit of 0.50 and a k -index limit of 17. All intensities were corrected for Lorentz-Polarization and absorption effects $[\mu(\text{MoK}\alpha) = 38.0 \text{ cm}^{-1}]$. A modified version of the program

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H	K	L	F (OBS)	F (CALC)	H	K	L	F (OBS)	F (CALC)
2	0	0	10.9	13.1	1	15	0	43.4	42.8
4	0	0	67.0	68.8	3	15	0	15.8	15.6
6	0	0	163.3	166.5	5	15	0	45.2	43.8
8	0	0	53.9	55.7	1	17	0	30.6	29.2
3	1	0	142.9	144.8	3	17	0	25.5	24.9
5	1	0	48.9	49.4	2	0	1	204.2	212.4
7	1	0	31.6	31.9	4	0	1	107.9	109.7
9	1	0	19.3	18.4	6	0	1	69.3	70.1
2	2	0	63.2	64.1	8	0	1	47.2	47.5
4	2	0	41.3	40.8	3	1	1	82.8	82.5
6	2	0	23.8	23.1	5	1	1	20.5	20.2
8	2	0	16.9	17.2	7	1	1	6.9	5.6
3	3	0	85.6	87.9	2	2	1	65.1	63.6
5	3	0	11.3	10.8	4	2	1	98.5	100.4
7	3	0	39.0	39.2	6	2	1	20.6	21.1
2	4	0	66.1	69.8	8	2	1	25.9	26.3
4	4	0	32.5	33.0	3	3	1	59.4	58.4
6	4	0	71.1	71.0	5	3	1	27.4	29.9
8	4	0	9.5	2.9	7	3	1	41.5	39.0
1	5	0	33.3	36.7	2	4	1	49.1	45.6
3	5	0	84.5	86.9	4	4	1	63.2	65.2
5	5	0	21.2	21.5	6	4	1	39.0	38.8
7	5	0	58.5	58.0	8	4	1	26.5	27.0
2	6	0	36.5	38.6	1	5	1	51.5	52.3
4	6	0	22.4	21.4	5	5	1	129.2	131.8
6	6	0	45.5	46.4	5	5	1	57.3	57.8
8	6	0	5.9	3.8	7	5	1	38.2	36.3
3	7	0	51.6	54.6	2	6	1	30.7	32.8
5	7	0	13.7	14.0	4	6	1	58.7	59.9
7	7	0	20.0	20.5	6	6	1	65.2	65.5
2	8	0	21.3	22.0	8	6	1	33.3	33.3
4	8	0	32.4	33.3	3	7	1	115.7	120.6
6	8	0	21.5	22.8	5	7	1	28.3	27.0
8	8	0	16.9	17.2	7	7	1	21.7	20.6
3	9	0	118.1	125.9	2	8	1	62.1	62.2
5	9	0	6.2	5.6	4	8	1	51.1	53.0
7	9	0	65.0	61.8	6	8	1	45.2	45.6
2	10	0	3.9	7.6	8	8	1	37.0	36.6
4	10	0	25.3	24.8	3	9	1	38.9	40.5
6	10	0	42.9	41.7	5	9	1	65.4	65.4
1	11	0	44.6	47.2	7	9	1	23.8	22.9
3	11	0	46.9	47.6	2	10	1	48.2	46.8
5	11	0	13.1	11.9	4	10	1	39.3	39.7
7	11	0	27.2	25.5	6	10	1	18.9	18.5
2	12	0	16.6	15.5	1	11	1	55.5	56.0
4	12	0	4.8	2.2	3	11	1	24.0	24.0
6	12	0	22.4	21.3	5	11	1	44.1	43.0
1	13	0	5.8	7.7	7	11	1	45.7	43.4
3	13	0	127.9	129.1	2	12	1	7.5	4.2
5	13	0	7.0	12.3	4	12	1	18.0	16.8
2	14	0	16.0	16.8	6	12	1	10.8	11.5
4	14	0	22.2	22.3	1	13	1	62.9	64.1
6	14	0	41.3	38.5	3	13	1	28.4	28.5

H	K	L	F (OBS)	F (CALC)	H	K	L	F (OBS)	F (CALC)
5	13	1	49.8	48.0	6	10	2	16.0	16.3
2	14	1	26.8	26.5	1	11	2	49.3	51.6
4	14	1	23.6	23.2	3	11	2	28.8	28.1
6	14	1	25.3	24.9	5	11	2	43.9	44.0
1	15	1	34.9	34.5	7	11	2	19.3	21.2
3	15	1	11.2	10.8	0	12	2	55.6	57.9
5	15	1	23.6	22.6	2	12	2	30.0	29.1
1	17	1	22.2	23.2	4	12	2	20.3	20.1
3	17	1	25.4	30.1	6	12	2	48.6	46.6
2	0	2	98.9	96.7	1	13	2	53.4	54.8
4	0	2	125.0	123.0	3	13	2	13.1	13.4
6	0	2	2.3 *	2.4	5	13	2	42.1	40.5
8	0	2	29.1	29.4	2	14	2	11.1	11.0
1	1	2	4.4	5.4	4	14	2	20.9	21.4
3	1	2	38.6	39.1	1	15	2	24.5	24.3
5	1	2	29.3	29.5	3	15	2	47.3	44.9
7	1	2	14.5	15.9	5	15	2	31.9	32.0
2	2	2	40.1	41.9	1	17	2	21.6	20.6
4	2	2	33.9	33.3	3	17	2	13.4	13.6
6	2	2	65.0	66.1	0	0	3	3.3	0.0
8	2	2	40.8	40.2	2	0	3	20.4	19.5
1	3	2	123.2	118.9	4	0	3	22.0	21.0
3	3	2	46.4	45.2	6	0	3	4.7	1.6
5	3	2	75.1	73.0	8	0	3	20.7	21.2
7	3	2	46.4	48.6	1	1	3	34.3	34.9
2	4	2	33.3	31.7	3	1	3	29.1	26.9
4	4	2	25.0	21.1	5	1	3	41.6	41.8
6	4	2	34.3	34.4	7	1	3	9.0	9.9
8	4	2	26.9	26.1	0	2	3	206.5	205.5
1	5	2	79.6	75.0	2	2	3	92.9	87.4
3	5	2	63.1	63.3	4	2	3	39.9	40.7
5	5	2	15.3	15.1	6	2	3	106.7	109.2
7	5	2	26.6	27.5	8	2	3	30.2	31.2
0	6	2	21.4	19.5	1	3	3	26.9	23.8
2	6	2	111.1	112.4	3	3	3	101.0	102.8
4	6	2	50.2	49.9	5	3	3	40.8	41.4
6	6	2	62.7	63.6	7	3	3	25.3	25.1
8	6	2	41.6	41.4	0	4	3	32.8	30.0
3	7	2	42.0	42.4	2	4	3	59.6	59.9
5	7	2	64.1	64.6	4	4	3	47.5	47.4
7	7	2	37.1	37.6	6	4	3	15.7	17.3
0	8	2	12.0	11.1	8	4	3	33.8	33.4
2	8	2	12.2	10.9	1	5	3	118.4	112.5
4	8	2	24.1	23.6	3	5	3	33.6	33.1
6	8	2	14.0	14.2	5	5	3	30.5	30.6
8	8	2	14.6	13.0	7	5	3	43.3	44.3
1	9	2	29.5	31.8	0	6	3	115.4	115.7
3	9	2	83.4	82.0	2	6	3	38.9	36.9
5	9	2	20.5	21.6	4	6	3	100.3	101.2
7	9	2	34.4	33.8	6	6	3	36.6	38.6
0	10	2	34.0	35.1	8	6	3	28.0	28.1
2	10	2	61.9	63.4	1	7	3	72.1	75.3
4	10	2	50.4	49.6	3	7	3	81.1	84.0

H	K	L	F (OBS)	F (CALC)	H	K	L	F (OBS)	F (CALC)
5	7	3	35.6	35.4	4	4	4	22.8	19.9
7	7	3	72.2	71.8	6	4	4	16.5	18.2
0	8	3	37.2	38.2	8	4	4	25.9	26.4
2	8	3	43.7	42.2	1	5	4	10.6	8.8
4	8	3	23.5	23.0	3	5	4	57.9	56.7
6	8	3	44.3	45.9	5	5	4	25.0	23.5
1	9	3	39.3	39.0	7	5	4	28.0	26.2
3	9	3	7.1	8.5	0	6	4	61.7	59.8
5	9	3	32.4	31.2	2	6	4	80.0	80.3
7	9	3	24.3	25.0	4	6	4	41.1	40.9
0	10	3	22.7	22.1	6	6	4	54.7	55.1
2	10	3	36.2	36.4	8	6	4	23.9	23.4
4	10	3	18.3	19.2	1	7	4	66.3	69.9
6	10	3	25.9	26.0	3	7	4	51.5	51.4
1	11	3	14.9	15.1	5	7	4	48.3	48.6
3	11	3	103.2	106.3	7	7	4	39.8	39.2
5	11	3	19.0	20.7	0	8	4	68.0	70.1
7	11	3	28.0	26.8	2	8	4	57.3	60.6
0	12	3	45.9	48.9	4	8	4	31.5	32.6
2	12	3	34.2	35.4	6	8	4	21.4	21.6
4	12	3	26.9	27.0	1	9	4	4.6	4.0
6	12	3	12.1	13.0	3	9	4	24.9	25.5
1	13	3	35.1	36.7	5	9	4	14.2	15.3
3	13	3	6.9	3.4	7	9	4	6.2	6.3
5	13	3	26.6	26.8	0	10	4	48.1	48.4
0	14	3	3.9	2.7	2	10	4	48.3	48.8
2	14	3	15.0	14.2	4	10	4	13.8	13.1
4	14	3	17.9	18.3	6	10	4	43.4	43.8
1	15	3	34.5	34.0	1	11	4	74.5	77.5
3	15	3	56.4	55.4	3	11	4	22.4	21.8
5	15	3	32.1	30.9	5	11	4	53.6	54.8
1	17	3	41.2	39.4	0	12	4	47.5	47.5
3	17	3	10.8	9.4	2	12	4	50.0	50.1
0	0	4	95.0	88.2	4	12	4	60.3	60.5
2	0	4	125.6	121.8	6	12	4	30.9	30.9
4	0	4	100.4	97.9	1	13	4	58.0	59.9
6	0	4	20.9	20.6	3	13	4	8.8	7.7
8	0	4	9.8	11.5	5	13	4	38.2	37.1
1	1	4	93.1	88.9	0	14	4	14.0	14.1
3	1	4	74.6	72.7	2	14	4	7.6	5.4
5	1	4	22.9	22.3	4	14	4	40.0	38.4
7	1	4	63.0	63.3	1	15	4	52.4	50.4
0	2	4	14.6	13.8	3	15	4	12.0	12.6
2	2	4	115.3	113.3	1	17	4	28.3	26.7
4	2	4	103.2	104.7	0	0	5	1.9	0.0
6	2	4	38.8	38.7	2	0	5	104.2	100.9
8	2	4	47.6	48.9	4	0	5	55.0	53.9
1	3	4	94.2	90.6	6	0	5	46.3	44.2
3	3	4	105.8	102.7	8	0	5	19.2	18.4
5	3	4	56.7	54.2	1	1	5	97.4	96.8
7	3	4	8.7	8.1	3	1	5	68.0	67.7
0	4	4	84.0	82.4	5	1	5	62.3	60.1
2	4	4	37.2	32.1	7	1	5	31.2	30.6

H	K	L	F (OBS)	F (CALC)	H	K	L	F (OBS)	F (CALC)
0	2	5	39.3	39.6	2	0	6	69.0	69.4
2	2	5	65.0	63.3	4	0	6	12.7	11.0
4	2	5	50.7	49.0	6	0	6	56.1	56.0
6	2	5	9.5	8.4	1	1	6	77.1	77.6
8	2	5	22.6	22.7	3	1	6	45.7	45.5
1	3	5	29.8	29.7	5	1	6	50.8	50.4
3	3	5	33.1	32.5	7	1	6	13.0	12.7
5	3	5	39.8	39.8	0	2	6	11.6	10.4
7	3	5	23.7	23.1	2	2	6	43.8	45.0
0	4	5	25.6	25.1	4	2	6	55.7	54.8
2	4	5	48.5	48.5	6	2	6	19.6	19.6
4	4	5	43.0	42.5	1	3	6	61.3	61.3
6	4	5	37.3	37.6	3	3	6	25.2	24.8
1	5	5	104.6	106.3	5	3	6	19.6	19.5
3	5	5	35.5	36.2	7	3	6	41.3	41.9
5	5	5	80.4	79.2	0	4	6	56.2	51.7
7	5	5	57.6	56.9	2	4	6	25.3	22.1
0	6	5	24.1	24.7	4	4	6	29.2	31.4
2	6	5	34.8	34.7	6	4	6	21.2	21.4
4	6	5	29.0	28.3	1	5	6	83.3	85.1
6	6	5	25.6	24.6	3	5	6	27.7	28.4
1	7	5	39.8	41.7	5	5	6	45.4	45.7
3	7	5	44.7	46.8	7	5	6	41.0	40.3
5	7	5	30.3	30.5	0	6	6	16.6	17.6
7	7	5	15.6	15.5	2	6	6	23.9	23.7
0	8	5	23.7	26.6	4	6	6	28.7	29.6
2	8	5	96.8	103.9	6	6	6	19.8	20.0
4	8	5	83.8	85.7	1	7	6	19.6	19.4
6	8	5	23.1	23.1	3	7	6	28.6	29.8
1	9	5	41.4	43.2	5	7	6	15.4	16.5
3	9	5	36.3	37.2	7	7	6	22.8	22.5
5	9	5	26.3	25.0	0	8	6	43.5	43.8
7	9	5	8.7	8.2	2	8	6	70.7	75.1
0	10	5	61.9	63.6	4	8	6	45.9	49.0
2	10	5	19.0	17.1	6	8	6	16.8	16.2
4	10	5	11.7	12.2	1	9	6	34.0	34.1
6	10	5	46.5	45.7	3	9	6	44.5	46.4
1	11	5	46.8	49.7	5	9	6	13.0	12.1
3	11	5	27.2	28.7	0	10	6	6.4	0.5
5	11	5	37.7	38.1	2	10	6	41.0	41.2
0	12	5	11.3	11.1	4	10	6	39.2	39.4
2	12	5	49.2	52.2	6	10	6	17.3	18.0
4	12	5	23.1	23.2	1	11	6	31.7	33.1
1	13	5	33.9	34.6	3	11	6	3.5	4.4
3	13	5	16.5	18.2	5	11	6	21.8	21.5
5	13	5	25.2	24.4	0	12	6	26.8	27.4
0	14	5	34.0	33.2	2	12	6	22.6	23.1
2	14	5	27.6	27.5	4	12	6	15.6	16.7
4	14	5	18.2	17.7	1	13	6	25.7	25.1
1	15	5	34.0	33.9	3	13	6	47.2	48.7
3	15	5	10.3	9.3	0	14	6	31.9	32.1
1	17	5	26.1	25.4	2	14	6	31.1	31.0
0	0	6	157.5	151.1	4	14	6	27.0	25.8

H	K	L	F (OBS)	F (CALC)	H	K	L	F (OBS)	F (CALC)
1	15	6	29.4	28.3	0	0	8	27.9	27.6
3	15	6	32.9	31.7	2	0	8	27.5	27.0
0	0	7	2.2 *	0.0	4	0	8	53.7	54.4
2	0	7	46.3	44.9	6	0	8	11.6	12.7
4	0	7	30.3	30.7	1	1	8	63.7	63.9
6	0	7	35.0	34.6	3	1	8	35.7	36.6
1	1	7	29.6	29.4	5	1	8	48.0	48.6
3	1	7	71.5	72.7	0	2	8	57.5	55.9
5	1	7	10.6	10.2	2	2	8	32.0	32.3
7	1	7	24.3	24.2	4	2	8	23.8	23.8
0	2	7	49.8	49.1	6	2	8	38.0	38.3
2	2	7	39.3	39.0	1	3	8	69.7	69.0
4	2	7	43.0	43.4	3	3	8	31.3	32.9
6	2	7	31.8	32.1	5	3	8	49.8	49.8
1	3	7	41.1	40.9	0	4	8	7.6	7.7
3	3	7	21.4	22.3	2	4	8	37.1	38.2
5	3	7	7.9	7.3	4	4	8	29.2	28.2
7	3	7	25.7	25.0	6	4	8	27.2	28.7
0	4	7	33.4	33.6	1	5	8	54.5	55.0
2	4	7	44.0	46.5	3	5	8	27.9	28.8
4	4	7	43.7	45.4	5	5	8	41.0	41.5
6	4	7	26.8	27.8	0	6	8	14.8	14.7
1	5	7	36.7	37.3	2	6	8	47.0	49.1
3	5	7	98.7	102.2	4	6	8	37.8	38.9
5	5	7	27.3	28.7	6	6	8	26.1	25.5
0	6	7	41.7	41.3	1	7	8	31.7	32.4
2	6	7	17.1	18.4	3	7	8	13.7	13.4
4	6	7	21.9	21.8	5	7	8	7.9	8.0
6	6	7	29.3	30.4	0	8	8	8.0	7.2
1	7	7	14.8	15.8	2	8	8	31.1	30.7
3	7	7	32.2	35.5	4	8	8	28.0	28.2
5	7	7	34.7	35.5	1	9	8	26.7	26.9
0	8	7	110.6	115.6	3	9	8	37.6	39.1
2	8	7	29.0	30.7	5	9	8	24.0	23.1
4	8	7	13.5	13.7	0	10	8	31.6	31.8
6	8	7	61.5	64.6	2	10	8	56.0	58.7
1	9	7	52.8	52.6	4	10	8	50.3	51.0
3	9	7	25.4	25.5	1	11	8	21.2	20.3
5	9	7	39.3	38.6	3	11	8	13.7	14.2
0	10	7	21.5	21.7	0	12	8	54.6	53.4
2	10	7	29.1	29.5	2	12	8	27.0	26.8
4	10	7	51.3	52.9	1	13	8	19.2	19.1
1	11	7	21.3	21.1	0	14	8	19.8	6.3
3	11	7	27.0	26.6	0	0	9	2.5 *	0.0
5	11	7	7.6	6.5	2	0	9	9.0	6.3
0	12	7	43.2	43.8	4	0	9	4.9	0.8
2	12	7	9.1	10.5	1	1	9	41.0	40.4
4	12	7	10.6	11.2	3	1	9	28.6	28.8
1	13	7	19.8	19.4	5	1	9	43.7	44.9
3	13	7	9.1	9.1	0	2	9	60.9	60.2
0	14	7	41.6	40.0	2	2	9	37.3	39.4
2	14	7	12.1	11.8	4	2	9	21.1	21.9
1	15	7	20.9	21.1	1	3	9	38.4	35.9

H	K	L	F (OBS)	F (CALC)	I	H	K	L	F (OBS)	F (CALC)
3	3	9	46.5	48.5		3	3	11	3.0 *	8.5
5	3	9	48.4	50.1		0	4	11	2.7 *	1.1
0	4	9	52.4	52.6		2	4	11	13.8	12.8
2	4	9	23.7	24.2		1	5	11	29.6	29.5
4	4	9	16.0	16.8		0	6	11	19.1	19.2
1	5	9	49.8	48.0		2	6	11	36.6	36.7
3	5	9	17.4	18.6		1	7	11	42.3	40.3
5	5	9	27.0	28.3		0	0	12	14.8	14.9
0	6	9	14.8	14.3						
2	6	9	30.3	30.2						
4	6	9	24.7	25.8						
1	7	9	30.5	28.0						
3	7	9	23.7	23.5						
0	8	9	15.2	14.4						
2	8	9	38.8	38.2						
4	8	9	38.8	39.3						
1	9	9	12.3	11.9						
3	9	9	12.2	12.4						
0	10	9	48.8	48.0						
2	10	9	23.0	23.6						
1	11	9	14.9	14.1						
0	12	9	26.7	25.9						
0	0	10	49.7	49.0						
2	0	10	19.7	20.7						
4	0	10	25.1	24.7						
1	1	10	31.3	29.4						
3	1	10	22.2	22.7						
0	2	10	7.4	4.6						
2	2	10	18.5	19.2						
4	2	10	22.8	24.9						
1	3	10	15.5	14.2						
3	3	10	73.6	77.0						
0	4	10	16.5	15.3						
2	4	10	20.8	20.1						
4	4	10	17.2	17.5						
1	5	10	9.9	8.2						
3	5	10	24.6	25.5						
0	6	10	56.9	55.8						
2	6	10	2.6 *	4.0						
4	6	10	12.3	12.5						
1	7	10	12.1	11.6						
3	7	10	38.1	38.5						
0	8	10	30.8	29.4						
2	8	10	12.9	12.4						
1	9	10	10.4	9.2						
0	10	10	60.5	59.1						
0	0	11	5.0	0.0						
2	0	11	12.5	12.6						
1	1	11	36.1	34.2						
3	1	11	8.1	6.3						
0	2	11	7.6	6.3						
2	2	11	23.3	23.6						
1	3	11	56.8	53.4						