

The crystal structure of jordanite, $\text{Pb}_{28}\text{As}_{12}\text{S}_{46}$ *

By TETSUZO ITO** and WERNER NOWACKI

Abteilung für Kristallographie und Strukturlehre, Universität Bern

(Received 7 June 1973)

Auszug

Natürlicher Jordanit aus dem Binnatal (Schweiz) ist monoklin, Raumgruppe $P2_1/m$, mit $a = 8,918(1)$, $b = 31,899(4)$, $c = 8,462(1)$ Å und $\beta = 117,79(1)^\circ$. Die Elementarzelle ist entlang der a - und der c -Achse ungefähr halbiert. Von der Viertel-Struktur ausgehend wurde die vollständige Struktur mittels einer Art Minimal-Residual-Methode (der Methode der Hauptverschiebungen) gelöst und durch gewöhnliche Fourier- und Kleinste-Quadrate-Methoden bis zu $R = 7,0\%$ verfeinert.

Die Jordanitstruktur ist ein deformierter PbS-Strukturtyp. Die Elementarzelle enthält 40 Me- und 46 S-Atomlagen. Die 12 unabhängigen Me-Lagen verteilen sich auf drei Schichten $y \approx 0,05$, $\approx 0,15$ und $\approx 0,25$ (die Spiegelebene), mit vier Me-Lagen, 3 Pb + As, in jeder Schicht. Zwischen diesen Me-Schichten befinden sich S-Schichten; drei zusätzliche S-Atome liegen in der dritten Me-Schicht, die eine gemischte (Me-S)-Schicht darstellt. Einige der Lagen sind statistisch besetzt; eine Pb-Lage der ersten Schicht ist von 0,50 Pb + 0,50 As, eine andere Pb-Lage in der dritten Schicht von 0,88 Pb besetzt. Dies ergibt eine Formel­einheit von $\text{Pb}_{27,8}\text{As}_{12,0}\text{S}_{45,8}$ pro Elementarzelle, mit der idealen Formel $\text{Pb}_{28}\text{As}_{12}\text{S}_{46}$.

Die voll besetzten Pb-Lagen der ersten, zweiten bzw. dritten Schicht sind von sechs [mittlerer (Pb—S)-Abstand = 3,01 Å], sieben [3,04 Å] bzw. acht [3,08 Å] S-Atomen koordiniert. Die S-Koordination um die As-Atome ist trigonal-pyramidal mit einem mittleren (As—S)-Abstand von 2,25 Å. Die AsS_3 -Pyramiden sind voneinander getrennt (Typus $I.c_1$ der Klassifikation von NOWACKI).

Abstract

Natural jordanite from Binnatal, Switzerland is monoclinic, space group $P2_1/m$, with $a = 8.918(1)$, $b = 31.899(4)$, $c = 8.462(1)$ Å and $\beta = 117.79(1)^\circ$.

* Contribution no. 233; paper no. 69 on sulfides. — Preliminary communication in *Wiss. Verh. Schweiz. Natf. Gesellschaft, Luzern, 1972*.

** Present address: The Institute of Physical and Chemical Research, Rikagakukenyusho, Wako-shi, Saitama, 351 Japan.

The unit cell is approximately halved along both the a and c axes. Starting from the one-fourth substructure, the complete structure was solved by a kind of minimum residual method (the method of key shifts), and was refined by ordinary Fourier and least-squares methods ($R = 7.0\%$).

The structure of jordanite is a deformed PbS-type structure. The unit cell contains 40 metal and 46 sulfur atom sites. The twelve independent metal sites are distributed on three layers at $y \approx 0.05$, ≈ 0.15 and ≈ 0.25 (the mirror plane), with four metal sites, 3 Pb + As, on each layer. These metal layers are interleaved by sulfur layers; three additional S atoms are added to the third metal layer to form a metal-sulfur mixed layer. Some of the sites have statistical nature; one Pb site on the first layer is occupied by 0.50 Pb + 0.50 As, another Pb site on the third layer is occupied by 0.88 Pb. Thus, the unit-cell content is $\text{Pb}_{27.8}\text{As}_{12.0}\text{S}_{45.8}$, with the ideal formula $\text{Pb}_{28}\text{As}_{12}\text{S}_{46}$.

The fully occupied Pb atoms on the first, second and the third layers are coordinated with six (average Pb—S = 3.01 Å), seven (3.04 Å) and eight (3.08 Å) S atoms, respectively. The sulfur coordinations about the As atoms are ordinary trigonal pyramids with an average As—S = 2.25 Å. The AsS_3 pyramids are isolated from each other (type I.c.1 of the classification of NOWACKI).

Introduction

The precise chemical composition of jordanite has been the subject of considerable discussion (SOLLY, 1900; PALACHE, RICHMOND and WINCHELL, 1938; FISHER, 1940; PEACOCK and BERRY, 1940; DOUGLASS, MURPHY and PABST, 1954; WUENSCH and NOWACKI, 1966). The formulae which have been proposed on the basis of the chemical analyses of natural material can be summarized by the range of composition $\text{Pb}_{26-28}\text{As}_{14}\text{S}_{46-49}$. On the other hand, ROLAND (1968) proposed a new formula, $\text{Pb}_{28-x}\text{As}_{12}\text{S}_{46-x}$ [$0.8 < x < 1.4$], from silica-tube quenching experiments and density measurements of synthetic jordanite; moreover, he concluded that jordanite is most probably a high-temperature dimorph of gratonite, $\text{Pb}_{27}\text{As}_{12}\text{S}_{45}$, the structure of which has been established by x-ray work (RIBÁR and NOWACKI, 1969; RÖSCH, 1963). More recently, however, KUTOGLU (1969) proposed an older formula, $\text{Pb}_{27}\text{As}_{14}\text{S}_{48}$, for synthetic jordanite.

Jordanite is a typical superstructure based on the PbS-type substructure. The unit cell is approximately halved along both the a and c axes. The one-fourth substructure (the average atomic arrangement over four closely related subcells) has been determined by WUENSCH and NOWACKI (1966). The present paper deals with the structure determination of the complete structure of natural jordanite. As described below, the obtained unit-cell content is $\text{Pb}_{27.8}\text{As}_{12.0}\text{S}_{45.8}$, with the ideal formula, $\text{Pb}_{28}\text{As}_{12}\text{S}_{46}$.

Crystal data

A specimen of jordanite (sample code Jord. Nr. 1) from Binnatal, Switzerland was used for the present investigation. A fragment was cut out of the specimen with a razor, and it was made into a sphere with a radius of 0.078 mm by BOND's (1951) method. The powder attached to the surface was dissolved away with a hot aqueous HNO_3 solution. Diffraction patterns showed jordanite to be monoclinic. The lattice constants were obtained from three equatorial Weissenberg photographs (about a , b and $[201]$ axes), taken with a back-reflection double-radius camera. Diffraction patterns of Si powder ($a = 5.43074 \text{ \AA}$) were used for calibration. The wave lengths used were 1.54051 and 1.54433 \AA for $\text{CuK}\alpha_1$ and α_2 radiations, respectively. The results of the least-squares calculations agree fairly well with those given by NOWACKI, ITAKA, BÜRKI and KUNZ (1961) (Table 1)¹.

As was already pointed out by DOUGLASS, MURPHY and PABST (1954), the set of lattice constants given in Table 1 (the reduced cell of jordanite) should carefully be distinguished from another very similar set: $a' = 8.987(1) \text{ \AA}$, $\beta' = 118.61(1)^\circ$, $b' = b$, $c' = c$ and $V' = V$. The transformation is given by: $\mathbf{a}' = \mathbf{a} + \mathbf{c}$, $\mathbf{b}' = -\mathbf{b}$ and $\mathbf{c}' = -\mathbf{c}$.

The observed systematic absences of reflections were only $0k0$ with k odd. Therefore, permitted space groups are $P2_1$ or $P2_1/m$. Since the mineral is not piezoelectric (NOWACKI *et al.*, 1961) and possesses morphology of symmetry $2/m$, the space group was assumed to be $P2_1/m^2$.

Table 1. Lattice constants of jordanite

	Jordanite		Galena*
	Present work	NOWACKI <i>et al.</i> (1961)	
a	8.918(1) \AA	8.96(4) \AA	8.39 \AA
b	31.899(4)	31.92(1)	34.24
c	8.462(1)	8.45(3)	8.39
β	117.79(1)°	117° 50(10)'	120°
V	2129.5 \AA^3	2137.1 \AA^3	2085.3 \AA^3

* $a = [\bar{1}\bar{1}0]_{\text{Pbs}}$, $b = (10/3) [111]_{\text{Pbs}}$ and $c = [\bar{1}01]_{\text{Pbs}}$, where $a_{\text{Pbs}} = 5.93 \text{ \AA}$.

¹ Throughout the paper, the estimated standard deviations are given in parentheses in an abbreviated form; for example, 8.918(1) means 8.918 ± 0.001 .

² The results of the present analysis do not rule out the other possible space group $P2_1$. However, even if the correct space group is $P2_1$, deviation from the symmetry of $P2_1/m$ seems to be hardly significant (see also the footnote ⁴).

Since chemical and microprobe analyses on natural jordanite from Binnatal have detected at most negligible amount of Sb (cf. Table 7), it was assumed that the crystal used did not contain Sb.

Intensity measurements

The intensities were measured with an automatic diffractometer of the equi-inclination type (Buerger-Supper-Pace) using Ni-filtered $\text{CuK}\alpha$ radiation. The diffracted beams were detected with a proportional counter. The spherical crystal was rotated in the ω -scan mode about the b (0 to 37th layers) and the a (0 to 9th layers) axes. The scanning speed was varied from 0.5° (for higher angles) to 1.0° per minute (for lower angles). The background was measured before and after each Bragg reflection for the time approximately equal to the scan time of the reflection. About 4000 independent reflections were measured, of which 3200 were considered to be observed [$I > 2.33\sigma(I)$]. They were corrected for Lorentz, polarization and absorption (sphere with $\mu r = 9.7$ for $\text{CuK}\alpha$ radiation) effects.

Structure determination

Approximate structure

Starting from the one-fourth substructure of WUENSCH and NOWACKI (1966), an approximate complete structure of jordanite was solved by a kind of minimum residual method (the method of key shifts; ITO, 1973). Since the procedure of key shifts of jordanite is described in detail in the above reference, only the results of the analysis are given in Table 2. The R value at this stage was 33% for all 3200 observed reflections.

Isotropic refinement

The approximate structure was refined by least-squares (block-diagonal approximation) and Fourier methods. In the least-squares calculations, unit weights were given to all reflections, and the atomic scattering factors for the neutral atoms were used³. Two cycles of isotropic refinement of the twelve metal atoms of Table 2 reduced R from 33 to 28%. The B value of As(11) showed tendency to diverge and that of Pb(12), which had been considered to be As, became exceptionally low (0.5 \AA^2). The corresponding Fourier map also gave a very

³ *International tables for x-ray crystallography* (1962), Vol. III, pp. 202 (S and As) and 210 (Pb). Birmingham: Kynoch Press.

Table 2. *Approximate coordinates of jordanite as deduced by the method of key shifts*
 The overall temperature factor used was $B = 1.7 \text{ \AA}^2$

Designation of atoms		x/a	y/b	z/c
this paper	Ito (1973)			
Pb(1)	Pb(111)	0.440	0.059	0.346
Pb(2)	Pb(112)	440	048	831
Pb(3)	Pb(121)	912	041	322
As(4)	As(122)	912	046	822
Pb(5)	Pb(211)	266	140	001
As(6)	As(212)	266	140	501
Pb(7)	Pb(221)	794	150	017
Pb(8)	Pb(222)	794	150	517
Pb(9)	Pb(311)	131	250	162
Pb(10)	Pb(312)	116	250	677
As(11)	As(321)	543	250	147
Pb(12)	As(322)	543	250	647

low peak for As(11) and a high peak for Pb(12). At the same time, the map revealed ten reasonable sulfur peaks. Therefore, in the next cycle, As(11) was eliminated, the atomic species of Pb(12) was changed from As to Pb and the ten S atoms, S(1) to S(10), were added (altogether 21 atoms). After additional four cycles, R was 17%. In the Fourier map, As(11) disappeared from the mirror plane; instead, three additional sulfur peaks surrounding the absent As(11) position in a triangular arrangement appeared on the plane. In addition, a peak with approximately the same peak height as that of a sulfur atom appeared about 0.7 Å below (by symmetry also above) the As(11) position; the peak together with the above three sulfur peaks formed a trigonal pyramid typical for the AsS_3 pyramid. Therefore, the peak was assigned as As with half occupancy; As(11) now split into two halves and the three S atoms, S(11) to S(13), were added in the next cycle (altogether 25 atoms). A few cycles of least-squares refinement together with the Fourier maps indicated that S(11) had also to be split into two halves, about 0.4 Å above and below the mirror plane. The R value at this stage was 11%.

Refinement of site occupancy

The results of the least-squares refinement ($R = 11\%$) gave abnormally high B values for Pb(2) and Pb(12) (3.9 and 3.2 Å², respectively). Both atoms were coordinated with six S atoms. The coordina-

tion about Pb(2) was an intermediate one between typical coordinations of Pb and As; the Pb—S distances were about 2.6 and 3.0 Å for the three shorter and three longer bonds, respectively. On the other hand, the coordination about Pb(12) was a typical one for Pb with the six Pb—S distances of about 3.0 Å. Therefore, it was assumed that the Pb(2) site was statistically occupied by Pb and As, and the Pb(12) site was fractionally occupied by Pb. The occupancies of the two sites were then refined in combination with the isotropic temperature factor of each site by a least-squares method (2×2 block-diagonal approximation). As for the Pb(2) site, preliminary calculations indicated that the distribution was approximately 0.5 Pb + 0.5 As. Therefore, the number of electrons of the site was refined using a unitary atomic scattering factor, $f = \{f(\text{Pb}) + f(\text{As})\}/(82 + 33)$, in a similar way as was applied to binnite by WUENSCH, TAKÉUCHI and NOWACKI (1966).

Table 3. Atomic coordinates of jordanite with standard deviations

Atom	x/a	y/b	z/c
Pb(1)	0.4469(2)	0.05466(4)	0.3504(2)
Pb(2)	4392(2)	05194(8)	8422(3)
Pb(3)	9040(2)	04119(4)	3167(2)
As(4)	9194(4)	05256(10)	8299(4)
Pb(5)	2648(2)	14226(5)	-0028(2)
As(6)	2758(5)	14284(12)	5082(5)
Pb(7)	7904(2)	15071(4)	0176(2)
Pb(8)	7925(2)	15021(4)	5149(2)
Pb(9)	1222(3)	25	1714(3)
Pb(10)	1215(3)	25	6896(3)
As(11)	6158(9)	2265(2)	1766(10)
Pb(12)	5504(4)	25	6395(4)
S(1)	3095(9)	0031(3)	0123(11)
S(2)	3067(10)	0051(3)	5504(12)
S(3)	0460(9)	0862(2)	1005(10)
S(4)	0511(9)	0853(2)	6864(11)
S(5)	6520(9)	0969(3)	2028(10)
S(6)	6733(9)	0910(2)	7073(11)
S(7)	4061(10)	1767(3)	3744(12)
S(8)	4021(11)	1774(3)	7699(11)
S(9)	0307(9)	1791(3)	3838(10)
S(10)	9940(10)	1935(2)	8688(11)
S(11)	3783(17)	2617(4)	055(2)
S(12)	7520(15)	25	032(2)
S(13)	7521(15)	25	455(2)

Table 4. Thermal parameters of jordanite with standard deviations

The thermal parameters refer to the expression:

$$T = \exp \{-2\pi^2 (b_{11}h^2a^{*2} + \dots + 2b_{12}hka^*b^* + \dots)\}$$

B_{eq} is the equivalent isotropic temperature factor.

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	B_{eq}
Pb(1)	0.0203(6)	0.0191(5)	0.0215(6)	0.0032(5)	0.0082(5)	0.0012(5)	1.65 Å ²
Pb(2)	129(9)	469(15)	153(9)	— 70(8)	54(7)	— 111(9)	2.01
Pb(3)	143(5)	232(5)	206(6)	20(5)	43(5)	7(5)	1.65
As(4)	68(14)	93(15)	141(16)	— 4(12)	30(13)	— 28(13)	0.85
Pb(5)	197(6)	361(10)	219(7)	74(6)	79(5)	63(6)	2.10
As(6)	158(17)	.018(2)	.019(2)	24(15)	39(14)	33(15)	1.54
Pb(7)	192(6)	191(5)	190(6)	3(5)	80(5)	2(5)	1.54
Pb(8)	180(6)	165(5)	162(6)	— 1(5)	65(5)	— 1(5)	1.38
Pb(9)	225(9)	258(10)	208(9)	0	80(8)	0	1.88
Pb(10)	233(9)	237(10)	232(9)	0	114(8)	0	1.83
As(11)	.015(3)	.007(4)	.022(4)	.001(3)	.005(3)	— .000(3)	1.25
Pb(12)	.0404(14)	.0160(10)	.0388(14)	0	.0172(12)	0	2.55
S(1)	.003(3)	.022(4)	.018(4)	.001(3)	— .002(3)	— .011(3)	1.34
S(2)	10(3)	11(4)	29(4)	2(3)	12(3)	7(3)	1.22
S(3)	7(3)	12(4)	9(3)	— 4(3)	— 2(3)	— 1(3)	0.89
S(4)	9(3)	11(4)	18(4)	1(3)	9(3)	1(3)	0.88
S(5)	10(3)	16(4)	8(3)	— 7(3)	— 1(3)	— 1(3)	1.04
S(6)	9(3)	9(4)	16(4)	2(3)	6(3)	2(3)	0.87
S(7)	7(4)	37(5)	22(4)	5(4)	8(3)	1(4)	1.71
S(8)	21(4)	17(4)	11(4)	5(3)	5(3)	5(3)	1.38
S(9)	2(3)	16(4)	13(4)	0(3)	2(3)	1(3)	0.86
S(10)	16(4)	8(4)	15(4)	— 1(3)	11(3)	— 4(3)	0.92
S(11)	6(6)	6(8)	15(7)	— 4(4)	2(5)	2(5)	0.79
S(12)	7(5)	38(8)	23(6)	0	7(5)	0	1.79
S(13)	13(5)	17(6)	26(6)	0	6(5)	0	1.56

The crystal structure of jordanite

Table 5. (Continued)

k	$ F_o $	F_c	k	$ F_o $	F_c	k	$ F_o $	F_c	k	$ F_o $	F_c	k	$ F_o $	F_c	k	$ F_o $	F_c	k	$ F_o $	F_c								
5	398	-398	29	50	46	33	87	-98	2	k	2	5	k	2	-9	k	3	9	45	-33	28	22	20					
6	85	-87	30	51	-48	34	133	-105										10	41	64	30	38	-40					
7	49	-45	31	19	13	35	31	-26	0	937	-933	0	325	333	0	56	60	12	32	-34	31	167	-73					
8	48	-37	32	37	37	36	89	95	1	290	282	2	64	-35	1	47	98	12	106	103	32	37	35					
9	88	88		-4	k	2	37	63	-81	2	57	-42	3	55	-34	2	39	37	13	122	-127	34	23	-22				
10	29	-29							3	75	69	4	68	65	3	55	55	14	39	25	35	46	-55					
11	59	-58	0	855	894		-1	k	2	4	36	30	5	53	-36	4	43	64	15	49	40							
12	33	-33	1	340	361	1	140	-153	5	85	-95	6	52	-47	5	29	12	16	88	85		-1	k	3				
13	101	93	2	70	68	9	52	-41	7	52	44	7	40	-40	6	57	-56	17	52	43	0	39	31					
14	322	329	3	90	10	11	309	399	8	43	-35	8	36	-22	7	44	49	18	43	42	2	81	66					
15	31	25	5	76	-83	12	34	36	9	147	153	9	160	-155	9	28	22	20	40	-37	3	57	64					
16	83	-83	7	46	-33	17	32	27	10	691	686	10	394	-398	10	37	-28	21	39	43	25	139	-128					
17	85	-25	9	232	234	19	34	-14	11	194	-202	11	40	-26	11	34	26	22	55	-44	27	29	27					
18	15	-25	9	232	234	19	34	-14	11	194	-202	11	40	-26	11	34	26	22	55	-44	27	29	27					
19	100	-103	10	644	-650	21	330	-347	12	44	39	13	108	119	14	36	-29	23	87	87	8	63	-57					
20	43	44	11	247	-244	22	25	-26	13	71	-67	14	103	-101	17	21	-15	24	21	-10	12	87	-84					
21	23	25	12	59	-47	23	59	55	14	54	-57	15	48	-55	18	38	42	26	97	-101	13	146	-153					
22	64	-39	13	83	-84	27	28	-35	15	68	-74	17	33	34	19	60	-41	27	45	-9	14	114	-113					
23	64	-39	13	83	-84	27	28	-35	15	68	-74	17	33	34	19	60	-41	27	45	-9	14	114	-113					
24	64	-39	13	83	-84	27	28	-35	15	68	-74	17	33	34	19	60	-41	27	45	-9	14	114	-113					
25	73	69	14	56	30	29	31	-24	16	35	-19	19	92	86	20	33	30	28	64	-69	16	152	-154					
26	285	-282	16	39	27	31	303	324	19	108	-114	21	82	80				30	56	-53	19	57	59					
27	29	-26	18	71	-69	32	31	17	20	460	-453	22	115	-114	0	44	18	31	52	-62	20	95	-95					
28	53	53	19	181	-180	33	76	80	21	299	206	24	21	14	1	46	45	32	28	11	22	95	100					
29	44	-38	20	441	432	35	35	-31	22	102	-95	25	47	48	2	31	-10	33	78	-84	23	148	149					
30	72	-70	21	218	212	36	12	-6	23	152	145	27	27	8	3	57	58				24	60	70					
31	54	56	22	101	103	37	46	64	24	32	24	28	24	18	4	76	-86				25	51	-51					
32	31	-36	23	150	150		0	k	2	25	52	-57			5	26	-13	0	46	45	26	109	120					
33	43	25	23	48	-49				26	41	37			6	k	2	6	87	84	11	75	31	-18					
34	192	-180	26	42	-44	0	147	152	28	89	-94	0	30	11	7	71	69	2	51	-54	28	70	74					
35	356	354	28	84	88	1	89	-91	29	52	49	1	90	85	9	25	12	3	119	-126	29	54	-58					
36	40	-39	29	90	90	2	170	-179	30	251	254	2	23	-22	10	29	-26	4	103	-108	30	52	49					
37	88	99	30	231	-241	3	398	388	31	126	-124	3	36	-33	11	50	42	5	47	-60	31	17	8					
38	107	100	31	128	-129	4	461	-471	32	30	-36	4	38	39	12	37	-12	102	-106	32	43	-47						
39	15	42	-39	33	29	-31	5	178	172	34	48	-41	5	379	-384	15	43	29	8	56	-55	33	81	-90				
40	37	34	34	42	30	6	330	329	35	55	55	6	57	55	16	36	-21	10	31	-27	34	42	-44					
41	112	102	35	33	34	7	546	546		3	k	2	7	42	-18	17	44	-50	11	63	-68		0	k	3			
42	244	-241		-3	k	2	8	312	314		1	80	80	9	9	32	11	18	33	-22	13	85	73		0	221	226	
43	56	51				9	97	-102				10	80	9	9	32	11	18	33	-22	13	85	73					
44	130	138	3	229	-218	10	162	-172	2	71	70	11	56	-58	20	43	-33	16	22	-24	1	66	56					
45	48	48	4	224	231	11	109	105	3	207	-211	12	29	24	21	112	-111	17	120	130	2	48	65					
46	20	19	5	99	-97	12	110	109	4	196	192	14	127	-123	22	45	41	18	32	-18	8	40	27					
47	26	8	6	107	-115	13	352	-358	5	103	-109	15	312	315	23	27	-17	21	63	66	9	71	76					
48	26	8	6	107	-115	13	352	-358	5	103	-109	15	312	315	23	27	-17	21	63	66	9	71	76					
49	26	8	6	107	-115	13	352	-358	5	103	-109	15	312	315	23	27	-17	21	63	66	9	71	76					
50	171	-176	11	70	-64	16	216	-218	8	57	-70	19	101	-104				24	76	-72	13	67	-49					
51	263	263	13	162	169	17	251	-250	9	54	49	20	32	-22				25	31	30	14	69	-54					
52	328	-317	14	139	-152	18	137	-162	10	25	24	21	40	41	0	30	27	26	37	-40	18	85	-87					
53	167	144	15	188	190	19	109	-115	11	55	-52	22	28	-20				-36	27	64	-52	19	47	-47				
54	199	196	16	90	91	20	143	145	12	60	-54	24	88	83	3	63	63	28	28	-13	20	73	71					
55	140	-131	17	56	-62	21	98	-67	13	104	87	25	198	-214	4	45	-44	30	17	-21	22	47	44					
56	273	-276	18	163	-163	22	46	-41	14	50	-47				7	k	2	5	72	79	-38	24	105	89				
57	284	-289	19	135	-132	23	239	235	15	45	-45				6	49	-42	33	22	-5	25	33	-35					
58	220	-216	21	97	98	24	283	-281	16	303	296	0	84	91	7	84	89	34	31	25	27	27	31					
59	43	-30	23	189	-190	25	57	-51	17	300	300	1	70	72	9	29	-27				28	88	-83					
60	114	119	24	214	215	26	184	185	18	162	152	2	110	115	11	33	27	-3	k	3	30	35	-23					
61	140	-134	25	159	-160	27	110	108	19	32	-23	3	181	191	12	45	42	0	143	146	31	70	72					
62	191	192	26	26	9	28	116	127	20	50	-40	4	101	106	14	72	61	1	64	-68	33	66	68					
63	70	-72	27	77	74	29	81	-75	21	36	25	21	36	-25	34	34	-34				34	35	17	-19				
64	173	-174	28	113	120	30	60	-62	22	51	48	6	101	-99	16	66	59	6	21	20								
65	110	100	29	113	112	31	55	61	23	34	-30	7	149	154	17	42	-41	7	43	-23		1	k	3				
66	187	185	30	49	39	32	25	-22	24	33	11	8	45	-41	20	45	42	8	26	26	0	61	-55					
67	225	-218	31	167	-173	33	113	-122	25	85	78	9	36	31	22	31	-25	9	183	-181	1	61	-74					
68	180	177	32	46	-35	34	134	162	26	185	-185	10	47	-38	23	32	-33	10	41	-29	2	96	82					
69	33	32	33	118	126	35	23	-21	27	208	-211	12	107	-111	24	65	-67	12	90	97	4	45	-31					
70	36	-30	34	115	-111	36	74	-75	28	24	-13	13	198	-204	26	92	-98	13	53	-50	5	110	111					
71	54	49	35	78	75	37	67	-83	29	42	40	14	113	-115	27	63												

