

## The crystal structure of hodgkinsonite



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With 8 figures

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### Auszug

Hodgkinsonit,  $\text{Zn}_2\text{Mn}[(\text{OH})_2|\text{SiO}_4]$ , ist ein pneumatolytisches Mineral von Franklin, New Jersey, mit Gitterkonstanten:  $a = 8,171$ ,  $b = 5,316$ ,  $c = 11,761 \text{ \AA}$ ,  $\beta = 95^\circ 15'$ ;  $Z = 4$ , Raumgruppe  $P2_1/a$ . Die Intensitäten der Reflexe  $hkl$  wurden mit Hilfe eines Einkristall-Zählrohr-Diffraktometers (equi-inclination) gemessen. Die Struktur wurde aus der dreidimensionalen Patterson-Synthese mit Hilfe der Minimum-Funktion ermittelt. Atom-Koordinaten und isotrope Temperaturfaktoren wurden nach der Methode der kleinsten Quadraten bis zu  $R = 0,067$  verfeinert. Korrektur für anomale Dispersion in bezug auf die Mn-Atome wurde berücksichtigt.

Das  $\text{SiO}_4$ -Tetraeder ist fast regelmäßig mit mittlerem Si—O Abstand  $1,626 \text{ \AA}$  und O—O Abstand  $2,655 \text{ \AA}$ . Die zwei Zn-Atome sind von vier O-Atomen in Form eines verzerrten Tetraeders umgeben; mittlere Zn—O-Abstände  $1,969 \text{ \AA}$  und  $1,974 \text{ \AA}$  und O—O-Abstände  $3,211 \text{ \AA}$  und  $3,216 \text{ \AA}$ . Das Mn-Atom ist von fünf OH-Gruppen und einem O-Atom umgeben, welche ein ziemlich stark verzerrtes Oktaeder bilden. Mittlerer Mn—O Abstand  $2,222 \text{ \AA}$  und O—O Abstand  $3,133 \text{ \AA}$ . Die  $\text{ZnO}_4$ -Tetraeder haben mit den  $\text{SiO}_4$ -Tetraedern eine gemeinsame Spitze und formen zweidimensionale  $\text{Zn}_2\text{SiO}_4$ -Netze, (A), parallel (001). Ähnlicherweise bilden die  $\text{MnO}_6$ -Oktaeder zweidimensionale Netze, (B), parallel (001), welche zwei  $\text{Zn}_2\text{SiO}_4$ -Netze verbinden. Das Bauprinzip ist  $\dots ABAABA \dots$  der  $c$ -Achse entlang. Es besteht keine Isotypie zwischen Hodgkinsonit und Norbergit,  $\text{Mg}_3[(\text{OH})_2|\text{SiO}_4]$ ; das Mineral gehört der Humit-Gruppe nicht an.

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### Abstract

Hodgkinsonite,  $\text{Zn}_2\text{Mn}[(\text{OH})_2|\text{SiO}_4]$ , is a pneumatolytic mineral of Franklin, New Jersey, with lattice constants:  $a = 8.171$ ,  $b = 5.316$ ,  $c = 11.761$  Å,  $\beta = 95^\circ 15'$ ;  $Z = 4$ , space group  $P2_1/a$ . Intensities  $hkl$  were collected with a single-crystal equi-inclination diffractometer. The structure was obtained from the three-dimensional Patterson synthesis by applying the minimum function. Atomic parameters and isotropic temperature factors were refined by least squares to  $R = 0.067$ . Correction for anomalous scattering of the Mn atoms was applied.

The  $\text{SiO}_4$  tetrahedron is almost regular with an average Si—O distance of 1.626 Å and average O—O distance of 2.655 Å. The two Zn atoms are surrounded by four O atoms forming a distorted tetrahedron. Average Zn—O distances are 1.969 Å and 1.974 Å and O—O distances 3.211 Å and 3.216 Å respectively. The Mn atom is octahedrally coordinated by five OH groups and one O atom. The average Mn—O distance is 2.222 Å and the corresponding O—O distance is 3.133 Å. The  $\text{ZnO}_4$  tetrahedra share a corner with the  $\text{SiO}_4$  tetrahedra and form two-dimensional networks  $\text{Zn}_2\text{SiO}_4$ , (*A*), parallel to (001). Similarly the  $\text{MnO}_6$  octahedra form two-dimensional networks, (*B*), extending parallel to (001), and link two  $\text{Zn}_2\text{SiO}_4$  networks together. The structural principle is . . . *ABAABA* . . . in the direction of the *c* axis. Hodgkinsonite is not isotypic with norbergite,  $\text{Mg}_3[(\text{OH})_2|\text{SiO}_4]$ , and does not belong to the humite group.

### Introduction

Hodgkinsonite,  $\text{Zn}_2\text{Mn}[(\text{OH})_2|\text{SiO}_4]$ , is a pink pneumatolytic mineral found at Franklin, New Jersey, U.S.A., in association with other zinc minerals, mostly franklinite and willemite. It was discovered by H. HODGKINSON and first studied morphologically and chemically by PALACHE and SCHALLER (1913), who named the mineral after its discoverer. Detailed optical, morphological and chemical study of the mineral, alone or in connection with other minerals from Franklin, was reported at various times again by PALACHE (1914, 1928, 1935). Recent reexamination of hodgkinsonite crystals by ROBERTS and QUODLING (1962) gave almost identical results. The crystals are monoclinic, usually elongated along the *c* axis, with a perfect (001) cleavage.

X-ray data concerning the unit cell and space group of hodgkinsonite were first given by the author (RENTZEPERIS, 1958). Part of corresponding data recently published by ROBERTS and QUODLING (1962) must, for reasons explained below, be considered as erroneous.

From the similarity of the chemical formula of hodgkinsonite with that of norbergite,  $\text{Mg}_2\text{Mg}[(\text{OH})_2|\text{SiO}_4]$  the mineral has been considered isotypic with the latter and grouped with the humite family. However, as hodgkinsonite is monoclinic and norbergite orthorhombic, and as,

in many instances, Zn behaves differently from Mg, it was thought very probable that hodgkinsonite might have a different structure from that of norbergite, and this actually proved to be the case. And since the high refractive index ( $\sim 1.74$ ) indicated a very probable oxygen substructure, the mineral was considered as very suitable for testing the resolving power of the three-dimensional minimum function (BUERGER, 1959) in such instances.

### Experimental

The desirability of having accurate settings for the single-crystal equi-inclination diffractometer used for collecting intensities led to a careful redetermination of the unit-cell constants with a precession camera and  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The new data differ only slightly from those already published by the author (RENTZEPERIS, 1958), the differences being within the experimental errors of the methods used then:

$$\begin{array}{ll} a = 8.170 \pm 0.002 \text{ \AA} & \beta = 95^\circ 15' \pm 5' \\ b = 5.316 \pm 0.002 \text{ \AA} & V = 508.67 \text{ \AA}^3 \\ c = 11.761 \pm 0.002 \text{ \AA} & a:b:c = 1.5370:1:2.2124 \end{array}$$

The angle  $\beta$  and the axial ratios are in very good agreement with those found by PALACHE (1914):  $\beta = 95^\circ 25'$ ,  $a:b:c = 1.538:1:1.1075$ . As in numerous other cases the  $c$  axis of the morphological result proves to be half its true value.

ROBERTS and QUODLING (1962) give the following values for the cell constants:  $a = 8.12 \pm 0.05 \text{ \AA}$ ,  $b = 5.30 \pm 0.05 \text{ \AA}$ ,  $c = 11.71 \pm 0.05 \text{ \AA}$ ,  $\beta = 95^\circ 15'$ . The values for  $a$  and  $c$  are so close to the value of

$$d_{100} = a \sin \beta = 8.136 \text{ \AA} \quad d_{001} = c \sin \beta = 11.712 \text{ \AA},$$

found in this investigation, that it seems almost certain that ROBERTS and QUODLING have actually reported their  $d_{100}$  and  $d_{001}$  values instead of  $a$  and  $c$ . Their proposed reorientation of the crystal axes by interchanging  $a$  and  $c$  in the original setting by PALACHE and SCHALLER (1913) cannot be considered as actually necessary.

For a unit-cell content of four formula units, a density of  $4.07 \text{ g} \cdot \text{cm}^{-3}$  is deduced, which compares well with  $3.91 \text{ g} \cdot \text{cm}^{-3}$  given by PALACHE and SCHALLER (1913),  $3.99 \text{ g} \cdot \text{cm}^{-3}$  by ROBERTS and QUODLING (1962) and  $4.01 \text{ g} \cdot \text{cm}^{-3}$  found by us with the help of a Clerici solution.

The observed reflections were:  $hkl$ , no conditions;  $0kl$ , no conditions;  $h0l$ ,  $h = 2n$ ;  $hk0$ , no conditions;  $0k0$ ,  $k = 2n$ . The only possible space group is  $P2_1/a$ .

At first an attempt was made to solve the structure by using two-dimensional data obtained from small, almost cylindrical, crystals by precession and Weissenberg methods. As no satisfactory solution was obtained in this way it was thought best to proceed with three-dimensional data. Small spheres of hodgkinsonite were ground in a device similar to that described by BOND (1951). A sphere of radius  $R = 0.185$  mm was selected and mounted optically along the shortest axis,  $b$ . Intensities were collected with a single-crystal equi-inclination diffractometer (BUERGER, 1960) using  $\text{CuK}\alpha$  radiation. The response of the Geiger counter was kept linear during all the measurements by using Al foils of measured absorption coefficient. The counting rate was always below 400 counts/second.

The diffractometer settings  $\gamma$  and  $\varphi$  were computed on the IBM 7090 computer at M.I.T. using the program written by PREWITT (1960, 1962). Six levels were measured with a total of 946 accessible reflections, none of which was actually zero. Intensities were measured as follows: using the suitable Al foil the background count for 100 sec was first obtained, then the reflection was scanned slowly (2/3 degree/min), and lastly the background on the other side of the reflection was measured again. The reproducibility of the measurements was of the order of 1 to 2%. The integrated intensity was obtained from

$$I = C - \left( \frac{B_1 + B_2}{2} \right) \cdot \frac{T}{100}$$

where  $C$  is the total count of the peak,  $B_1$  and  $B_2$  the background counts before and after the measurement of the peak, and  $T$  the time required to scan the peak. This data reduction was done on the IBM 7090 computer using the program DTRDA by BURNHAM (1961). The integrated intensities obtained from DTRDA were further corrected for spherical absorption and  $Lp$  factor using the program DTRDB by BURNHAM and a special program for spherical absorption by PREWITT (1962). Hodgkinsonite absorbs Cu radiation rather highly, having  $\mu = 344.80 \text{ cm}^{-1}$ , and for the sphere used,  $\mu R = 6.378$ . The values of the absorption coefficient  $A$  were obtained from the International Tables (1959).

All subsequent computations were carried out on the IBM 7090 computer at the Computation Center of M.I.T.

### Determination of the structure

A three-dimensional Patterson synthesis with sections normal to the  $b$  axis and at intervals of  $1/60$  along the three axes was computed using the program ERFR2 written by SLY, SHOEMAKER and VAN DEN HENDE (1962). Figures 1, 2, and 3 show three sections of the Patterson function at heights  $y = 0, 8/60$  and  $1/2$  (Harker section).

The general approach to the solution of the Patterson synthesis was as follows: Since the equipoints of the general position in space group  $P2_1/a$  are

$$x, y, z; \quad \bar{x}, \bar{y}, \bar{z}; \quad \frac{1}{2} - x, \frac{1}{2} + y, \bar{z}; \quad \frac{1}{2} + x, \frac{1}{2} - y, z;$$

it follows that an atom at a general position  $xyz$ , with its symmetry equivalent atoms, gives rise to the following peaks in the Patterson space:

- inversion peak at  $2x, 2y, 2z$ , of weight 1
- rotation peak at  $\frac{1}{2} - 2x, \frac{1}{2}, 2z$ , of weight 2 (Harker section)
- reflection peak at  $\frac{1}{2}, \frac{1}{2} - 2y, 0$ , of weight 2 (Harker line).

Owing to the center of symmetry on the Harker section, the peak  $\frac{1}{2} - 2x, \frac{1}{2}, 2z$  appears also at  $\frac{1}{2} + 2x, \frac{1}{2}, 2z$  and, if the origin of the section is shifted to  $\frac{1}{2}, \frac{1}{2}, 0$ , then this last peak will have coordinates  $2x, \frac{1}{2}, 2z$ . Consequently, a double rotation satellite on the Harker section would fall exactly on the corresponding single inversion peak every time the Harker section, with its origin shifted to  $\frac{1}{2}, \frac{1}{2}, 0$ , were superposed on a Patterson section at height  $2y$  containing the inversion peak  $2x, 2y, 2z$ . The authenticity of the single inversion peak could be further established by referring to the reflection satellite at height  $\frac{1}{2} - 2y$  on the Harker line  $\frac{1}{2}, y, 0$ . In this way one could find image points which would allow the application of the three-dimensional minimum function (BUERGER, 1959) and finally lead to the solution of the structure.

Before attempting to solve the Patterson synthesis the expected heights of the single and double peaks due to every kind of atom in the cell, relative to the height of the origin peak, were calculated. This showed that the double peaks due to the heavy atoms Zn and Mn were considerably lower than most of the prominent peaks on the Harker section and consequently the latter were probably multiple. The expected single Zn — Zn and Mn — Mn peaks were also much lower than many on the other sections but they were high enough to promise the possibility of finding image points for the minimum function.

Inspection of the Harker line showed a very intense peak at  $y = 22/60$  and a somewhat lower peak at  $y = 0$ . The second peak, because of its special position, was not considered at first. The height of the first peak suggested an accumulation of reflection satellites accompanying single inversion peaks which, according to the relations

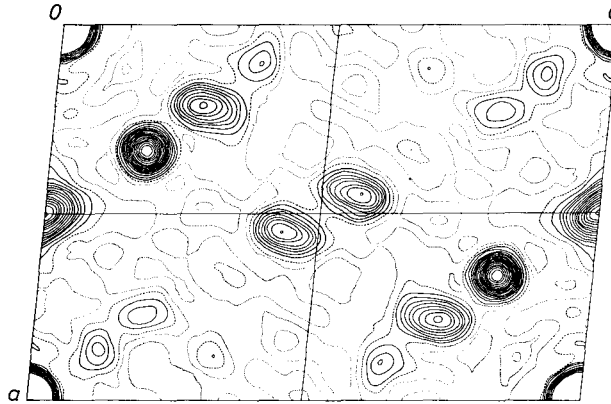


Fig. 1. Three-dimensional Patterson section  $P(x_0z)$

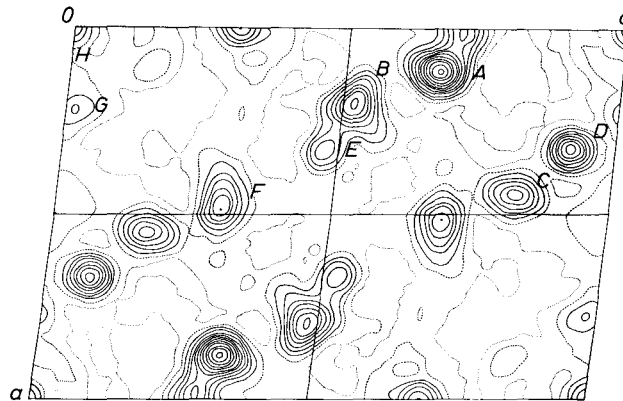


Fig. 2. Three-dimensional Patterson section  $P(x_{\frac{8}{60}}z)$

mentioned above, should lie around  $y = \frac{1}{2} - \frac{2}{60} = \frac{8}{60}$ . And in fact, superposition of the Harker section on section  $y = \frac{8}{60}$ , in the way indicated above, brought eight peaks of the asymmetric unit of the former into coincidence with corresponding peaks of the latter (Figs. 2, 3). Peak *A* on section  $y = \frac{8}{60}$ , Fig. 2, though certainly a multiple peak, was first considered as a possible Zn — Zn inversion peak and

superposed on the origin of section  $y = 0$ . The minimum function was then drawn in the way described by BUERGER (1959). The first  $M_2(x \frac{4}{60} z)$  obtained in this way (Fig. 4) showed six intense and several lower peaks. Of the intense peaks,  $B$  and  $C$  were attributed to the second Zn and the Mn atom because the corresponding inversion

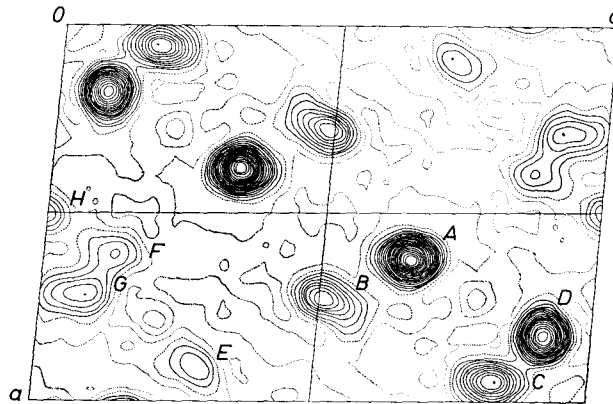


Fig. 3. Harker section  $P(x \frac{1}{2} z)$

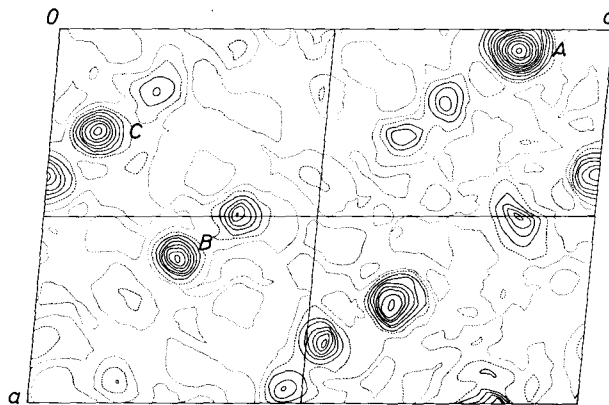


Fig. 4. Minimum function  $M_2(x \frac{4}{60} z)$  based on peak  $A$  of Fig. 2

peaks  $B$  and  $C$  on the Patterson section  $y = \frac{8}{60}$  had satisfactory satellites ( $B$  and  $C$ ) on the Harker section and, as mentioned, on the Harker line. Accordingly peaks  $B$  and  $C$  on section  $y = \frac{8}{60}$  were used as image points to form two more minimum functions  $M_2(x \frac{4}{60} z)$  in the same way as for peak  $A$ . As the atomic numbers of Zn and Mn do not differ very much, and as the peaks on the Patter-

son section were certainly multiple, the corresponding  $M_2$ 's were considered as approximately equivalent, and in this way the three  $M_2$  maps were combined to form a more powerful  $M_6(x \frac{4}{6} z)$ . This showed that very probably almost all the atoms of the asymmetric unit were at, or near, height  $y = \frac{4}{6}$ . Using the three probable heavy-atom locations as image points the sections of the Patterson synthesis were superposed in pairs differing by  $\frac{8}{6}$  (e.g., points  $A, B, C$  on section  $\frac{0}{6}$  were placed on the origin of section  $\frac{8}{6}$ , those of section  $\frac{2}{6}$  on the origin of section  $\frac{4}{6}$ , etc.) and the corresponding section of  $M_6$  was formed up to  $y = \frac{5}{6}$  (asymmetric unit). Fig. 5 (see p. 133) shows a projection of the maximum heights of  $M_6$  on (010). Most of the peaks lie around  $y = \frac{4}{6}$ , except for an intense peak at  $y = \frac{1}{6}$  and a few weaker peaks at heights  $\frac{1}{6}$  and  $\frac{1}{6}$ . This distribution of the peaks explains very well the appearance of the maxima on the Harker line.

As there were more peaks on the  $M_6$  map than the ten atoms in the asymmetric unit (hydrogen atoms ignored) the assignment of atoms to the peaks on the  $M_6$  was done, at least for some atoms, by taking into account the size of the  $\text{SiO}_4$  tetrahedron and interatomic distances  $\text{Zn} - \text{O}$  and  $\text{Mn} - \text{O}$  known from other structures. With the exception of two O atoms, for which there was an alternative position, all other atoms were more or less uniquely allocated, although there was the possibility of an interchange of position among the heavy atoms. The positions originally selected on the  $M_6$  map are marked with letters from  $A$  to  $J$  in the order  $\text{Zn}_{(1)}, \text{Zn}_{(2)}, \text{Mn}, \text{Si}, \text{O}_{(1)}, \text{O}_{(2)}, \text{O}_{(3)}, \text{O}_{(4)}, \text{OH}_{(1)}, \text{OH}_{(2)}$ .

A preliminary scale factor for the  $F_o$  values was determined by a structure-factor calculation with the three heavy atoms only. The program SFLSQ3 written by PREWITT (1962) was used for this calculation, as well as for all the subsequent structure-factor calculations and least-squares refinement (full matrix). The discrepancy factor

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|},$$

obtained from the first calculation, was  $R = 0.55$ , which dropped to 0.46 in the two subsequent least-squares cycles with all the 10 atoms of the asymmetric unit included. Half-ionized state for all the atoms was assumed and probable isotropic temperature factors, known from other silicates, were assigned to them. Atomic form factors were obtained from the International Tables (1962).

A three-dimensional difference synthesis at this stage indicated an interchange of position between  $Zn_{(1)}$  and Mn and between Si and  $O_{(3)}$ . Further, the weighting scheme by CRUICKSHANK *et al.* (1960) was introduced. With these changes  $R$  dropped to 0.35 in the following three least-squares cycles. A three-dimensional Fourier synthesis and the corresponding difference synthesis indicated the right structure immediately: The assumed Si atom ought to be interchanged with the Mn atom, and  $O_{(3)}$  and  $OH_{(1)}$  should be replaced by peaks  $K$  and  $L$  on the  $M_6$  map. In the next cycle  $R$  dropped to 0.188 and with two further cycles it stopped at 0.137.

### Refinement

At this stage examination of  $F_o$  and  $F_c$  values showed that for all the 90 fifth-level reflections  $F_c$  was systematically considerably larger than  $F_o$ . The ratio  $F_o/F_c$  for the 30 strongest reflections ( $F_c$  between 122 and 25) was found to lie close to 0.6, so a systematic error in collecting the intensities of this level was suspected. As the crystal had not been taken off the diffractometer it was found that the Geiger counter had been misset by  $1^\circ$  and consequently counted less than it should. With counter properly set the reflections of the fifth level were measured again. Before and after the measurement, checks were made to see whether reflections from other levels yielded the same number of counts as before. The values agreed to within 1 or 2%.

Before proceeding with further refinement the influence of the weighting scheme on the  $R$  value was checked by arranging the  $F_o$  values in increasing order, subdividing the set in groups of fifty, finding the  $R$  value for 10 reflections around the middle of each group and plotting the  $R$  values versus the average  $F_o$  value of the ten reflections. It was found that weak reflections were underweighted in comparison with the stronger ones. Constant  $a$  in the weighting scheme (CRUICKSHANK *et al.*, 1960) was accordingly increased.

The next cycle brought  $R$  down to 0.092 and then to 0.080, at which stage the change in the atomic parameters was so small that refinement of the atomic positions had practically converged. Variation of the isotropic temperature factors of the atoms dropped  $R$  to 0.078. Further refinement with anisotropic temperature factors improved  $R$  only slightly, 0.075. This, with the practically featureless appearance of the difference map, indicated that the thermal motion was substantially isotropic.

Table 1. Comparison between observed and calculated structure factors for hodgkinsonite.

h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>
0 0 1	34.9	33.0	4 0 $\overline{11}$	35.2	38.0	1 1 3	197.9	198.9	3 1 11	74.8	72.0
2	24.9	13.8	$\overline{12}$	3.0	6.6	4	65.9	65.7	12	43.6	42.6
3	97.8	104.2	$\overline{13}$	25.1	29.0	5	29.5	25.8	13	62.0	62.0
4	39.7	39.9	6 0 0	103.4	98.2	6	85.6	77.2	$\overline{1}$	66.6	66.0
5	38.4	44.6	1	82.9	74.5	7	4.0	2.3	$\overline{2}$	101.2	99.3
6	168.8	164.1	2	102.7	101.2	8	35.7	35.1	$\overline{3}$	7.2	2.8
7	21.6	21.6	3	43.0	40.4	9	63.1	63.5	$\overline{4}$	23.4	21.4
8	66.0	58.0	4	22.1	20.6	10	60.1	57.9	$\overline{5}$	99.6	104.4
9	25.9	21.3	5	28.6	28.7	11	28.4	25.3	$\overline{6}$	38.9	41.9
10	96.0	96.1	6	68.4	68.4	12	14.8	12.7	$\overline{7}$	23.0	22.5
11	97.5	98.5	7	39.7	38.6	13	6.5	5.6	$\overline{8}$	37.0	41.0
12	57.8	58.5	8	24.8	26.2	14	4.3	3.9	$\overline{9}$	4.4	4.3
13	72.3	75.2	9	17.9	19.1	$\overline{1}$	37.8	29.8	$\overline{10}$	40.6	42.5
14	24.0	23.1	10	7.8	7.3	$\overline{2}$	100.8	100.3	$\overline{11}$	83.3	90.0
2 0 0	14.1	11.2	$\overline{1}$	137.0	139.6	$\overline{3}$	109.8	112.7	$\overline{12}$	65.0	64.8
1	123.2	126.9	$\overline{2}$	84.0	80.6	$\overline{4}$	2.2	2.1	$\overline{13}$	43.9	48.7
2	62.3	68.3	$\overline{3}$	81.9	74.8	$\overline{5}$	7.2	10.1	$\overline{14}$	48.4	53.5
3	107.2	115.5	$\overline{4}$	70.7	74.1	$\overline{6}$	102.3	103.5	4 1 0	98.2	96.2
4	11.0	13.2	$\overline{5}$	20.7	21.0	$\overline{7}$	40.4	38.1	1	11.0	9.3
5	81.7	77.3	$\overline{6}$	14.1	10.8	$\overline{8}$	151.1	160.3	2	18.0	14.9
6	34.4	33.1	$\overline{7}$	78.8	84.1	$\overline{9}$	96.8	101.1	3	56.2	57.9
7	184.1	191.7	$\overline{8}$	19.4	20.2	$\overline{10}$	5.8	6.0	4	24.8	23.9
8	57.0	57.0	$\overline{9}$	2.9	3.2	$\overline{11}$	34.6	31.7	5	40.9	38.4
9	49.8	49.6	$\overline{10}$	73.0	79.4	$\overline{12}$	22.6	22.3	6	34.2	36.3
10	84.7	83.6	$\overline{11}$	14.2	17.8	$\overline{13}$	33.4	33.7	7	47.9	49.1
11	8.1	3.2	$\overline{12}$	32.3	33.1	$\overline{14}$	28.0	28.0	8	64.4	61.3
12	30.6	29.2	8 0 0	54.4	48.6	2 1 0	126.6	121.9	9	16.0	15.5
13	68.6	71.5	1	9.0	11.5	1	92.1	88.2	10	55.7	53.9
$\overline{1}$	75.1	76.0	2	7.0	10.8	2	95.3	83.8	11	22.1	21.6
$\overline{2}$	111.0	106.6	3	91.3	93.3	3	127.2	128.1	12	19.9	18.6
$\overline{3}$	215.5	243.5	4	35.6	33.7	4	43.7	39.6	$\overline{1}$	12.8	12.0
$\overline{4}$	15.6	11.8	5	31.1	35.7	5	10.3	3.4	$\overline{2}$	151.7	153.8
$\overline{5}$	134.2	135.4	6	37.9	41.1	6	12.5	8.9	$\overline{3}$	29.3	26.8
$\overline{6}$	150.1	164.3	7	56.3	58.0	7	24.3	23.5	$\overline{4}$	55.7	55.9
$\overline{7}$	30.7	31.0	$\overline{1}$	51.5	51.4	8	11.2	12.9	$\overline{5}$	27.2	23.9
$\overline{8}$	70.0	75.9	$\overline{2}$	17.5	18.2	9	48.2	46.9	$\overline{6}$	41.3	43.9
$\overline{9}$	55.4	60.6	$\overline{3}$	111.5	114.5	10	35.6	34.2	$\overline{7}$	10.1	11.5
$\overline{10}$	19.3	17.4	$\overline{4}$	36.0	37.1	11	59.6	56.7	$\overline{8}$	26.9	27.7
$\overline{11}$	36.4	39.4	$\overline{5}$	18.3	21.0	12	11.7	11.9	$\overline{9}$	10.1	8.6
$\overline{12}$	31.4	32.0	$\overline{6}$	83.1	89.7	13	18.8	19.1	$\overline{10}$	25.6	26.0
$\overline{13}$	26.2	28.0	$\overline{7}$	30.1	33.8	$\overline{1}$	43.1	40.9	$\overline{11}$	6.0	8.6
$\overline{14}$	82.8	89.4	$\overline{8}$	26.6	30.7	$\overline{2}$	55.6	53.0	$\overline{12}$	45.7	50.1
4 0 0	98.9	87.5	$\overline{9}$	13.7	16.1	$\overline{3}$	14.8	9.5	5 1 0	9.3	6.5
1	93.4	89.3	10 0 0	39.7	41.2	$\overline{4}$	72.9	67.4	1	70.4	69.5
2	46.2	41.1	1	12.1	15.0	$\overline{5}$	29.5	30.4	2	98.9	102.1
3	87.7	86.0	$\overline{1}$	14.7	15.9	$\overline{6}$	29.6	30.7	3	3.8	3.3
4	230.4	262.7	$\overline{2}$	67.2	70.3	$\overline{7}$	63.3	61.1	4	7.8	7.6
5	118.7	119.1	0 1 1	31.0	22.8	$\overline{8}$	26.4	26.1	5	51.8	52.9
6	26.8	23.4	2	91.6	59.9	$\overline{9}$	15.1	15.8	6	39.2	40.3
7	7.0	1.2	3	67.5	60.9	$\overline{10}$	76.4	76.9	7	79.9	77.8
8	11.9	10.2	4	134.9	128.8	$\overline{11}$	13.0	14.0	8	90.3	90.4
9	22.8	22.2	5	10.4	11.5	$\overline{12}$	20.6	21.5	9	32.6	29.4
10	94.7	98.7	6	116.7	110.8	$\overline{13}$	11.1	10.2	10	27.8	27.3
11	4.1	11.1	7	106.1	100.9	$\overline{14}$	20.6	21.7	11	16.1	16.7
12	36.5	35.8	8	7.4	8.0	3 1 0	24.9	13.3	$\overline{1}$	6.5	3.8
$\overline{1}$	146.4	147.8	9	34.2	31.0	1	152.0	158.3	$\overline{2}$	41.0	41.2
$\overline{2}$	114.0	116.2	10	21.1	21.2	2	49.6	43.9	$\overline{3}$	55.8	54.0
$\overline{3}$	35.6	34.0	11	17.1	14.1	3	21.2	19.1	$\overline{4}$	189.4	188.1
$\overline{4}$	18.4	19.4	12	30.4	28.0	4	80.9	74.2	$\overline{5}$	49.9	52.5
$\overline{5}$	32.4	29.1	13	39.0	40.7	5	70.3	70.7	$\overline{6}$	40.9	42.0
$\overline{6}$	58.5	58.8	14	24.3	24.6	6	23.5	22.4	$\overline{7}$	26.2	27.1
$\overline{7}$	141.3	135.8	1 1 0	33.6	32.1	7	80.2	82.7	$\overline{8}$	44.4	42.7
$\overline{8}$	50.1	53.4	1	54.9	44.5	8	5.0	6.2	$\overline{9}$	7.8	4.8
$\overline{9}$	81.5	85.6	2	19.5	15.4	9	7.3	4.7	$\overline{10}$	65.3	72.0
$\overline{10}$	68.2	68.5				10	74.8	69.3	$\overline{11}$	40.1	44.7

