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# Refinement of the Crystal Structure of Cuprosklodowskite, $Cu[(UO_2)_2(SiO_3OH)_2] \cdot 6H_2O$[1]

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## Abstract

The structure of cuprosklodowskite has been refined using three dimensional X-ray techniques. The space group is $P\bar{1}$ with $a = 7.052(5)$, $b = 9.267(8)$, $c = 6.655(5)$ Å, $\alpha = 109.23°(5)$, $\beta = 89.84°(5)$, $\gamma = 110.01°(7)$, and $Z = 2$. The structure consists of sheets of $[(UO_2)_2(SiO_4)_2]^{4-}$, formed by edge-sharing pentagonal-bipyramidal $UO_7$ groups and $SiO_4$ tetrahedra, separated by $[Cu(H_2O)_4]^{2+}$ ions and $H_2O$. The coordination polyhedron for $Cu^{2+}$ is a tetragonal bipyramid with axial Cu-O distance of 2.48 Å and an equatorial distance of 1.97 Å. In the $UO_7$ polyhedron the axial distances are 1.77 Å with equatorial distances ranging from 2.29 to 2.43 Å. The three oxygen Si–O distances in the $SiO_4$ tetrahedron which are shared with $UO_2^{2+}$ ions are 1.59, 160, and 1.61 Å while the distance to the unshared oxygen atom is 1.67 Å, lending support to the hypothesis that the 2 protons per formula unit, which are necessary for charge balance, are attached to the unshared silicate oxygen. The structure was found to contain one water molecule more than previously reported; the formula $Cu[(UO_2)_2(SiO_3OH)_2] \cdot 6H_2O$ is suggested.

## Introduction

The mineral cuprosklodowskite was first described by Vaes (1933) from the oxidized uranium ores of the Katanga region. An occurrence at Joachimsthal was independently described by Novacek (1935a) who named it jachimovite. The identity of the two minerals was recognized by both Novacek (1935b) and Billet (1936). Novacek (1935 a, b) determined the composition to approximate $CuO \cdot 2UO_3 \cdot 2SiO_2 \cdot 6H_2O$. All of these authors thought cuproklodowskite to be orthorhombic, but this was questioned by Vaes and Guillemin (1958) and by Frondel (1958). Melon and Dejace (1959) carefully studied the symmetry, morphology and optical properties of cuprosklodowskite and established the symmetry as triclinic with a single empirical formula in the unit cell.

The structure of cuprosklodowskite was determined by Piret-Meunier and van Meerssche (1963) to an $R$ value of 0.14 by two-dimensional projection methods. Their solution supports the composition as given by Novacek, and established the existence of the fundamental structural unit as a sheet of composition $[(UO_2)_2(SiO_4)_2]^{4-}$, essentially identical to that found in uranophane, $CuO \cdot 2UO_3 \cdot 2SiO_2 \cdot 6H_2O$, as described by Smith, Gruner, and Lipscomb (1957). The same structural unit was also found for sklodowskite, $MgO \cdot 2UO_3 \cdot 2SiO_2 \cdot 6H_2O$ (Mokeeva, 1958, 1964; Huynen and van Meerssche, 1962). According to the accepted empirical formulas of these three minerals, they are isostoichiometric, and prior to the deduction of their true symmetries they were assumed to be isostructural. This early assumption may explain the adherence to the empirical formulae even though the analyses for water are rarely in good agreement with that stoichiometry.

In all three structures there is a question of how the formal charge balance is to be accomplished. The structural unit, $[(UO_2)_2(SiO_4)_2]^{4-}$, is balanced by only one divalent cation, thus requiring the presence of two additional positive charges in the form of hydrogen ions as suggested in the case of cuprosklodowskite (Piret-Meunier and van Meers-

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sche, 1963) or hydronium ions (Smith *et al,* 1957; Huynen and van Meerssche, 1962), or by replacing either uranyl or silicate oxygen by hydroxyl (Huynen and van Meerssche, 1962; Mokeeva, 1958; Smith and Stohl, 1972). It was in the hope of illuminating this problem that the refinement of cuprosklodowskite was undertaken.

The material used in this study was from the Musonoi Mine, Kolwezi, Katanga, Zaire (formerly Belgian Congo), and was kindly supplied by William W. Pinch.

## Structure Refinement

The crystal chosen for data collection was a lathe-shaped cleavage fragment—100 × 47 × 36 microns—elongated parallel to [100] and flattened on the (010) face.

Lattice parameters and intensities were measured using graphite monochromatized Mo*Kα* radiation ($\lambda = 0.70930$ Å) and a Picker FACS-I diffractometer. The lattice parameters obtained by refinement of twelve high $2\theta$ reflections are in good agreement with those (Table 1) of Melon and Dejace (1959) except for significant differences in the *b*-axis length and the value of $\gamma$.

TABLE 1. Unit Cell Constants for Cuprosklodowskite

| | Melon & Dejace (1959) | Present Work |
|---|---|---|
| a | 7.04 Å | 7.052(5) Å |
| b | 9.18 | 9.267(8) |
| c | 6.66 | 6.655(5) |
| α | 109.23° | 109.23(5)° |
| β | 90.00° | 89.84(5)° |
| γ | 108.37° | 110.01(7)° |

A total of 1307 unique reflections with $2\theta \leq 50°$ were measured in a hemisphere of reciprocal space. Of these, 1143 were considered observed according to the criterion $I \geq 3\sigma(I)$ where $I$ is the intensity corrected for background, and $\sigma(I) = \{T + B + [0.015(T - B)]^2\}^{1/2}$ where $T$ is the total count and $B$ is the estimated background. Six bounding planes were used to define the crystal shape, and absorption corrections were calculated with a linear absorption coefficient of $\mu = 336$ cm$^{-1}$ (Larson, Cromer, and Roof, 1964).

The positional parameters reported by Piret-Meunier and van Meerssche (1963) were used directly in a least-squares refinement of the new data. In their interpretation, all atoms are in general positions, except for $Cu^{2+}$ and one oxygen—presumed to be a water molecule—which lie on centers of symmetry. Since the original structure data included no thermal parameters, reasonable isotropic thermal parameters

TABLE 2. Fractional Coordinates and Thermal Parameters (× $10^4$)

| Atom | x | y | z | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| U | 0.2589(1) | 0.210(1) | 0.6397(1) | 41(1) | 61(1) | 27(1) | 57(1) | 19(1) | 39(1) |
| Cu | 0.5(0) | 0.5(0) | 0(0) | 158(7) | 79(4) | 178(6) | 61(9) | 45(11) | 99(8) |
| Si | 0.7735(5) | 0.0526(4) | 0.8573(4) | 69(8) | 68(6) | 39(8) | 63(12) | 30(13) | 43(11) |
| 0(1) | 0.353(1) | 0.235(1) | 0.699(1) | 95(24) | 101(16) | 101(21) | 77(34) | 23(37) | 123(31) |
| 0(2) | 0.838(1) | 0.193(1) | 0.416(1) | 73(23) | 136(18) | 103(21) | 130(35) | 45(36) | 131(33) |
| 0(3) | 0.588(1) | 0.024(1) | 0.692(1) | 98(23) | 125(16) | 26(18) | 147(33) | 66(33) | 89(29) |
| 0(4) | 0.932(1) | 0.018(1) | 0.690(1) | 60(21) | 108(15) | 36(19) | 104(30) | 41(32) | 78(28) |
| 0(5) (OH)? | 0.863(1) | 0.248(1) | 0.021(1) | 200(28) | 84(15) | 81(21) | 118(36) | 41(41) | 60(30) |
| 0(6) | 0.720(1) | 0.940(1) | 0.002(1) | 75(21) | 88(14) | 29(18) | 90(29) | 23(31) | 40(27) |
| 0(7) ($H_2O$) | 0.465(1) | 0.374(1) | 0.193(1) | 248(31) | 74(15) | 144(24) | 18(37) | -40(46) | 53(32) |
| 0(8) ($H_2O$) | 0.231(1) | 0.513(1) | 0.052(1) | 178(33) | 131(20) | 574(48) | 150(46) | 206(68) | 288(55) |
| 0(9) ($H_2O$) | 0.201(1) | 0.482(1) | 0.499(1) | 256(36) | 173(22) | 314(32) | 94(48) | 52(59) | 124(42) |

Extinction parameter = $2.3(5) \times 10^{-6}$

β's are defined by $\exp[-(h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2k\ell\beta_{23} + 2h\ell\beta_{13})]$

TABLE 3. Observed and Calculated Scattering Factors

| | | |
|---|---|---|
| *h* = 0 *l* = -7 | | |
| -1 | 53 | 58 |
| 0 | 45 | 50 |
| 1 | 60 | 62 |
| 2 | 64 | 65 |
| 3 | 67 | 69 |
| 4 | 45 | 46 |
| 5 | 62 | 59 |
| 6 | 48 | 48 |
| 7 | 51 | 52 |
| *h* = 0 *l* = -6 | | |
| -3 | 51 | 54 |
| -2 | 66 | 67 |
| -1 | 46 | 46 |
| 0 | 69 | 72 |
| 1 | 51 | 53 |
| 2 | 53 | 56 |
| 3 | 24 | 25 |
| 4 | 34 | 32 |
| 5 | -13 | 3 |
| 6 | -16 | 3 |
| 7 | 34 | 34 |
| 8 | -18 | 19 |
| 9 | 41 | 37 |
| *h* = 0 *l* = -5 | | |
| -5 | 33 | 36 |
| -4 | 25 | 24 |
| -3 | -18 | 22 |
| -2 | -16 | 6 |
| -1 | -15 | 8 |
| 0 | 34 | 38 |
| 1 | 35 | 34 |
| 2 | 67 | 65 |
| 3 | 54 | 54 |
| 4 | 80 | 79 |
| 5 | 77 | 78 |
| 6 | 91 | 92 |
| 7 | 64 | 64 |
| 8 | 75 | 75 |
| 9 | 53 | 49 |
| *h* = 0 *l* = -4 | | |
| -6 | -20 | 15 |
| -5 | 48 | 45 |
| -4 | 41 | 41 |
| -3 | 78 | 77 |
| -2 | 74 | 72 |
| -1 | 105 | 104 |
| 0 | 82 | 82 |
| 1 | 153 | 150 |
| 2 | 101 | 99 |
| 3 | 130 | 131 |
| 4 | 75 | 73 |
| 5 | 111 | 111 |
| 6 | 78 | 79 |
| 7 | 80 | 78 |
| 8 | 34 | 33 |
| 9 | 53 | 49 |
| 10 | 20 | 23 |
| *h* = 0 *l* = -3 | | |
| -7 | 51 | 52 |
| -6 | 69 | 71 |
| -5 | 68 | 71 |
| -4 | 117 | 119 |
| -3 | 100 | 99 |
| -2 | 109 | 107 |
| -1 | 102 | 99 |
| 0 | 145 | 141 |
| 1 | 123 | 118 |
| 2 | 113 | 111 |
| 3 | 41 | 42 |
| 4 | 88 | 90 |
| 5 | 35 | 35 |
| 6 | 40 | 39 |
| 7 | -14 | 5 |
| 8 | 22 | 18 |
| 9 | -18 | 7 |
| 10 | -20 | 2 |
| *h* = 0 *l* = -2 | | |
| -8 | 48 | 45 |
| -7 | 60 | 59 |
| -6 | 48 | 50 |
| -5 | 79 | 80 |
| -4 | 42 | 39 |
| -3 | 92 | 91 |
| -2 | 19 | 19 |
| -1 | 85 | 83 |
| 0 | -7 | 7 |
| 1 | 53 | 52 |
| 2 | 15 | 16 |
| 3 | 44 | 42 |
| 4 | 66 | 67 |
| 5 | -12 | 7 |
| 6 | 61 | 62 |
| 7 | 25 | 24 |
| 8 | 60 | 59 |
| 9 | 39 | 43 |
| 10 | 62 | 54 |
| *h* = 0 *l* = -1 | | |
| -9 | -20 | 14 |
| -8 | 33 | 30 |
| -7 | -17 | 8 |
| -6 | -16 | 17 |
| -5 | -15 | 2 |
| -4 | 22 | 19 |
| -3 | 34 | 34 |
| -2 | -8 | 6 |
| -1 | 91 | 89 |
| 0 | 53 | 50 |
| 1 | 127 | 130 |
| 2 | 108 | 107 |
| 3 | 127 | 130 |
| 4 | 109 | 110 |
| 5 | 157 | 159 |
| 6 | 99 | 99 |
| 7 | 107 | 109 |
| 8 | 64 | 64 |
| 9 | 77 | 74 |
| 10 | 51 | 48 |
| *h* = 0 *l* = 0 | | |
| -9 | -14 | 5 |
| -8 | 42 | 40 |
| -7 | 17 | 18 |
| -6 | 70 | 72 |
| -5 | 75 | 72 |
| -4 | 157 | 158 |
| -3 | 106 | 105 |
| -2 | 195 | 195 |
| -1 | 148 | 146 |
| 0 | 172 | 361 |
| 1 | 147 | 146 |
| 2 | 193 | 195 |
| 3 | 105 | 105 |
| 4 | 156 | 158 |
| 5 | 73 | 72 |
| 6 | 70 | 72 |
| 7 | -17 | 18 |
| 8 | 42 | 40 |
| 9 | -14 | 5 |
| *h* = 0 *l* = 1 | | |
| -10 | 49 | 48 |
| -9 | 80 | 74 |
| -8 | 64 | 64 |
| -7 | 110 | 109 |
| -6 | 101 | 99 |
| -5 | 159 | 159 |
| -4 | 110 | 110 |
| -3 | 127 | 130 |
| -2 | 108 | 107 |
| -1 | 126 | 130 |
| 0 | 53 | 50 |
| 1 | 91 | 89 |
| 2 | 11 | 6 |
| 3 | 34 | 34 |
| 4 | 20 | 19 |
| 5 | -15 | 2 |
| 6 | 21 | 17 |
| 7 | -17 | 8 |
| 8 | 29 | 30 |
| 9 | -20 | 14 |
| *h* = 0 *l* = 2 | | |
| -10 | 60 | 54 |
| -9 | 42 | 43 |
| -8 | 63 | 59 |
| -7 | 21 | 24 |
| -6 | 63 | 62 |
| -5 | -12 | 7 |
| -4 | 65 | 67 |
| -3 | 42 | 42 |
| -2 | 14 | 16 |
| -1 | 53 | 52 |
| 0 | 9 | 7 |
| 1 | 86 | 83 |
| 2 | 20 | 19 |
| 3 | 91 | 91 |
| 4 | 40 | 39 |
| 5 | 77 | 80 |
| 6 | 49 | 50 |
| 7 | 59 | 59 |
| 8 | 47 | 45 |
| *h* = 0 *l* = 3 | | |
| -10 | -20 | 2 |
| -9 | -14 | 7 |
| -8 | 20 | 18 |
| -7 | -13 | 5 |
| -6 | 39 | 39 |
| -5 | 35 | 35 |
| -4 | 89 | 90 |
| -3 | 41 | 42 |
| -2 | 113 | 111 |
| -1 | 123 | 118 |
| 0 | 145 | 141 |
| 1 | 101 | 99 |
| 2 | 108 | 107 |
| 3 | 99 | 99 |
| 4 | 118 | 119 |
| 5 | 68 | 71 |
| 6 | 68 | 71 |
| 7 | 54 | 52 |
| *h* = 0 *l* = 4 | | |
| -10 | 20 | 23 |
| -9 | 55 | 49 |
| -8 | 33 | 33 |
| -7 | 81 | 78 |
| -6 | 81 | 79 |
| -5 | 110 | 111 |
| -4 | 74 | 73 |
| -3 | 129 | 131 |
| -2 | 101 | 99 |
| -1 | 153 | 150 |
| 0 | 82 | 82 |
| 1 | 105 | 104 |
| 2 | 73 | 72 |
| 3 | 79 | 77 |
| 4 | 36 | 41 |
| 5 | 44 | 45 |
| 6 | -20 | 15 |
| *h* = 0 *l* = 5 | | |
| -9 | 51 | 49 |
| -8 | 76 | 75 |
| -7 | 64 | 64 |
| -6 | 93 | 92 |
| -5 | 77 | 78 |
| -4 | 79 | 79 |
| -3 | 54 | 54 |
| -2 | 65 | 65 |
| -1 | 32 | 34 |
| 0 | 37 | 38 |
| 1 | -15 | 8 |
| 2 | -17 | 6 |
| 3 | 25 | 22 |
| 4 | 26 | 24 |
| 5 | 30 | 36 |
| *h* = 0 *l* = 6 | | |
| -9 | 38 | 37 |
| -8 | -18 | 19 |
| -7 | 33 | 34 |
| -6 | -12 | 3 |
| -5 | -13 | 3 |
| -4 | 30 | 32 |
| -3 | 27 | 25 |
| -2 | 56 | 56 |
| -1 | 50 | 53 |
| 0 | 71 | 72 |
| 1 | 45 | 46 |
| 2 | 66 | 67 |
| 3 | 51 | 54 |
| *h* = 0 *l* = 7 | | |
| -7 | 56 | 52 |
| -6 | 49 | 48 |
| -5 | 57 | 59 |
| -4 | 44 | 46 |
| -3 | 67 | 69 |
| -2 | 62 | 65 |
| -1 | 59 | 62 |
| 0 | 46 | 50 |
| 1 | 59 | 58 |
| *h* = 1 *l* = -7 | | |
| -1 | -19 | 7 |
| 0 | -18 | 13 |
| 1 | 39 | 38 |
| 2 | 37 | 40 |
| 3 | 58 | 55 |
| 4 | 48 | 49 |
| 5 | 78 | 76 |
| 6 | 62 | 64 |
| 7 | 68 | 68 |
| *h* = 1 *l* = -6 | | |
| -3 | 46 | 45 |
| -2 | 71 | 72 |
| -1 | 63 | 68 |
| 0 | 93 | 95 |
| 1 | 87 | 90 |
| 2 | 103 | 101 |
| 3 | 85 | 84 |
| 4 | 85 | 84 |
| 5 | 66 | 67 |
| 6 | 79 | 77 |
| 7 | 51 | 49 |
| 8 | 43 | 45 |
| *h* = 1 *l* = -5 | | |
| -5 | 65 | 66 |
| -4 | 72 | 74 |
| -3 | 88 | 89 |
| -2 | 65 | 66 |
| -1 | 78 | 79 |
| 0 | 63 | 64 |
| 1 | 96 | 95 |
| 2 | 52 | 50 |
| 3 | 50 | 49 |
| 4 | 37 | 34 |
| 5 | 50 | 51 |
| 6 | 23 | 22 |
| 7 | 27 | 26 |
| 8 | -17 | 3 |
| 9 | 20 | 15 |
| *h* = 1 *l* = -4 | | |
| -6 | 46 | 41 |
| -5 | 40 | 43 |
| -4 | 58 | 58 |
| -3 | 38 | 38 |
| -2 | 48 | 47 |
| -1 | 37 | 37 |
| 0 | 52 | 52 |
| 1 | 17 | 11 |
| 2 | 37 | 35 |
| 3 | -12 | 3 |
| 4 | -12 | 3 |
| 5 | 32 | 32 |
| 6 | 30 | 31 |
| 7 | 38 | 41 |
| 8 | 38 | 36 |
| 9 | 60 | 56 |
| *h* = 1 *l* = -3 | | |
| -8 | -21 | 24 |
| -7 | 29 | 32 |
| -6 | -18 | 15 |
| -5 | 28 | 28 |
| -4 | -14 | 2 |
| -3 | -14 | 16 |
| -2 | 28 | 27 |
| -1 | 45 | 42 |
| 0 | 80 | 80 |
| 1 | 73 | 70 |
| 2 | 119 | 121 |
| 3 | 82 | 83 |
| 4 | 130 | 133 |
| 5 | 95 | 96 |
| 6 | 107 | 108 |
| 7 | 71 | 72 |
| 8 | 75 | 72 |
| 9 | 53 | 47 |
| *h* = 1 *l* = -2 | | |
| -8 | -19 | 15 |
| -7 | 36 | 37 |
| -6 | 39 | 40 |
| -5 | 83 | 83 |
| -4 | 85 | 85 |
| -3 | 135 | 135 |
| -2 | 95 | 93 |
| -1 | 146 | 142 |
| 0 | 175 | 166 |
| 1 | 150 | 151 |
| 2 | 89 | 90 |
| 3 | 92 | 95 |
| 4 | 76 | 77 |
| 5 | 97 | 98 |
| 6 | 39 | 38 |
| 7 | 37 | 38 |
| 8 | 31 | 23 |
| 9 | 29 | 26 |
| *h* = 1 *l* = -1 | | |
| -9 | 48 | 51 |
| -8 | 70 | 68 |
| -7 | 64 | 64 |
| -6 | 94 | 95 |
| -5 | 104 | 105 |
| -4 | 112 | 111 |
| -3 | 56 | 57 |
| -2 | 114 | 114 |
| -1 | 84 | 80 |
| 0 | 118 | 118 |
| 1 | 38 | 39 |
| 2 | 59 | 61 |
| 3 | 28 | 27 |
| 4 | 44 | 46 |
| 5 | 19 | 15 |
| 6 | 26 | 24 |
| 7 | 24 | 17 |
| 8 | -14 | 2 |
| 9 | 23 | 23 |
| *h* = 1 *l* = 0 | | |
| -10 | 39 | 39 |
| -9 | 60 | 57 |
| -8 | 36 | 39 |
| -7 | 61 | 63 |
| -6 | 38 | 39 |
| -5 | 61 | 61 |
| -4 | 45 | 43 |
| -3 | 50 | 51 |
| -2 | 11 | 11 |
| -1 | 31 | 33 |
| 0 | 31 | 33 |
| 1 | 18 | 17 |
| 2 | 48 | 50 |
| 3 | 39 | 40 |
| 4 | 57 | 57 |
| 5 | 41 | 39 |
| 6 | 60 | 60 |
| 7 | 35 | 36 |
| 8 | 61 | 56 |
| 9 | 42 | 38 |
| *h* = 1 *l* = 1 | | |
| -10 | 22 | 21 |
| -9 | -14 | 7 |
| -8 | -14 | 12 |
| -7 | 18 | 18 |
| -6 | -14 | 10 |
| -5 | 38 | 39 |
| -4 | 31 | 30 |
| -3 | 56 | 58 |
| -2 | 38 | 38 |
| -1 | 113 | 114 |
| 0 | 73 | 70 |
| 1 | 129 | 129 |
| 2 | 37 | 37 |
| 3 | 121 | 122 |
| 4 | 92 | 91 |
| 5 | 104 | 104 |
| 6 | 56 | 59 |
| 7 | 74 | 72 |
| 8 | 49 | 48 |
| *h* = 1 *l* = 2 | | |
| -10 | 33 | 27 |
| -9 | -18 | 22 |
| -8 | 43 | 40 |
| -7 | 34 | 33 |
| -6 | 101 | 101 |
| -5 | 69 | 70 |
| -4 | 100 | 111 |
| -3 | 69 | 71 |
| -2 | 160 | 162 |
| -1 | 166 | 157 |
| 0 | 158 | 152 |
| 1 | 91 | 89 |
| 2 | 137 | 138 |
| 3 | 85 | 84 |
| 4 | 90 | 90 |
| 5 | 38 | 40 |
| 6 | 42 | 40 |
| 7 | 20 | 17 |
| *h* = 1 *l* = 3 | | |
| -10 | 52 | 48 |
| -9 | 74 | 71 |
| -8 | 71 | 73 |
| -7 | 105 | 106 |
| -6 | 96 | 98 |
| -5 | 130 | 134 |
| -4 | 81 | 82 |
| -3 | 127 | 129 |
| -2 | 64 | 61 |
| -1 | 95 | 94 |
| 0 | 39 | 36 |
| 1 | 41 | 38 |
| 2 | 21 | 19 |
| 3 | -15 | 8 |
| 4 | 36 | 32 |
| 5 | -14 | 7 |
| 6 | 31 | 34 |
| 7 | 29 | 20 |
| *h* = 1 *l* = 4 | | |
| -10 | 65 | 59 |
| -9 | 39 | 33 |
| -8 | 47 | 47 |
| -7 | 19 | 24 |
| -6 | 40 | 40 |
| -5 | -12 | 5 |
| -4 | 12 | 7 |
| -3 | 44 | 42 |
| -2 | -13 | 2 |
| -1 | 57 | 57 |
| 0 | 31 | 30 |
| 1 | 52 | 49 |
| 2 | 35 | 35 |
| 3 | 58 | 56 |
| 4 | 38 | 43 |
| 5 | 47 | 50 |
| 6 | 32 | 32 |
| *h* = 1 *l* = 5 | | |
| -10 | -19 | 14 |
| -9 | -13 | 3 |
| -8 | 29 | 27 |
| -7 | 22 | 19 |
| -6 | 52 | 53 |
| -5 | 32 | 33 |
| -4 | 49 | 49 |
| -3 | 47 | 46 |
| -2 | 95 | 96 |
| -1 | 61 | 62 |
| 0 | 82 | 83 |
| 1 | 62 | 61 |
| 2 | 91 | 91 |
| 3 | 72 | 74 |
| 4 | 68 | 69 |
| *h* = 1 *l* = 6 | | |
| -9 | 46 | 46 |
| -8 | 44 | 45 |
| -7 | 79 | 79 |
| -6 | 62 | 63 |
| -5 | 88 | 88 |
| -4 | 80 | 79 |
| -3 | 102 | 102 |
| -2 | 87 | 89 |
| -1 | 93 | 97 |
| 0 | 65 | 69 |
| 1 | 74 | 74 |
| 2 | 41 | 47 |
| 3 | 43 | 46 |
| *h* = 1 *l* = 7 | | |
| -8 | 69 | 66 |
| -7 | 63 | 63 |
| -6 | 77 | 76 |
| -5 | 46 | 49 |
| -4 | 57 | 57 |
| -3 | 36 | 40 |
| -2 | 40 | 41 |
| -1 | 22 | 16 |
| 0 | -19 | 10 |
| *h* = 2 *l* = -7 | | |
| -1 | 48 | 51 |
| 6 | 52 | 50 |
| *h* = 2 *l* = -6 | | |
| -4 | 50 | 53 |
| -3 | 55 | 59 |
| -2 | 41 | 41 |
| -1 | 58 | 59 |
| 6 | 38 | 39 |
| 7 | 25 | 26 |
| *h* = 2 *l* = -5 | | |
| -5 | -19 | 13 |
| -4 | -18 | 15 |
| -3 | -17 | 8 |
| -2 | -13 | 3 |
| -1 | 53 | 52 |
| 6 | 68 | 67 |
| 7 | 76 | 74 |
| 8 | 52 | 49 |
| *h* = 2 *l* = -4 | | |
| -7 | 22 | 20 |
| -6 | 45 | 46 |
| -5 | 45 | 46 |
| -4 | 75 | 75 |
| -3 | 80 | 78 |
| -2 | 96 | 95 |
| -1 | 90 | 90 |
| 6 | 64 | 65 |
| 7 | 32 | 33 |
| 8 | 39 | 39 |
| *h* = 2 *l* = -3 | | |
| -8 | 46 | 49 |
| -7 | 64 | 67 |
| -6 | 59 | 61 |
| -5 | 108 | 108 |
| -4 | 81 | 79 |
| -3 | 98 | 96 |
| -2 | 65 | 64 |
| -1 | 114 | 112 |
| 0 | 83 | 80 |
| 6 | -13 | 2 |
| 7 | -16 | 8 |
| 8 | -18 | 7 |
| 9 | -14 | 5 |
| *h* = 2 *l* = -2 | | |
| -9 | 41 | 41 |
| -8 | 50 | 48 |
| -7 | 40 | 43 |
| -6 | 57 | 56 |
| -5 | 37 | 35 |
| -4 | 53 | 51 |
| -3 | 15 | 16 |
| -2 | 30 | 30 |
| -1 | -9 | 3 |
| 0 | 10 | 4 |
| 5 | 48 | 48 |
| 6 | 28 | 29 |
| 7 | 48 | 49 |
| 8 | 47 | 43 |
| 9 | 51 | 48 |
| *h* = 2 *l* = -1 | | |
| -9 | 33 | 26 |
| -8 | -18 | 4 |
| -7 | -17 | 14 |
| -6 | -15 | 6 |
| -5 | 20 | 16 |
| -4 | 28 | 29 |
| -3 | -10 | 7 |
| -2 | 73 | 71 |
| -1 | 27 | 27 |
| 0 | 99 | 102 |
| 5 | 88 | 90 |
| 6 | 92 | 94 |
| 7 | 57 | 58 |
| 8 | 67 | 65 |
| *h* = 2 *l* = 0 | | |
| -10 | -19 | 6 |
| -9 | 30 | 28 |
| -8 | 18 | 19 |
| -7 | 47 | 47 |
| -6 | 67 | 66 |
| -5 | 102 | 102 |
| -4 | 105 | 106 |
| -3 | 98 | 102 |
| -2 | 140 | 142 |
| -1 | 195 | 204 |
| 0 | 145 | 149 |
| 5 | 49 | 52 |
| 6 | -17 | 21 |
| 7 | 31 | 32 |
| 8 | -14 | 7 |
| *h* = 2 *l* = 1 | | |
| -10 | 66 | 62 |
| -9 | 59 | 57 |
| -8 | 87 | 88 |
| -7 | 83 | 83 |
| -6 | 129 | 130 |
| -5 | 87 | 87 |
| -4 | 99 | 102 |
| -3 | 77 | 78 |
| -2 | 94 | 98 |
| -1 | 44 | 43 |
| 0 | 73 | 72 |
| 6 | -17 | 6 |
| 7 | -19 | 23 |
| 8 | -14 | 12 |
| *h* = 2 *l* = 2 | | |
| -10 | 47 | 44 |
| -9 | 48 | 48 |
| -8 | 35 | 35 |
| -7 | 42 | 44 |
| -6 | 29 | 29 |
| -5 | 46 | 45 |
| -4 | -9 | 7 |
| -3 | -8 | 4 |
| -2 | 12 | 10 |
| -1 | -14 | 4 |
| 0 | 21 | 20 |
| 5 | 42 | 43 |
| 6 | 49 | 49 |
| 7 | 43 | 42 |
| *h* = 2 *l* = 3 | | |
| -10 | -19 | 11 |
| -9 | -13 | 7 |
| -8 | 17 | 3 |
| -7 | 22 | 18 |
| -6 | 16 | 16 |
| -5 | 58 | 58 |
| -4 | 18 | 16 |
| -3 | 76 | 77 |
| -2 | 73 | 71 |
| -1 | 116 | 114 |
| 0 | 73 | 71 |
| 5 | 68 | 69 |
| 6 | 53 | 48 |
| *h* = 2 *l* = 4 | | |
| -10 | 41 | 36 |
| -9 | 33 | 29 |
| -8 | 58 | 58 |
| -7 | 72 | 73 |
| -6 | 85 | 86 |
| -5 | 74 | 75 |
| -4 | 100 | 101 |
| -3 | 101 | 101 |
| -2 | 133 | 131 |
| -1 | 92 | 91 |
| 0 | 100 | 98 |
| 5 | 25 | 21 |
| *h* = 2 *l* = 5 | | |
| -10 | 49 | 49 |
| -9 | 75 | 72 |
| -8 | 63 | 64 |
| -7 | 93 | 95 |
| -6 | 79 | 81 |
| -5 | 92 | 91 |
| -4 | 65 | 64 |
| -3 | 80 | 80 |
| -2 | 46 | 47 |
| -1 | 57 | 57 |
| 0 | -14 | 6 |
| *h* = 2 *l* = 6 | | |
| -9 | 30 | 30 |
| -8 | 44 | 41 |
| -7 | -16 | 17 |
| -6 | -16 | 14 |
| -5 | -15 | 14 |
| -4 | -16 | 13 |
| -3 | 33 | 36 |
| -2 | 41 | 43 |
| -1 | 57 | 58 |
| 0 | 37 | 41 |
| *h* = 2 *l* = 7 | | |
| -8 | 46 | 45 |
| -7 | 44 | 42 |
| -6 | 57 | 56 |
| -5 | 42 | 42 |
| -4 | 70 | 69 |
| -3 | 62 | 64 |
| -2 | 65 | 67 |
| -1 | 49 | 53 |
| *h* = 3 *l* = -7 | | |
| -1 | -13 | 3 |
| 0 | 20 | 23 |
| 1 | 25 | 27 |
| 2 | 42 | 39 |
| 3 | 40 | 36 |
| 4 | 58 | 59 |
| *h* = 3 *l* = -6 | | |
| -3 | 55 | 57 |
| -2 | 52 | 54 |
| -1 | 78 | 81 |
| 0 | 72 | 72 |
| 1 | 90 | 90 |
| 2 | 71 | 71 |
| 3 | 78 | 79 |
| 4 | 58 | 59 |
| 5 | 76 | 75 |
| 6 | 44 | 45 |
| *h* = 3 *l* = -5 | | |
| -5 | 65 | 66 |
| -4 | 84 | 82 |
| -3 | 64 | 65 |
| -2 | 72 | 75 |
| -1 | 61 | 64 |
| 0 | 92 | 93 |
| 1 | 58 | 58 |
| 2 | 58 | 59 |
| 3 | 42 | 42 |
| 4 | 57 | 57 |
| 5 | 33 | 33 |
| 6 | 32 | 34 |
| 7 | -18 | 10 |
| *h* = 3 *l* = -4 | | |
| -7 | 50 | 51 |
| -6 | 44 | 45 |
| -5 | 64 | 65 |
| -4 | 44 | 44 |
| -3 | 61 | 62 |
| -2 | 44 | 45 |
| -1 | 70 | 71 |
| 0 | 24 | 24 |
| 1 | 59 | 59 |
| 2 | -13 | 7 |
| 3 | 24 | 26 |
| 4 | 26 | 26 |
| 5 | -15 | 13 |
| 6 | 39 | 38 |
| 7 | 35 | 26 |
| 8 | 55 | 52 |
| *h* = 3 *l* = -3 | | |
| -8 | 36 | 36 |
| -7 | -19 | 20 |
| -6 | 39 | 35 |
| -5 | -16 | 8 |
| -4 | 30 | 28 |
| -3 | 19 | 17 |
| -2 | 17 | 19 |
| -1 | 64 | 63 |
| 0 | 56 | 55 |
| 1 | 100 | 101 |
| 2 | 75 | 76 |
| 3 | 117 | 120 |
| 4 | 90 | 91 |
| 5 | 103 | 105 |
| 6 | 73 | 73 |
| 7 | 73 | 71 |
| 8 | 52 | 50 |
| *h* = 3 *l* = -2 | | |
| -9 | -20 | 11 |
| -8 | 37 | 34 |
| -7 | 35 | 34 |
| -6 | 75 | 76 |
| -5 | 74 | 74 |
| -4 | 132 | 132 |
| -3 | 85 | 85 |
| -2 | 162 | 156 |
| -1 | 141 | 137 |
| 0 | 175 | 177 |
| 1 | 92 | 93 |
| 2 | 119 | 123 |
| 3 | 74 | 77 |
| 4 | 111 | 113 |
| 5 | 40 | 43 |
| 6 | 51 | 52 |
| 7 | 25 | 25 |
| 8 | 33 | 32 |
| *h* = 3 *l* = -1 | | |
| -9 | 69 | 71 |
| -8 | 61 | 61 |
| -7 | 96 | 99 |
| -6 | 99 | 100 |
| -5 | 125 | 124 |
| -4 | 78 | 76 |
| -3 | 129 | 128 |
| -2 | 96 | 92 |
| -1 | 134 | 133 |
| 0 | 62 | 63 |
| 1 | 71 | 72 |
| 2 | 44 | 44 |
| 3 | 43 | 44 |
| 4 | -15 | 4 |
| 5 | -16 | 20 |
| 6 | -17 | 10 |
| 7 | -14 | 2 |
| 8 | 23 | 20 |
| *h* = 3 *l* = 0 | | |
| -10 | 58 | 57 |
| -9 | 42 | 41 |
| -8 | 68 | 67 |
| -7 | 34 | 39 |
| -6 | 69 | 70 |
| -5 | 37 | 38 |
| -4 | 60 | 61 |
| -3 | -11 | 8 |
| -2 | 41 | 41 |
| -1 | 40 | 40 |
| 0 | 23 | 22 |
| 1 | 62 | 62 |
| 2 | 33 | 30 |
| 3 | 66 | 66 |
| 4 | 37 | 41 |
| 5 | 64 | 64 |
| 6 | 37 | 39 |
| 7 | 61 | 58 |
| *h* = 3 *l* = 1 | | |
| -10 | -19 | 6 |
| -9 | -14 | 13 |
| -8 | 21 | 20 |
| -7 | -14 | 7 |
| -6 | 41 | 44 |
| -5 | 32 | 31 |
| -4 | 69 | 70 |
| -3 | 58 | 60 |
| -2 | 110 | 109 |
| -1 | 105 | 102 |
| 0 | 124 | 125 |
| 1 | 75 | 75 |
| 2 | 115 | 116 |
| 3 | 104 | 105 |
| 4 | 100 | 100 |
| 5 | 68 | 71 |
| 6 | 68 | 68 |
| 7 | 58 | 53 |
| *h* = 3 *l* = 2 | | |
| -11 | 33 | 28 |
| -10 | 27 | 25 |
| -9 | 44 | 43 |
| -8 | 41 | 41 |
| -7 | 94 | 97 |
| -6 | 80 | 81 |
| -5 | 116 | 120 |
| -4 | 85 | 86 |
| -3 | 158 | 161 |
| -2 | 158 | 151 |
| -1 | 160 | 156 |
| 0 | 99 | 97 |
| 1 | 128 | 129 |
| 2 | 80 | 80 |
| 3 | 87 | 89 |
| 4 | 36 | 38 |
| 5 | 40 | 39 |
| 6 | -20 | 16 |
| *h* = 3 *l* = 3 | | |
| -11 | 49 | 47 |
| -10 | 72 | 70 |
| -9 | 71 | 69 |
| -8 | 98 | 99 |
| -7 | 93 | 95 |
| -6 | 114 | 117 |
| -5 | 81 | 83 |
| -4 | 103 | 104 |
| -3 | 62 | 60 |
| -2 | 69 | 68 |
| -1 | 34 | 34 |
| 0 | 16 | 16 |
| 1 | -15 | 13 |
| 2 | -16 | 11 |
| 3 | 33 | 30 |
| 4 | -19 | 18 |
| 5 | 35 | 33 |
| *h* = 3 *l* = 4 | | |
| -10 | 35 | 32 |
| -9 | 36 | 38 |
| -8 | 22 | 19 |
| -7 | 30 | 26 |
| -6 | -13 | 8 |
| -5 | -13 | 12 |
| -4 | 47 | 46 |
| -3 | 23 | 21 |
| -2 | 65 | 65 |
| -1 | 41 | 42 |
| 0 | 60 | 60 |
| 1 | 43 | 43 |
| 2 | 58 | 60 |
| 3 | 45 | 47 |
| 4 | 48 | 52 |
| *h* = 3 *l* = 5 | | |
| -10 | -18 | 9 |
| -9 | 31 | 29 |
| -8 | 22 | 25 |
| -7 | 52 | 55 |
| -6 | 44 | 44 |
| -5 | 54 | 51 |
| -4 | 54 | 55 |
| -3 | 86 | 87 |
| -2 | 68 | 70 |
| -1 | 75 | 76 |
| 0 | 61 | 61 |
| 1 | 83 | 81 |
| 2 | 70 | 71 |
| 3 | 60 | 62 |
| *h* = 3 *l* = 6 | | |
| -9 | 44 | 45 |
| -8 | 69 | 70 |
| -7 | 59 | 60 |
| -6 | 78 | 77 |
| -5 | 71 | 69 |
| -4 | 88 | 87 |
| -3 | 75 | 77 |
| -2 | 80 | 81 |
| -1 | 55 | 57 |
| 0 | 62 | 62 |
| 1 | 40 | 37 |
| *h* = 3 *l* = 7 | | |
| -7 | 64 | 62 |
| -6 | 41 | 39 |
| -5 | 43 | 43 |
| -4 | 23 | 29 |
| -3 | 22 | 29 |
| -2 | -19 | 10 |
| *h* = 4 *l* = -6 | | |
| -3 | 36 | 41 |
| -2 | 53 | 54 |
| -1 | 39 | 40 |
| 0 | 38 | 42 |
| 1 | -18 | 18 |
| 2 | -17 | 16 |
| 3 | -13 | 5 |
| 4 | -12 | 9 |
| 5 | 31 | 32 |
| *h* = 4 *l* = -5 | | |
| -5 | -20 | 14 |
| -4 | -14 | 1 |
| -3 | -17 | 4 |
| -2 | 32 | 34 |
| -1 | 35 | 37 |
| 0 | 62 | 63 |
| 1 | 54 | 53 |
| 2 | 74 | 74 |
| 3 | 70 | 70 |
| 4 | 81 | 81 |
| 5 | 62 | 62 |
| 6 | 68 | 66 |
| *h* = 4 *l* = -4 | | |
| -6 | 33 | 38 |
| -5 | 65 | 65 |
| -4 | 67 | 65 |
| -3 | 87 | 86 |
| -2 | 77 | 78 |
| -1 | 112 | 110 |
| 0 | 91 | 89 |
| 1 | 102 | 102 |
| 2 | 62 | 64 |
| 3 | 85 | 84 |
| 4 | 63 | 65 |
| 5 | 62 | 61 |
| 6 | 33 | 32 |
| 7 | 42 | 36 |
| *h* = 4 *l* = -3 | | |
| -8 | 58 | 57 |
| -7 | 58 | 60 |
| -6 | 89 | 90 |
| -5 | 80 | 79 |
| -4 | 89 | 85 |
| -3 | 69 | 66 |
| -2 | 93 | 91 |
| -1 | 76 | 76 |
| 0 | 72 | 71 |
| 1 | 28 | 27 |
| 2 | 51 | 53 |
| 3 | 16 | 18 |
| 4 | 31 | 29 |
| 5 | -13 | 2 |
| 6 | -18 | 10 |
| 7 | 23 | 7 |
| *h* = 4 *l* = -2 | | |
| -9 | 48 | 47 |
| -8 | 42 | 40 |
| -7 | 57 | 55 |
| -6 | 34 | 34 |
| -5 | 54 | 53 |
| -4 | -14 | 15 |
| -3 | 46 | 42 |
| -2 | -13 | 6 |
| -1 | 21 | 21 |
| 1 | -12 | 11 |
| 2 | 34 | 36 |
| 3 | -14 | 13 |
| 4 | 46 | 46 |
| 5 | 23 | 22 |
| 6 | 50 | 46 |
| 7 | 37 | 36 |
| *h* = 4 *l* = -1 | | |
| -9 | -14 | 8 |
| -8 | -14 | 13 |
| -7 | -15 | 1 |
| -6 | -16 | 10 |
| -5 | 19 | 17 |
| -4 | -14 | 8 |
| -3 | 53 | 53 |
| -2 | 30 | 29 |
| -1 | 85 | 87 |
| 0 | 61 | 62 |
| 1 | 91 | 92 |
| 2 | 72 | 76 |
| 3 | 111 | 112 |
| 4 | 77 | 77 |
| 5 | 90 | 88 |
| 6 | 53 | 51 |
| 7 | 67 | 62 |
| *h* = 4 *l* = 0 | | |
| -10 | 24 | 26 |
| -9 | -18 | 16 |
| -8 | 48 | 49 |
| -7 | 48 | 48 |
| -6 | 100 | 101 |
| -5 | 76 | 78 |
| -4 | 114 | 115 |
| -3 | 97 | 99 |
| -2 | 173 | 181 |
| -1 | 105 | 108 |
| 0 | 126 | 128 |
| 1 | 71 | 72 |
| 2 | 103 | 105 |
| 3 | 57 | 62 |
| 4 | 53 | 55 |
| 5 | -18 | 20 |
| 6 | 33 | 31 |
| *h* = 4 *l* = 1 | | |
| -10 | 57 | 54 |
| -9 | 80 | 78 |
| -8 | 74 | 75 |
| -7 | 113 | 113 |
| -6 | 79 | 81 |
| -5 | 96 | 97 |
| -4 | 65 | 67 |
| -3 | 87 | 89 |
| -2 | 43 | 45 |
| -1 | 66 | 64 |
| 0 | -14 | 9 |
| 1 | 37 | 36 |
| 2 | -16 | 11 |
| 3 | -15 | 10 |
| 4 | -18 | 11 |
| 5 | 22 | 3 |
| 6 | 29 | 20 |
| *h* = 4 *l* = 2 | | |
| -10 | 51 | 49 |
| -9 | 25 | 28 |
| -8 | 47 | 47 |
| -7 | 16 | 18 |
| -6 | 50 | 51 |
| -5 | -12 | 11 |
| -4 | 23 | 23 |
| -3 | 21 | 19 |
| -2 | -13 | 11 |
| -1 | 35 | 33 |
| 0 | -14 | 11 |
| 1 | 49 | 50 |
| 2 | 24 | 25 |
| 3 | 58 | 57 |
| 4 | 38 | 37 |
| 5 | 46 | 46 |
| *h* = 4 *l* = 3 | | |
| -10 | -19 | 8 |
| -9 | -13 | 2 |
| -8 | -16 | 19 |
| -7 | 17 | 17 |
| -6 | 52 | 50 |
| -5 | 24 | 23 |
| -4 | 66 | 66 |
| -3 | 63 | 60 |
| -2 | 100 | 98 |
| -1 | 70 | 66 |
| 0 | 81 | 79 |
| 1 | 75 | 73 |
| 2 | 91 | 95 |
| 3 | 59 | 62 |
| 4 | 64 | 64 |
| *h* = 4 *l* = 4 | | |
| -10 | 23 | 25 |
| -9 | 58 | 57 |
| -8 | 56 | 58 |
| -7 | 84 | 85 |
| -6 | 63 | 63 |
| -5 | 95 | 94 |
| -4 | 83 | 83 |
| -3 | 121 | 119 |
| -2 | 80 | 78 |
| -1 | 94 | 92 |
| 0 | 69 | 68 |
| 1 | 71 | 72 |
| 2 | 50 | 48 |
| 3 | 44 | 44 |
| *h* = 4 *l* = 5 | | |
| -10 | 64 | 64 |
| -9 | 59 | 58 |
| -8 | 82 | 83 |
| -7 | 72 | 72 |
| -6 | 78 | 78 |
| -5 | 60 | 59 |
| -4 | 64 | 66 |
| -3 | 45 | 45 |
| -2 | 46 | 47 |
| -1 | 21 | 9 |
| 0 | -19 | 10 |
| 1 | -20 | 10 |
| *h* = 4 *l* = 6 | | |
| -8 | -18 | 14 |
| -7 | 20 | 14 |
| -6 | 18 | 14 |
| -5 | -18 | 10 |
| -4 | 32 | 33 |
| -3 | 35 | 37 |
| -2 | 52 | 51 |
| -1 | 32 | 38 |
| *h* = 5 *l* = -6 | | |
| -2 | 74 | 75 |
| -1 | 70 | 73 |
| 0 | 82 | 82 |
| 1 | 72 | 71 |
| 2 | 70 | 69 |
| 3 | 59 | 59 |
| *h* = 5 *l* = -5 | | |
| -4 | 60 | 59 |
| -3 | 60 | 63 |
| -2 | 53 | 54 |
| -1 | 72 | 72 |
| 0 | 46 | 46 |
| 1 | 45 | 46 |
| 2 | 31 | 30 |
| 3 | 45 | 40 |
| 4 | 21 | 24 |
| *h* = 5 *l* = -4 | | |
| -6 | 47 | 46 |
| -5 | 33 | 34 |
| -4 | 37 | 37 |
| -3 | 29 | 31 |
| -2 | 32 | 36 |
| -1 | 23 | 18 |
| 0 | 17 | 23 |
| 1 | -12 | 3 |
| 2 | -15 | 2 |
| 3 | 24 | 22 |
| 4 | 26 | 24 |
| 5 | 29 | 32 |
| *h* = 5 *l* = -3 | | |
| -7 | -20 | 19 |
| -6 | -14 | 2 |
| -5 | -17 | 11 |
| -4 | 19 | 20 |
| -3 | 22 | 24 |
| -2 | 53 | 55 |
| -1 | 53 | 53 |
| 0 | 81 | 80 |
| 1 | 65 | 67 |
| 2 | 93 | 94 |
| 3 | 75 | 76 |
| 4 | 86 | 86 |
| 5 | 63 | 62 |
| 6 | 57 | 59 |
| *h* = 5 *l* = -2 | | |
| -8 | 30 | 33 |
| -7 | 52 | 55 |
| -6 | 67 | 66 |
| -5 | 91 | 89 |
| -4 | 79 | 77 |
| -3 | 105 | 100 |
| -2 | 109 | 107 |
| -1 | 109 | 110 |
| 0 | 81 | 83 |
| 1 | 74 | 75 |
| 2 | 63 | 66 |

TABLE 3, Continued

| | | |
|---|---|---|
| 3 | 72 | 73 |
| 4 | 39 | 40 |
| 5 | 37 | 35 |
| 6 | 24 | 22 |
| $h = 5$ $l = -1$ | | |
| -9 | 47 | 50 |
| -8 | 73 | 71 |
| -7 | 73 | 76 |
| -6 | 87 | 85 |
| -5 | 57 | 59 |
| -4 | 78 | 77 |
| -3 | 61 | 58 |
| -2 | 77 | 81 |
| -1 | 37 | 37 |
| 0 | 45 | 46 |
| 1 | 27 | 22 |
| 2 | 25 | 30 |
| 3 | -14 | 2 |
| 4 | -14 | 13 |
| 5 | -19 | 10 |
| $h = 5$ $l = 0$ | | |
| -10 | 38 | 37 |
| -9 | 43 | 46 |
| -8 | 32 | 35 |
| -7 | 42 | 44 |
| -6 | 33 | 33 |
| -5 | 31 | 30 |
| -4 | -16 | 10 |
| -3 | 16 | 12 |
| -2 | -14 | 8 |
| -1 | -15 | 3 |
| 0 | 25 | 27 |
| 1 | 22 | 25 |
| 2 | 40 | 40 |
| 3 | 33 | 35 |
| 4 | 46 | 44 |
| 5 | 37 | 34 |
| $h = 5$ $l = 1$ | | |
| -10 | -20 | 9 |
| -9 | -14 | 7 |
| -8 | -18 | 5 |
| -7 | 23 | 21 |
| -6 | -15 | 14 |
| -5 | 40 | 40 |
| -4 | 28 | 29 |
| -3 | 65 | 65 |
| -2 | 54 | 56 |
| -1 | 84 | 83 |
| 0 | 49 | 47 |
| 1 | 88 | 87 |
| 2 | 71 | 71 |
| 3 | 83 | 82 |
| 4 | 55 | 55 |
| 5 | 60 | 57 |
| $h = 5$ $l = 2$ | | |
| -10 | 26 | 27 |
| -9 | 27 | 30 |
| -8 | 60 | 61 |
| -7 | 60 | 61 |
| -6 | 78 | 78 |
| -5 | 64 | 65 |
| -4 | 105 | 105 |
| -3 | 113 | 109 |
| -2 | 112 | 110 |
| -1 | 83 | 83 |
| 0 | 89 | 92 |
| 0 | 95 | 92 |
| 1 | 71 | 70 |
| 2 | 72 | 71 |
| 3 | 36 | 37 |
| 4 | 33 | 34 |
| $h = 5$ $l = 3$ | | |
| -10 | 56 | 56 |
| -9 | 79 | 78 |
| -8 | 77 | 78 |
| -7 | 94 | 95 |
| -6 | 70 | 71 |
| -5 | 90 | 88 |
| -4 | 54 | 53 |
| -3 | 72 | 70 |
| -2 | 34 | 32 |
| -1 | 35 | 31 |
| 0 | -17 | 4 |
| 1 | -18 | 5 |
| 2 | 26 | 19 |
| 3 | -21 | 7 |
| $h = 5$ $l = 4$ | | |
| -10 | 40 | 38 |
| -9 | 21 | 25 |
| -8 | 35 | 32 |
| -7 | -12 | 11 |
| -6 | -15 | 6 |
| -5 | 18 | 17 |
| -4 | -16 | 6 |
| -3 | 38 | 33 |
| -2 | 24 | 23 |
| -1 | 37 | 37 |
| 0 | 25 | 30 |
| 1 | 42 | 43 |
| 2 | 40 | 38 |
| $h = 5$ $l = 5$ | | |
| -9 | 19 | 13 |
| -8 | 38 | 37 |
| -7 | 28 | 27 |
| -6 | 39 | 39 |
| -5 | 37 | 38 |
| -4 | 65 | 68 |
| -3 | 53 | 56 |
| -2 | 69 | 67 |
| -1 | 55 | 51 |
| 0 | 71 | 72 |
| $h = 5$ $l = 6$ | | |
| -7 | 70 | 70 |
| -6 | 67 | 65 |
| -5 | 81 | 80 |
| -4 | 76 | 76 |
| -3 | 76 | 77 |
| $h = 6$ $l = -5$ | | |
| -3 | 20 | 19 |
| -2 | -19 | 21 |
| -1 | 44 | 43 |
| 0 | 43 | 37 |
| 1 | 55 | 55 |
| 2 | 52 | 53 |
| $h = 6$ $l = -4$ | | |
| -5 | 54 | 52 |
| -4 | 70 | 68 |
| -3 | 68 | 66 |
| -2 | 92 | 89 |
| -1 | 79 | 78 |
| 0 | 90 | 87 |
| 1 | 63 | 62 |
| 2 | 76 | 75 |
| 3 | 61 | 61 |
| $h = 6$ $l = -3$ | | |
| -7 | 78 | 77 |
| -6 | 70 | 71 |
| -5 | 83 | 80 |
| -4 | 68 | 63 |
| -3 | 84 | 84 |
| -2 | 72 | 71 |
| -1 | 69 | 70 |
| 0 | 40 | 40 |
| 1 | 48 | 49 |
| 2 | 31 | 29 |
| 3 | 24 | 30 |
| 4 | 19 | 10 |
| $h = 6$ $l = -2$ | | |
| -8 | 45 | 50 |
| -7 | 38 | 41 |
| -6 | 47 | 49 |
| -5 | 29 | 28 |
| -4 | 41 | 39 |
| -3 | 18 | 14 |
| -2 | 24 | 23 |
| -1 | -15 | 4 |
| 0 | -15 | 8 |
| 1 | 24 | 19 |
| 2 | -17 | 14 |
| 3 | 29 | 35 |
| 4 | 25 | 24 |
| $h = 6$ $l = -1$ | | |
| -8 | -21 | 1 |
| -6 | -18 | 12 |
| -5 | -17 | 10 |
| -4 | 44 | 40 |
| -3 | 37 | 34 |
| -2 | 67 | 69 |
| -1 | 61 | 62 |
| 0 | 78 | 78 |
| 1 | 77 | 76 |
| 2 | 91 | 91 |
| 3 | 79 | 78 |
| 4 | 76 | 74 |
| $h = 6$ $l = 0$ | | |
| -9 | 38 | 40 |
| -8 | 47 | 49 |
| -7 | 77 | 80 |
| -6 | 76 | 80 |
| -5 | 97 | 95 |
| -4 | 100 | 101 |
| -3 | 142 | 134 |
| -3 | 129 | 134 |
| -2 | 109 | 111 |
| -1 | 108 | 108 |
| 0 | 80 | 79 |
| 1 | 87 | 87 |
| 2 | 63 | 63 |
| 3 | 50 | 50 |
| 4 | -21 | 26 |
| $h = 6$ $l = 1$ | | |
| -9 | 69 | 70 |
| -8 | 93 | 94 |
| -7 | 78 | 79 |
| -6 | 85 | 85 |
| -5 | 66 | 67 |
| -4 | 72 | 73 |
| -3 | 54 | 52 |
| -2 | 47 | 49 |
| -1 | 20 | 20 |
| 0 | -19 | 23 |
| 1 | -15 | 3 |
| 2 | -20 | 3 |
| 3 | -15 | 8 |
| $h = 6$ $l = 2$ | | |
| -9 | 27 | 34 |
| -8 | 18 | 25 |
| -7 | 31 | 29 |
| -6 | -15 | 4 |
| -5 | 18 | 5 |
| -4 | 17 | 13 |
| -3 | -17 | 10 |
| -2 | 26 | 28 |
| -1 | 32 | 25 |
| 0 | 44 | 43 |
| 1 | 34 | 35 |
| 2 | 51 | 51 |
| $h = 6$ $l = 3$ | | |
| -9 | 24 | 19 |
| -8 | 22 | 24 |
| -7 | 42 | 43 |
| -6 | 34 | 35 |
| -5 | 59 | 59 |
| -4 | 60 | 62 |
| -3 | 87 | 83 |
| -2 | 68 | 68 |
| -1 | 72 | 71 |
| 0 | 66 | 69 |
| 1 | 78 | 79 |
| $h = 6$ $l = 4$ | | |
| -9 | 54 | 56 |
| -8 | 69 | 70 |
| -7 | 64 | 64 |
| -6 | 77 | 75 |
| -5 | 79 | 76 |
| -4 | 95 | 92 |
| -3 | 72 | 72 |
| -2 | 79 | 73 |
| -1 | 60 | 57 |
| 0 | 60 | 57 |
| $h = 6$ $l = 5$ | | |
| -7 | 59 | 61 |
| -6 | 48 | 45 |
| -5 | 51 | 47 |
| -4 | 30 | 33 |
| -3 | 34 | 30 |
| -2 | -14 | 5 |
| $h = 7$ $l = -3$ | | |
| 2 | 63 | 62 |
| $h = 7$ $l = -2$ | | |
| 2 | 62 | 64 |
| $h = 7$ $l = -1$ | | |
| 2 | -21 | 7 |

were arbitrarily assigned for this refinement. The structure refined to an $R$ of 0.076, but the thermal parameter of the oxygen assigned to the special position became very large. A difference Fourier using all atoms except the special-position oxygen located an oxygen in a general position approximately 1.5 Å from the center of symmetry. Using these oxygen positions and anisotropic thermal parameters, the structure was refined by least squares methods. The function minimized was $\Sigma\omega(|F_o| - |F_c{}^*|)^2$ where $\omega$ is the weight defined as $1/\sigma^2(F_o)$ and

$$F_c{}^* = kF_c/\left\{1 + 2g\left(\frac{e^2}{mc^2V}\right)^2 \text{Lp } X \left[\frac{(1+\cos^2 2\alpha)(\cos^2 2\alpha + \cos^4 2\theta)}{(\cos^2 2\alpha + \cos^2 2\theta)^2}\right]^2 F_c{}^2\right\}^{1/4}$$

in which $k$ is a scale constant, Lp is the Lorentz-polarization factor, $g$ is the extinction coefficient (Zachariasen, 1967; Larson, 1967), $V$ is the unit cell volume, $\alpha$ is the monochromator angle, and $F_c$ is the structure factor calculated in the usual way. Scattering factors for the ions $U^{6+}$, $Si^{4+}$, $Cu^{2+}$, and $O^{2-}$ (*International Tables for X-ray Crystallography,* Vol. IV) were used, and appropriate anomalous dispersion corrections were applied (Cromer and Liberman, 1970). The final parameters listed in Table 2 yield an $R = 0.0303$ and $R_w = 0.0263$, where $R = \Sigma|\Delta F|/\Sigma|F_o|$ and $R_w = [\Sigma\omega(\Delta F)^2/\Sigma\omega F_o{}^2]^{1/2}$. Table 3 gives the value of observed and calculated structure factors.

The resultant structure is in general agreement with that found by Piret-Meunier and van Meerssche, except that we have found one additional oxygen in the unit cell, having moved an oxygen from a special to a general position. Attempts to refine the structure in space group $P1$, or in $P\bar{1}$ with the new general position oxygen site only half occupied, did not yield a reasonable alternative. The structure solution thus supports the conclusion that the empirical formula should be written $CuO \cdot 2UO_3 \cdot 2SiO_2 \cdot 7H_2O$.

## Composition

Independent corroboration of the stoichiometry found through the structure refinement was undertaken by performing a thermogravimetric analysis. The analyses by Novacek (1935a,b), on which the published stoichiometry is based, were performed on three samples of 2.0, 4.5, and 8.5 mg weight respectively. The thermogravimetric analysis was performed on a 25.4 mg sample heated in nitrogen to a temperature of 650°C. Loss in weight equivalent to $4H_2O$ occurred between 75° and 150°C; weight loss equivalent to an additional $2H_2O$ occurred between 200–250°C; and a weight loss equivalent to one more water molecule occurred gradually between 300°–650°C. A separate sample (14.8 mg), heated to 650°C, lost weight equivalent to nearly $7H_2O$, and showed no further weight loss up to 800°C. Pertinent analytical data are given in Table 4.

The density of several crystal aggregates (8.27, 8.86, 8.22 mg) was measured using a Berman balance, the results ranging from 3.82-3.84 g/cm³. The calculated value for unit cells containing hydrogen equivalent to $6H_2O$ and $7H_2O$ are 3.815 and 3.893

TABLE 4. Water Loss on Heating Cuprosklodowskite

| | $CuO \cdot 2UO_3 \cdot 2S \cdot O_2 \cdot 7H_2O$ | | Sample 1 (25.4 mg) | Sample 2 (14.8 mg) |
|---|---|---|---|---|
| | | 75-150° C | | |
| % Wt Loss | 8.03 | | 7.89 | -- |
| Δ $H_2O$ | -4 | | -3.93 | -- |
| | | 200-250°C | | |
| % Wt Loss | 4.01 | | -1.97 | -- |
| Δ $H_2O$ | -2 | | 1.97 | -- |
| | | 300-650°C | | |
| % Wt Loss | 2.01 | | 1.97 | -- |
| Δ $H_2O$ | -1 | | -0.98 | -- |
| | | Total | | |
| % Wt Loss | 14.05 | | 13.80 | 13.75 |
| Δ $H_2O$ | -7 | | -6.88 | -6.86 |

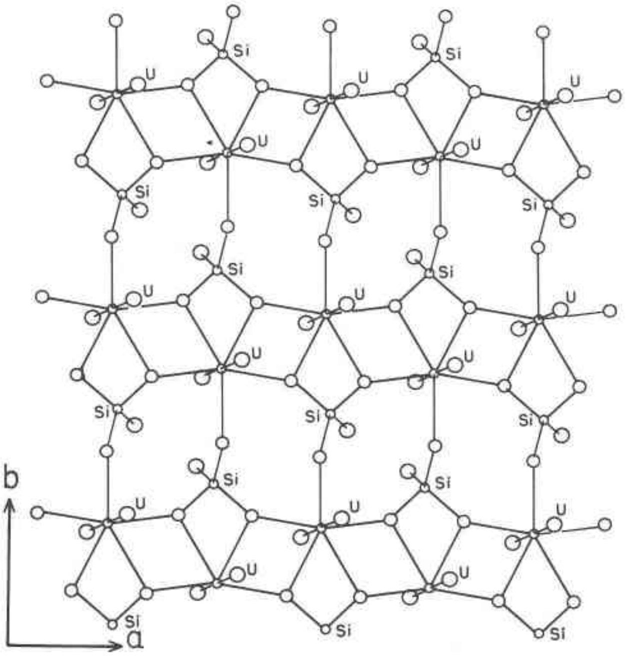

FIG. 1. Projection of the uranyl silicate layer.

g/cm$^3$, respectively. Since the crystal aggregates may contain considerable air space, and the analyses indicate slightly less than $7H_2O$, the data can be considered to be in reasonable agreement with the higher water content stoichiometry. These data corroborate the stoichiometry deduced in the structure refinement.

TABLE 5. Selected Intermolecular Distances and Angles

| Uranium Coordination | | Copper Coordination (T Site Symmetry) | |
|---|---|---|---|
| U-O(1) | 1.77(1) | Cu-O(1) | 2.48(1) |
| O(2) | 1.77(1) | O(7) | 1.96(1) |
| O(3) | 2.43(1) | O(8) | 1.96(1) |
| O(3)' | 2.34(1) | | |
| O(4) | 2.32(1) | O(1)-O(7) | 92.3(3) |
| O(4)' | 2.43(1) | O(8) | 92.5(4) |
| O(6) | 2.29(1) | O(7)-O(8) | 91.5(4) |
| O(1)-O(2) | 178.9(4) | Silicon coordination | |
| O(3) | 91.8(3) | | |
| O(3)' | 91.0(3) | Si-O(3) | 1.60(1) |
| O(4) | 91.4(3) | O(4) | 1.61(1) |
| O(4)' | 90.2(3) | O(5) | 1.67(1) |
| O(6) | 90.4(3) | O(6) | 1.59(1) |
| O(2)-O(3) | 89.3(3) | O(3)-O(4) | 98.8(4) |
| O(3)' | 89.4(3) | O(5) | 109.4(4) |
| O(4) | 87.9(3) | O(6) | 115.3(4) |
| O(4)' | 90.3(3) | | |
| O(6) | 88.7(3) | O(4)-O(5) | 110.3(4) |
| | | O(4)-O(6) | 115.2(4) |
| O(3)-O(3)' | 68.2(3) | O(5)-O(6) | 107.7(4) |
| O(4) | 60.4(2) | | |
| O(4)' | 80.9(2) | | |
| O(4)-O(4)' | 67.9(3) | | |
| O(4)-O(6) | 82.6(2) | | |

## Discussion of the Structure

As stated earlier, the fundamental structural unit consists of sheets of composition $[(UO_2)_2(SiO_4)_2]^{4-}$. These are made up of chains, formed by edge-sharing pentagonal-bipyramidal $UO_7$ polyhedra and $SiO_4$ tetrahedra, joined to one another via an Si-O-U linkage to form the sheets (Fig. 1). The chains parallel the direction of elongation, [100], and the sheets parallel the perfect (010) cleavage. It should be noted that the two uranyl oxygens and one of the silicate oxygens are not involved in the intra-sheet bonding. The $Cu^{2+}$ ion lies on a center of symmetry and is bonded to four water molecules in an approximately square-planar array at distances of 1.96 Å. Additionally, the copper has two uranyl oxygen neighbors from adjacent sheets at 2.48 Å completing the distorted octahedral coordination. Pertinent interatomic distances and angles are listed in Table 5. A stereoscopic view of the structure is given in Figure 2.

The charge-balancing mechanism in cuprosklodowskite may be reflected in a number of possible interatomic distances. First among these would be a search for some indication of hydrogen bonding. The shortest oxygen-oxygen distances are those involving oxygens of the $SiO_4$ tetrahedron, the shortest (2.44 Å) being a shared edge with the uranium coordination polyhedron. Those oxygens which are interpreted as water molecules [O(7) and O(8) in the copper coordination sphere, and O(9) which is not cation coordinated] do not display exceptionally short O–O bonds. However, some distances on the order of 2.70-2.80 Å may have some significance. The copper-coordinated water molecules O(7) and O(8) lie, respectively, at distances of 2.76 Å from O(9), the uncoordinated water, and 2.70 Å from O(5), the unshared Si oxygen. The evidence for hydrogen bonding is not clear, and the existence of hydrogen as hydronium ions remains indeterminate.

The possibility that one of the uranyl oxygens is actually a hydroxyl as suggested by Mokeeva (1958) and by Smith and Stohl (1972) is not supported, in that the U–O bonds are short and equal 1.77 Å within the standard deviation. This strongly suggests that the ions are identical and of high negative charge, *i.e.*, oxygen rather than hydroxyl.

The third possibility is that hydroxyl ion is present in the silicon coordination sphere, as suggested by Smith and Stohl (1972). Silicon has three oxygen

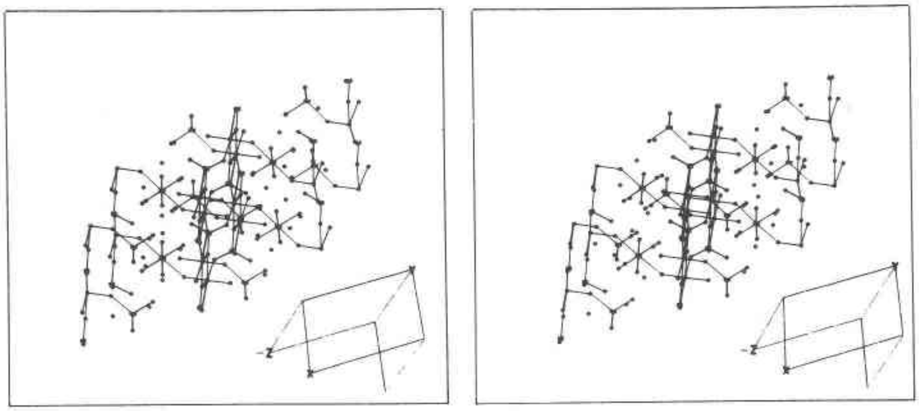

FIG. 2. Stereoscopic view of the cuprosklodowskite structure. The translational directions for the unit cell are shown at bottom, right.

neighbors at nearly equal distances (1.59-1.61 Å), all of which are shared by uranium. The remaining oxygen, O(5), which is unshared by other cations, lies at the significantly greater distance of 1.67 Å. Furthermore this oxygen is the nearest neighbor of the unshared uranyl oxygen, O(2), although the distance of 2.82 Å is not particularly meaningful in terms of hydrogen bonding. The possibility of O(5) being a hydroxyl ion is strongly suggested. Although the evidence is not unequivocal, it seems to favor writing the structural formula of cuprosklodowskite as $Cu[(UO_2)_2(SiO_3OH)_2] \cdot 6H_2O$.

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