# NATIONAL BUREAU OF STANDARDS REPORT

10 441

Progress Report

on

# THE CRYSTAL STRUCTURE OF $CaKAsO_4 \cdot 8H_2O$

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

# NATIONAL BUREAU OF STANDARDS

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# THE CRYSTAL STRUCTURE OF $CaKAsO_4 \cdot 8H_2O$

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# The Crystal Structure of $CaKAsO_4 \cdot 8H_2O$

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# Abstract

$CaKAsO_4 \cdot 8H_2O$ crystallizes in the orthorhombic unit cell $\underline{a}$ = 7.146(1) Å, $\underline{b}$ = 11.696(2) Å, $\underline{c}$ = 7.100(2) Å at 25°C with cell contents of 2[$CaKAsO_4 \cdot 8H_2O$]. The structure has been refined to $\underline{R_w}$ = 0.037, $\underline{R}$ = 0.043 in space-group Cm2m using 1023 observed reflections corrected for absorption. Allowance was made for anomalous dispersion and secondary isotropic extinction.

All ions in $CaKAsO_4 \cdot 8H_2O$ are completely hydrated. Ca coordinates to eight water oxygens with Ca...O distances in the range 2.459(5) Å to 2.490(3) Å. K coordinates to eight water oxygens with K...O distances ranging from 2.746(3) Å to 2.960(7) Å. The coordination polyhedra of Ca and K share a face of four water molecules. The oxygens of the $AsO_4$ ion are the acceptors in hydrogen bonds from 16 water molecules and form no bonds with the cations. The two crystallographically different As—O distances in the $AsO_4^{3-}$ ion are 1.682(4) Å and 1.684(4) Å when uncorrected for thermal motion, and 1.690 Å and 1.692 Å with the riding model correction.

The structure of $CaKAsO_4 \cdot 8H_2O$ is related to that of $MgNH_4PO_4 \cdot 6H_2O$, struvite. This structural type may be common to several calcium phosphates and related compounds.

# The Crystal Structure of $CaKAsO_4 \cdot 8H_2O$

## Introduction

In crystallization, nucleation is an important step which could conceivably control the identities and forms of materials that grow to macroscopic sizes. For various reasons[1] studies of hydrates may give valuable clues to the existence of possible precursors or nuclei of crystallization in aqueous environments. In biological mineralization, hydration of ions is likely to play a significant role, and the formation of ion pairs or higher complexes may be important. We found in our study of $CaCO_3 \cdot 6H_2O$[1] that the crystal structure contains $[CaCO_3]^\circ$ ion pairs which are completely hydrated. All Ca ions in $CaCO_3 \cdot 6H_2O$ are in ion pairs. To examine the hydration of Ca and the possible retention in the solid state of ion pairs involving $XO_4$ ions, in this case $AsO_4^{3-}$, we have determined the crystal structure of $CaKAsO_4 \cdot 8H_2O$. Prior to this work, the formula was believed to be $CaKAsO_4 \cdot 7H_2O$. The related salts $CaKPO_4 \cdot 8H_2O$ and $CaNH_4PO_4 \cdot 8H_2O$ were also prepared. The structure determination was carried out on $CaKAsO_4 \cdot 8H_2O$ because it is the only one that is sufficiently stable at room temperature. The salt $CaNH_4AsO_4 \cdot 8H_2O$ was not made.

## Data collection and structure refinement

$CaKAsO_4 \cdot H_2O$ was prepared by mixing 20 $cm^3$ of 0.1 $m \cdot \ell^{-1}$ $CaCl_2$ solution, 25 $cm^3$ 1.0 $m \cdot \ell^{-1}$ tri-potassium citrate solution and 10 $cm_3$ 3.0 $m \cdot \ell^{-1}$ KOH solution at 0°C and then adding 10 $cm^3$ 0.2 $m \cdot \ell^{-1}$ $K_2HAsO_4$ solution. The resultant mixture was kept at 0°C; precipitation of $CaKAsO_4 \cdot 8H_2O$ began after about 2 hours.

The crystal used in the data collection was an approximately square plate with dimensions 0.06 mm x 0.10 mm x 0.12 mm. It was mounted on the goniometer head in our usual way[2].

Formula (ideal): $CaKAsO_4 \cdot 8H_2O$
cell: orthorhombic
$\underline{a} = 7.146(1)$ Å at 25°C
$\underline{b} = 11.696(2)$
$\underline{c} = 7.100(2)$
volume = 593.40 $Å^3$
space-group Cm2m; cell contents $2[CaKAsO_4 \cdot 8H_2O]$
reciprocal lattice extinctions: $h + k = 2n + 1$ for $hk\ell$.
density calculated from refractive indices = 2.10 $g \cdot cm^{-3}$ [3]
density calculated from unit cell = 1.933 $g \cdot cm^{-3}$.

In general, the data collection and data processing procedure given in reference 2 was followed. The $\theta$-$2\theta$ scans here were carried out at 0.5°/min for $2\theta$. Each background was counted for 40 sec. Absorption corrections were made assuming $\mu(Mo) = 39.6\ cm^{-1}$. The maximum and minimum transmission factors were 0.83 and 0.66, respectively. 2163 reflections were collected from the $hk\ell$ and $\bar{h}k\ell$ octants of the reciprocal lattice and were merged into a unique set of 1071, of which 1023 were "observed" and 48 are "unobserved". "Unobserved" reflections are those less than $2\sigma(I)$ above background.

The structure of $CaKAsO_4 \cdot 8H_2O$ was solved from a sharpened Patterson map (calculated from the $E^2-1$ coefficients, where E is the quasi-normalized structure factor[4]) and from subsequent $F_0$ electron density syntheses. The scattering factors used were those of the neutral atoms. They were taken from references 5 and 6 for the X-ray 67[7] refinements and from reference 8 for the refinements using the program RFINE, written by L. W. Finger of the Carnegie Institute of Washington. The structure with hydrogens excluded was refined isotropically to $\underline{R_w} = 0.067$, $\underline{R} = 0.068$ using X-ray 67. The quantity minimized was $\Sigma w(F_0 - F_c)^2$. Unobserved reflections calculating more than $2\sigma(F_{hk\ell})$ above background were included. Three cycles of anisotropic refinement varying all unconstrained parameters decreased $\underline{R_w}$ to 0.054 and $\underline{R}$ to 0.056.

The hydrogen positions were found in a difference electron density synthesis calculated after the last cycle in this refinement. The next largest peaks after the hydrogen atoms were equivalent to about 1/2 of an electron between As and O(1), and about 1/3 of an electron at 0.5, 0.35, 0.25. Because of its proximity to As and O(1), the former peak cannot be attributed to an atom. The latter peak is in a void in the structure, but is, however, only 2.30 Å from O(5) and 2.39 Å from O(2).

It is 2.30 Å from H(3) and 2.65 Å from K. Thus, because it does not seem to fill all the requirements of any one chemical species, it is attributed to the background.

The structure including hydrogen atoms with variable positional parameters but with the hydrogen thermal parameters fixed at B = 1.0 $Å^2$ was then refined anisotropically to $\underline{R_w}$ = 0.040, $\underline{R}$ = 0.047 in three cycles using Finger's least-squares program RFINE. Correction was made for secondary isotropic extinction. Although the environments of the oxygen atoms are not very different, the surprising result that the two crystallographically different As—O distances in the $AsO_4$ group were 1.664(4) Å and 1.701(4) Å was obtained. After correction for anomalous dispersion was included in the refinement, the As—O distances became essentially equal, as would be expected from consideration of their similar environments. The values of f' and f" were taken from Cromer[9]. The parameters from the third cycle ($\underline{R_w}$ = 0.037, $\underline{R}$ = 0.043) of this series of refinements are given in Table 1. (The values for equivalent refinement of the other enantiomorph are $\underline{R_w} = 0.049$, $\underline{R} = 0.054$.) The observed and calculated structure factors are given in Table 2. The average shift/error in the last cycle was 0.19 excluding hydrogen parameters and 0.35 for all parameters. The standard deviation of an observation of unit weight, $[\Sigma w(|F_o|-|F_c|)^2/(1071 - 57)]^{\frac{1}{2}}$, was 1.60. The largest correlation coefficient was 0.41 between $(\underline{B}_{22},\underline{B}_{12})$ of O(4); all others were below 0.17. Because the isotropic secondary extinction parameter refined to -0.00000100(7) cm, it was constrained to zero in the final refinements. The physically unreasonable negative value obtained may be due to small errors in the absorption corrections.

The space-group Cm2m requires the chemical formula to contain an even number of water molecules unless there are statistical vacancies in some of the water positions. The thermal parameters of the oxygens of the water molecules are fairly close to those of the oxygens in the $AsO_4$ ions and thus the formula is probably $CaKAsO_4 \cdot 8H_2O$ with no statistical vacancies. To check this, a sample of $CaKAsO_4 \cdot 8H_2O$ was heated quickly (~1 min) to constant weight at 400°C; a weight loss of eight moles of water per formula weight was obtained.

Three sets of hydrogen positions, (i) from the difference electron density synthesis, (ii) from the least-squares refinements, and (iii) calculated idealized positions, are given in Table 3. All distances and angles involving hydrogen in the tables or the text were obtained using these calculated hydrogen positions.

## Description of the Structure

The structure of $CaKAsO_4$ is shown in Figure 1. The Ca and K ions and the oxygen of the O(4) water molecule lie on mirror planes parallel to (001). The $AsO_4$ ions lie on mirror planes halfway between these cation planes. The O(3) and O(5) water molecules lie approximately halfway between the cation planes and the anion planes. Also, mirror planes containing both cations and anions and the oxygen of the O(3) water molecule exist parallel to (100).

All the ions in $CaKAsO_4 \cdot 8H_2O$ are completely hydrated, and thus there are no direct bonds between ions themselves. There are eight water molecules in the coordination polyhedra of the Ca and K ions and 16 in the coordination polyhedron of the $AsO_4$ ion. Each of the water molecules in the structure is bonded to the Ca, K and $AsO_4$ ions. The coordination polyhedra of Ca and K share a face of four water molecules.

The Ca ion environment.--The environment of the Ca ion, which lies on the intersection of two mirror planes, is detailed in Table 4 and Figure 1. The Ca ion is coordinated to eight oxygens of water molecules arranged in an approximately square antiprism. The range of Ca...O distances, 2.459 Å to 2.490 Å, is unusually small and indicates strong bonding to all these oxygens. The shortest O...O distance in this polyhedron is 2.789 Å for O(3)...O(4). All other O...O distances are a little over 3 Å. The shortest Ca...O distances are to the approximate square of water oxygens O($3^{I}$, $3^{II}$, $4^{I}$, $4^{II}$) (Figure 1), which is also part of the K ion environment. However, these oxygens are the weakest bonded to K. The longest Ca...O bonds are to those water oxygens in edges common to the coordination polyhedra of Ca and K. These oxygens, O($5^{I}$, $5^{II}$, $5^{III}$, $5^{IV}$), are strongly bonded to K though not as strongly as they are to Ca.

The K ion environment.--The details of the environment of the K ion are given in Table 4 and Figure 1. K is bonded to eight water oxygens arranged in a distorted square antiprism.

As would be expected, K is relatively far (2.918 Å, 2.960 Å) from the coordination polyhedron face which involves water oxygens O($3^{III}$, $3^{IV}$) and O($4^{III}$, $4^{IV}$) (for $K^{I}$, Figure 1) and which is shared with the $Ca^{II}$ coordination polyhedron. The $K^{I}$ ion instead forms stronger K...O (2.746 Å) bonds to the O($5^{I}$, $5^{II}$, $5^{V}$, $5^{VI}$) water oxygens in the opposite face of the coordination polyhedron.

The edges of this face are also edges in the Ca coordination polyhedron. The shortest K...Ca distance, $K^{I}...Ca^{II}$ = 3.66 Å, is along (010), across the shared face comprised of water oxygens of types O($3^{III}$, $3^{IV}$) and O($4^{III}$, $4^{IV}$).

The $AsO_4$ group and its environment.--The details of the $AsO_4$ group and its environment are given in Table 5. The two unique As-O distances are not significantly different, which is consistent with the lack of cations and very strong hydrogen bonds in their environments. The O-As-O angles across the mirror planes are significantly different from the other O-As-O angles. The reason seems to be that the hydrogen bonds from the water molecules are strong enough to pull O(1) and O(2) away from the mirror plane to angles greater than the tetrahedral angle. (It has been our experience that groups such as $PO_4^{3-}$ are easily distorted from tetrahedral symmetry.) The O(1)-As-O(2) angle of 107.5° is, therefore, regarded as a concomitant result. The $AsO_4$ group is extensively hydrogen bonded, O(1) and O(2) each being the acceptor in four hydrogen bonds (Tables 5 and 6). There is no coordination between the $AsO_4$ group and the Ca and K cations.

The environments of the water molecules.--The environments of the water molecules are detailed in Table 6. The water molecules in Figure 1 and in the tables have the idealized geometry O-H = 0.958 Å and ∠H-O-H = 104.5°. The hydrogen bonds were made as linear as possible in the calculation of the probable hydrogen positions. Water oxygens O(3) and O(4) lie on mirror planes; O(5) is in a general position. All the oxygens of the water molecules are bonded to the Ca and K ions and all the hydrogens are hydrogen bonded to the oxygens in the $AsO_4$ group. There is no hydrogen bonding between water molecules. The O(3) and O(4) water molecules are bonded strongly to Ca, less strongly to K, and are the donors in hydrogen bonds of average strength to O(2) and O(1) of the $AsO_4$ group. The O(5) water molecule is bonded slightly less strongly to Ca but more strongly to K than are O(3) and O(4), and appears to form slightly stronger hydrogen bonds to the $AsO_4$ group. As would be expected to minimize repulsions, the cations and hydrogens are arranged in approximately tetrahedral directions about each water oxygen.

## Discussion

The average As-O distance in $CaKAsO_4 \cdot 8H_2O$ is 1.685 Å, corrected for thermal motion, and the individual As-O distances are equal within experimental error. Essentially equal As-O distances are expected from the close similarity of the environments of the oxygen atoms of the As-O group. Inclusion of anomalous scattering effects, therefore, seemingly resulted in a refinement of the As-O bond lengths from unreasonable to reasonable values.

Other recently determined crystal structures which contain $AsO_4$ groups are $CaHAsO_4 \cdot 2H_2O$[11] (the mineral pharmacolite) and $2H_3AsO_4 \cdot H_2O$[12]. In the refinement of the crystal structure of $CaHAsO_4 \cdot 2H_2O$, corrections for anomalous scattering were made but no corrections for extinction or absorption were included. Further, the As-O bond lengths in $CaHAsO_4 \cdot 2H_2O$ are perturbed by the cationic environment and by the presence of a covalently bonded hydrogen atom.

Nevertheless, three of the As-O distances average to 1.672 Å, close to those observed here. The fourth As-O distance involves the oxygen with the covalently bonded hydrogen atom and is 1.729(9) Å. In the determination of the crystal structure of $2H_3AsO_4 \cdot H_2O$, the data were collected photographically using unfiltered Cu(Kα) radiation and were corrected for absorption. Only isotropic refinement was carried out, and no correction was made for anomalous scattering. The As-O distances in this relatively imprecise structural determination range from 1.594 Å to 1.695 Å and average to 1.652 Å. The environment of the $AsO_4$ group in $2H_3AsO_4 \cdot H_2O$ is similar to that in $CaKAsO_4 \cdot 8H_2O$ and more nearly equal As-O distances would be expected than those given for $2H_3AsO_4 \cdot H_2O$

It is interesting to note that no ion pairs between Ca and $AsO_4$ are formed in the $CaKAsO_4 \cdot 8H_2O$ structure, although $[CaCO_3]^\circ$ ion pairs were found in the structure of $CaCO_3 \cdot 6H_2O$[1] and both the $CaKAsO_4 \cdot 8H_2O$ structure and the $CaCO_3 \cdot 6H_2O$ structure contain large amounts of water. Reasonable evidence for the presence of $[CaHPO_4]^\circ$ and $[CaH_2PO_4]^+$ ion pairs in calcium phosphate solutions has been given[13]. The formation of higher complexes[14] than pairs in these solutions may be unlikely.

The complete hydration of the Ca ion in the crystal structure of $CaKAsO_4 \cdot 8H_2O$ is the only solid-state example known to us with certainty. The complete hydration of the K ion is surprising and is likewise the only solid-state example known to us with certainty. Because no cation-anion bonds are formed in $CaKAsO_4 \cdot 8H_2O$, the low thermal stability of the related series of compounds given in Table 7 is undoubtedly a consequence of the importance of hydrogen bonding in the structures. In this connection, arsenates are known to form more stable hydrates than phosphates, and some calcium arsenate hydrates (see, for example, references 15 and 16) have no stable counterpart among the calcium phosphates. Thus a study of hydrated calcium arsenates should provide details of possible precursors of crystallization in calcium arsenate and calcium phosphate systems.

The structure of $CaKAsO_4 \cdot 8H_2O$ (Figure 1) resembles that of $MgNH_4PO_4 \cdot 6H_2O$, struvite[17] (Figure 2), though the two structures are not isomorphous. The $MgNH_4PO_4 \cdot 6H_2O$ structure has space-group $Pmn2_1$; the space-group of $CaKAsO_4 \cdot 8H_2O$ is Cm2m. The structures of both compounds contain layers of $XO_4$ ions and water molecules. The layers are parallel to (001) with $\underline{z} \sim 0$ in $MgNH_4PO_4 \cdot 6H_2O$, and parallel to (010) with $\underline{y} \sim 0$ in $CaKAsO_4 \cdot 8H_2O$. Hydrated cations lie between these layers. In $MgNH_4PO_4 \cdot 6H_2O$, Mg is coordinated to six water oxygens arranged in an approximate octahedron. The Ca ion in $CaKAsO_4 \cdot 8H_2O$ lies near the site of Mg in $MgNH_4PO_4 \cdot 6H_2O$, but is coordinated to the oxygens of eight water molecules. This difference in cation coordinations is reflected in the different numbers of waters of crystallization in the formulas of the two compounds.

In $MgNH_4PO_4 \cdot 6H_2O$, the $PO_4$ group is positioned so that the $NH_4$ ion hydrogen bonds to O(1) of the $PO_4$ group[17,18]. In $CaKAsO_4 \cdot 8H_2O$, the $AsO_4$ group is in a special position at the intersection of two mirror planes and cannot have the orientation $PO_4$ has in $MgNH_4PO_4 \cdot 6H_2O$. Its orientation is such that the oxygen atoms are not near the K ion, which occupies a site in $CaKAsO_4 \cdot 8H_2O$ near that of $NH_4^+$ in $MgNH_4PO_4 \cdot 6H_2O$. The polyhedron of eight water oxygens which surround K satisfactorily in $CaKAsO_4 \cdot 8H_2O$ may not be big enough for $NH_4$

in $MgNH_4PO_4 \cdot 6H_2O$ . The hydrogen bonds from $NH_4$ to its environment are apparently too weak to increase the size of the coordination polyhedron by inducing more water molecules to crystallize in $MgNH_4PO_4 \cdot 6H_2O$. Unlike the $AsO_4$ group in $CaKAsO_4 \cdot 8H_2O$, the $PO_4$ group in $MgNH_4PO_4 \cdot 6H_2O$ forms bonds with cations.

$MgNH_4PO_4 \cdot 6H_2O$ exists as the biomineral struvite and has been found in excreta[19,20] from various forms of life, in human urinary calculi[21], in human lungs[22], and in canned goods such as lobster[23] and salmon[17]. After removal from the environment in which it formed, struvite changes[19] into $MgHPO_4 \cdot 3H_2O$, newberyite.[24]

$CaNH_4PO_4 \cdot 8H_2O$, the calcium analogue of struvite, is very unstable and decomposes to $Ca_5(PO_4)_3OH$, the major inorganic phase in the body, within minutes at room temperature, even in an aqueous environment. (As was remarked in the introduction, $CaKAsO_4 \cdot 8H_2O$ was studied here because it was one of the most stable members of the series.) Because of its unstability, $CaNH_4PO_4 \cdot 8H_2O$ probably does not exist as a biomineral, since it would then have to be stable at 37°C. It is conceivable, however, that it exists transiently even at 37°C as a highly hydrated nucleus important in the early stages of crystallization of biominerals. The high hydration of the ions in $CaNH_4PO_4 \cdot 8H_2O$ and its fairly high rate of growth (of the order of 1 mm/h) during its preparation near 0°C suggest that it is easily produced in an aqueous environment under favorable conditions.

The structural relationship of $CaKAsO_4 \cdot 8H_2O$ to $MgNH_4PO_4 \cdot 6H_2O$ speaks for the stability of this overall structural type, which may be called the struvite-type structure, after $MgNH_4PO_4 \cdot 6H_2O$. The compounds given in Tables 7 and 8 are some other probable members of this structural type. "Structural type" is used here in the sense that the structures show overall similarities, not in the sense that they are isomorphous or nearly so.

Four structural types have emerged in calcium phosphates and related compounds. These four types are:

(i) $M_5(XO_4)_3Y$, the apatite type, of which there are many examples (over 70 are listed in Wyckoff[25]);

(ii) $MXO_4$-sheet containing compounds: $CaSO_4 \cdot 2H_2O$[26], $CaHPO_4 \cdot 2H_2O$[27,28,29], $Ca(H_2PO_4)_2 \cdot H_2O$[30,31,32], $CaHPO_4$[33,31,34], and probably $Ca_2(NH_2)H_7(PO_4)_4 \cdot 2H_2O$[3], $Ca_2KH_7(PO_4)_4 \cdot 2H_2O$[3] and $CaClH_2PO_4 \cdot H_2O$[3] contain corrugated $CaPO_4$ sheets; $Ca_2PO_4Cl$[35] and probably $CaIH_2PO_4 \cdot 4H_2O$[3] contain planar sheets;

(iii) $(M,N,\square)_4(XO_4)_2$ or glaserite-type after $K_3Na(SO_4)_2$ (glaserite): $Ca_5(PO_4)_2SiO_4$[36] and $Ca_7Mg_9(Ca,Mg)_2(PO_4)_{12}$[37] both have structures related to the glaserite structure but with systematic cation vacancies, denoted □ in the general formula above; $\alpha$-$Ca_3(PO_4)_2$ [37,38] $CaNaPO_4$ [39], $Ca_4Na_2(PO_4)_4$ [39], and the high temperature solid solution between $\alpha$-$Ca_2SiO_4$ and $\bar{\alpha}$-$Ca_3(PO_4)_2$ [40,41] may be other examples of glaserite-type structures with systematic cation vacancies; $CaK_3(PO_4)_2$ [42] is probably a monoclinic distortion of the $K_3Na(SO_4)_2$ structure.

(iv) $M^{II}N^{I}XO_4\cdot nH_2O$ or struvite-type after $MgNH_4PO_4\cdot 6H_2O$ (struvite) where n is 6 to 8 and N is a larger cation than M. Several compounds which probably have struvite-type structures are given in Tables 7 and 8.

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### Table 1. Atomic Parameters of $CaKAsO_4 \cdot 8H_2O$

| Atom | x | y | z | $B^*_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ca mm** | 0.0 | 0.3750(1) | 0.5 | 1.16(4) | 1.20(5) | 1.04(5) | -- | -- | -- |
| K mm | 0.5 | 0.1877 | 0.5 | 1.40(5) | 1.94(7) | 2.33(7) | -- | -- | -- |
| As mm | 0.0 | 0.0 | 0.0 | 0.89(2) | 0.77(2) | 0.87(2) | -- | -- | -- |
| O(1) m | 0.0 | 0.0793(4) | 0.1977(5) | 1.9(1) | 1.4(1) | 1.2(1) | -- | -- | -0.4(1) |
| O(2) m | 0.3027(5) | 0.4214(4) | 0.0 | 1.2(1) | 1.9(2) | 1.7(1) | -0.5(1) | -- | -- |
| O(3) m | 0.5 | 0.0031(6) | 0.2235(5) | 1.9(1) | 2.4(1) | 1.4(1) | -- | -- | -0.1(2) |
| O(4) m | 0.2228(5) | -0.0003(7) | 0.5 | 1.6(1) | 3.2(2) | 1.8(1) | 1.0(2) | -- | -- |
| O(5) 1 | 0.2119(4) | 0.2697(3) | 0.2824(4) | 2.2(1) | 1.3(1) | 1.7(1) | -0.1(1) | .09(7) | -0.07(8) |

Figures in parentheses are standard errors in last significant figure quoted, and were computed in the final cycle of full-matrix least-squares refinement.

* Thermal parameters have the form $\exp -1/4[a^{*2}B_{11}h^2 + b^{*2}B_{22}k^2 + c^{*2}B_{33}\ell^2 + 2a^*b^*B_{12}hk + 2a^*c^*B_{13}h\ell + 2b^*c^*B_{23}k\ell]$

** Symmetry of atom site.

symmetry elements: $x,y,z$; $-x,y,z$; $-x,y,-z$; $x,y,-z$; $\frac{1}{2}+x$, $\frac{1}{2}+y$, $z$; $\frac{1}{2}-x$, $\frac{1}{2}+y,z$; $\frac{1}{2}-x$, $\frac{1}{2}+y$, $-z$; $\frac{1}{2}+x$, $\frac{1}{2}+y,-z$.

Table 2 Observed and calculated structure factors for $CaKAsO_4 \cdot 8H_2O$

| | | | |
|---|---|---|---|
| H,0,0 | | | |
| 2 | 795 | 734 | 0 |
| 4 | 1470 | 1456 | 0 |
| 6 | 755 | 765 | 0 |
| 8 | 463 | 479 | 0 |
| 10 | 444 | 446 | 0 |
| 12 | 196 | 198 | 0 |
| H,0,1 | | | |
| 0 | 86 | 31 | 500 |
| 2 | 194 | 193 | 0 |
| 4 | 40 | 21 | 500 |
| 6 | 146 | 150 | 0 |
| 8 | 26* | 0 | 0 |
| 10 | 59 | 57 | 0 |
| 12 | 33* | 19 | 0 |
| H,0,2 | | | |
| 0 | 688 | 681 | 0 |
| 2 | 633 | 667 | 0 |
| 4 | 559 | 581 | 0 |
| 6 | 468 | 473 | 0 |
| 8 | 332 | 331 | 0 |
| 10 | 264 | 264 | 0 |
| 12 | 179 | 178 | 0 |
| H,0,3 | | | |
| 0 | 145 | 117 | 500 |
| 2 | 359 | 355 | 500 |
| 4 | 107 | 107 | 500 |
| 6 | 27* | 19 | 0 |
| 8 | 93 | 97 | 500 |
| 10 | 54 | 27 | 0 |
| 12 | 54 | 30 | 500 |
| H,0,4 | | | |
| 0 | 1541 | 1505 | 0 |
| 2 | 508 | 552 | 0 |
| 4 | 994 | 914 | 0 |
| 6 | 532 | 560 | 0 |
| 8 | 363 | 363 | 0 |
| 10 | 350 | 350 | 0 |
| 12 | 166 | 165 | 0 |
| H,0,5 | | | |
| 0 | 97 | 91 | 0 |
| 2 | 373 | 380 | 0 |
| 4 | 75 | 66 | 0 |
| 6 | 183 | 194 | 0 |
| 8 | 70 | 61 | 0 |
| 10 | 60 | 59 | 0 |
| H,0,6 | | | |
| 0 | 710 | 705 | 0 |
| 2 | 481 | 474 | 0 |
| 4 | 520 | 535 | 0 |
| 6 | 373 | 385 | 0 |
| 8 | 288 | 286 | 0 |
| 10 | 242 | 242 | 0 |
| H,0,7 | | | |
| 0 | 75 | 64 | 0 |
| 2 | 159 | 152 | 500 |
| 4 | 45 | 18 | 500 |
| 6 | 31* | 9 | 500 |
| 8 | 76 | 71 | 500 |
| 10 | 38* | 25 | 0 |
| H,0,8 | | | |
| 0 | 489 | 481 | 0 |
| 2 | 292 | 301 | 0 |
| 4 | 385 | 360 | 0 |
| 6 | 273 | 281 | 0 |
| 8 | 193 | 198 | 0 |
| 10 | 188 | 186 | 0 |
| H,0,9 | | | |
| 0 | 44 | 19 | 0 |
| 2 | 180 | 151 | 0 |
| 4 | 34* | 26 | 0 |
| 6 | 98 | 86 | 0 |
| 8 | 48 | 31 | 0 |
| H,0,10 | | | |
| 0 | 425 | 418 | 0 |
| 2 | 251 | 255 | 0 |
| 4 | 325 | 329 | 0 |
| 6 | 232 | 241 | 0 |
| 8 | 179 | 179 | 0 |
| H,0,11 | | | |
| 0 | 44* | 52 | 0 |
| 2 | 37* | 13 | 500 |
| 4 | 37* | 21 | 0 |
| 6 | 37* | 26 | 0 |
| H,0,12 | | | |
| 0 | 188 | 177 | 0 |
| 2 | 172 | 157 | 0 |
| 4 | 163 | 151 | 0 |
| H,1,0 | | | |
| 1 | 346 | 392 | 99 |
| 3 | 130 | 165 | 190 |
| 5 | 399 | 388 | 69 |
| 7 | 72 | 87 | 965 |
| 9 | 151 | 145 | 71 |
| 11 | 62 | 59 | 952 |
| H,1,1 | | | |
| 1 | 939 | 970 | 6 |
| 3 | 781 | 781 | 36 |
| 5 | 599 | 608 | 986 |
| 7 | 433 | 433 | 23 |
| 9 | 265 | 266 | 0 |
| 11 | 240 | 244 | 999 |
| H,1,2 | | | |
| 1 | 432 | 514 | 897 |
| 3 | 224 | 213 | 245 |
| 5 | 442 | 470 | 903 |
| 7 | 117 | 96 | 177 |
| 9 | 164 | 163 | 935 |
| 11 | 66 | 56 | 1000 |
| H,1,3 | | | |
| 1 | 717 | 754 | 992 |
| 3 | 556 | 569 | 980 |
| 5 | 459 | 477 | 7 |
| 7 | 369 | 382 | 980 |
| 9 | 227 | 232 | 9 |
| 11 | 229 | 221 | 980 |
| H,1,4 | | | |
| 1 | 191 | 191 | 27 |
| 3 | 45 | 53 | 766 |
| 5 | 224 | 234 | 33 |
| 7 | 40 | 38 | 851 |
| 9 | 116 | 109 | 45 |
| 11 | 39* | 44 | 961 |
| H,1,5 | | | |
| 1 | 598 | 603 | 1 |
| 3 | 500 | 501 | 55 |
| 5 | 421 | 449 | 968 |
| 7 | 333 | 343 | 45 |
| 9 | 208 | 218 | 983 |
| 11 | 200 | 197 | 6 |
| H,1,6 | | | |
| 1 | 271 | 270 | 992 |
| 3 | 166 | 162 | 87 |
| 5 | 265 | 269 | 974 |
| 7 | 90 | 81 | 95 |
| 9 | 131 | 120 | 1 |
| 11 | 67 | 58 | 19 |
| H,1,7 | | | |
| 1 | 419 | 416 | 995 |
| 3 | 360 | 382 | 970 |
| 5 | 316 | 323 | 14 |
| 7 | 262 | 272 | 963 |
| 9 | 173 | 170 | 11 |
| H,1,8 | | | |
| 1 | 88 | 95 | 971 |
| 3 | 59 | 16 | 113 |
| 5 | 101 | 116 | 964 |
| 7 | 32* | 15 | 194 |
| 9 | 63 | 56 | 997 |
| H,1,9 | | | |
| 1 | 257 | 263 | 979 |
| 3 | 222 | 227 | 29 |
| 5 | 225 | 228 | 948 |
| 7 | 185 | 171 | 30 |
| 9 | 118 | 126 | 960 |
| H,1,10 | | | |
| 1 | 137 | 134 | 43 |
| 3 | 111 | 80 | 68 |
| 5 | 143 | 129 | 43 |
| 7 | 39* | 50 | 64 |
| H,1,11 | | | |
| 1 | 260 | 236 | 994 |
| 3 | 228 | 216 | 981 |
| 5 | 201 | 191 | 3 |
| H,1,12 | | | |
| 1 | 77 | 58 | 9 |
| 3 | 88 | 43 | 151 |
| H,2,0 | | | |
| 0 | 878 | 776 | 943 |
| 2 | 962 | 916 | 69 |
| 4 | 459 | 458 | 987 |
| 6 | 351 | 350 | 994 |
| 8 | 257 | 255 | 33 |
| 10 | 161 | 159 | 944 |
| 12 | 109 | 113 | 14 |
| H,2,1 | | | |
| 0 | 896 | 861 | 988 |
| 2 | 910 | 920 | 52 |
| 4 | 568 | 555 | 26 |
| 6 | 496 | 491 | 16 |
| 8 | 281 | 290 | 50 |
| 10 | 235 | 242 | 11 |
| 12 | 158 | 147 | 44 |
| H,2,2 | | | |
| 0 | 946 | 917 | 934 |
| 2 | 595 | 583 | 45 |
| 4 | 356 | 361 | 937 |
| 6 | 155 | 168 | 832 |
| 8 | 65 | 71 | 927 |
| 10 | 140 | 148 | 911 |
| 12 | 33* | 31 | 837 |
| H,2,3 | | | |
| 0 | 255 | 276 | 862 |
| 2 | 651 | 662 | 22 |
| 4 | 252 | 262 | 977 |
| 6 | 362 | 372 | 991 |
| 8 | 218 | 224 | 37 |
| 10 | 159 | 162 | 988 |
| 12 | 136 | 132 | 33 |
| H,2,4 | | | |
| 0 | 461 | 460 | 924 |
| 2 | 384 | 397 | 28 |
| 4 | 356 | 378 | 967 |
| 6 | 228 | 243 | 955 |
| 8 | 181 | 181 | 10 |
| 10 | 123 | 140 | 975 |
| 12 | 86 | 86 | 989 |
| H,2,5 | | | |
| 0 | 761 | 769 | 26 |
| 2 | 526 | 532 | 50 |
| 4 | 504 | 515 | 37 |
| 6 | 398 | 409 | 30 |
| 8 | 246 | 251 | 61 |
| 10 | 241 | 228 | 26 |
| H,2,6 | | | |
| 0 | 407 | 404 | 954 |
| 2 | 89 | 69 | 19 |
| 4 | 252 | 245 | 972 |
| 6 | 135 | 142 | 939 |
| 8 | 81 | 94 | 993 |
| 10 | 112 | 119 | 934 |
| H,2,7 | | | |
| 0 | 111 | 129 | 971 |
| 2 | 369 | 376 | 34 |
| 4 | 132 | 134 | 4 |
| 6 | 206 | 214 | 9 |
| 8 | 162 | 147 | 50 |
| 10 | 103 | 97 | 0 |
| H,2,8 | | | |
| 0 | 251 | 276 | 916 |
| 2 | 102 | 114 | 900 |
| 4 | 192 | 199 | 924 |
| 6 | 129 | 134 | 889 |
| 8 | 85 | 92 | 940 |
| 10 | 117 | 102 | 897 |
| H,2,9 | | | |
| 0 | 341 | 338 | 24 |
| 2 | 247 | 241 | 46 |
| 4 | 266 | 264 | 34 |
| 6 | 215 | 213 | 28 |
| 8 | 162 | 141 | 60 |
| H,2,10 | | | |
| 0 | 201 | 180 | 955 |
| 2 | 142 | 132 | 5 |
| 4 | 156 | 143 | 970 |
| 6 | 122 | 114 | 960 |
| 8 | 86 | 87 | 995 |
| H,2,11 | | | |
| 0 | 104 | 99 | 51 |
| 2 | 211 | 191 | 68 |
| 4 | 123 | 106 | 71 |
| 6 | 135 | 124 | 53 |
| H,2,12 | | | |
| 0 | 154 | 140 | 917 |
| 2 | 35* | 55 | 823 |
| 4 | 104 | 103 | 915 |
| H,3,0 | | | |
| 1 | 1128 | 969 | 61 |
| 3 | 1029 | 972 | 156 |
| 5 | 699 | 713 | 995 |
| 7 | 461 | 466 | 129 |
| 9 | 371 | 366 | 31 |
| 11 | 204 | 203 | 70 |
| H,3,1 | | | |
| 1 | 285 | 285 | 218 |
| 3 | 189 | 196 | 922 |
| 5 | 184 | 203 | 753 |
| 7 | 140 | 149 | 901 |
| 9 | 55 | 72 | 778 |
| 11 | 100 | 92 | 846 |
| H,3,2 | | | |
| 1 | 1136 | 1153 | 19 |
| 3 | 873 | 979 | 11 |
| 5 | 699 | 700 | 29 |
| 7 | 462 | 471 | 15 |
| 9 | 389 | 383 | 40 |
| 11 | 212 | 220 | 12 |
| H,3,3 | | | |
| 1 | 471 | 500 | 802 |
| 3 | 193 | 203 | 897 |
| 5 | 347 | 375 | 784 |
| 7 | 124 | 141 | 919 |
| 9 | 131 | 143 | 794 |
| 11 | 86 | 100 | 846 |
| H,3,4 | | | |
| 1 | 666 | 667 | 32 |
| 3 | 614 | 632 | 108 |
| 5 | 507 | 535 | 999 |
| 7 | 345 | 354 | 99 |
| 9 | 292 | 311 | 27 |
| 11 | 180 | 174 | 52 |
| H,3,5 | | | |
| 1 | 40 | 56 | 793 |
| 3 | 133 | 137 | 895 |
| 5 | 27* | 36 | 172 |
| 7 | 120 | 124 | 883 |
| 9 | 30* | 17 | 197 |
| 11 | 63 | 70 | 847 |
| H,3,6 | | | |
| 1 | 594 | 591 | 44 |
| 3 | 517 | 523 | 57 |
| 5 | 455 | 462 | 33 |
| 7 | 315 | 322 | 56 |
| 9 | 285 | 280 | 46 |
| 11 | 156 | 164 | 39 |
| H,3,7 | | | |
| 1 | 231 | 247 | 842 |
| 3 | 151 | 136 | 936 |
| 5 | 229 | 250 | 813 |
| 7 | 98 | 88 | 944 |
| 9 | 109 | 112 | 814 |
| H,3,8 | | | |
| 1 | 372 | 366 | 17 |
| 3 | 335 | 325 | 44 |
| 5 | 298 | 308 | 6 |
| 7 | 224 | 215 | 46 |
| 9 | 200 | 197 | 26 |
| H,3,9 | | | |
| 1 | 52 | 75 | 794 |
| 3 | 100 | 102 | 851 |
| 5 | 48 | 44 | 223 |
| 7 | 95 | 87 | 847 |
| 9 | 34* | 23 | 760 |
| H,3,10 | | | |
| 1 | 292 | 282 | 53 |
| 3 | 284 | 262 | 87 |
| 5 | 245 | 234 | 32 |
| 7 | 189 | 182 | 90 |
| H,3,11 | | | |
| 1 | 79 | 94 | 888 |
| 3 | 74 | 68 | 983 |
| 5 | 94 | 95 | 847 |
| H,3,12 | | | |
| 1 | 191 | 182 | 27 |
| 3 | 192 | 168 | 29 |
| H,4,0 | | | |
| 0 | 1161 | 1013 | 990 |
| 2 | 143 | 115 | 124 |
| 4 | 500 | 455 | 5 |
| 6 | 155 | 162 | 903 |
| 8 | 157 | 154 | 993 |
| 10 | 127 | 125 | 921 |
| 12 | 36* | 35 | 950 |
| H,4,1 | | | |
| 0 | 443 | 431 | 35 |
| 2 | 1179 | 1133 | 59 |
| 4 | 508 | 509 | 56 |
| 6 | 493 | 481 | 39 |
| 8 | 378 | 373 | 56 |
| 10 | 219 | 217 | 31 |
| 12 | 191 | 190 | 45 |
| H,4,2 | | | |
| 0 | 726 | 709 | 214 |
| 2 | 265 | 265 | 951 |
| 4 | 307 | 343 | 796 |
| 6 | 180 | 197 | 808 |
| 8 | 147 | 145 | 941 |
| 10 | 119 | 129 | 773 |
| 12 | 41* | 59 | 949 |
| H,4,3 | | | |
| 0 | 586 | 588 | 4 |
| 2 | 652 | 661 | 27 |
| 4 | 486 | 498 | 13 |
| 6 | 395 | 410 | 15 |
| 8 | 291 | 306 | 33 |
| 10 | 214 | 214 | 15 |
| 12 | 165 | 155 | 25 |
| H,4,4 | | | |
| 0 | 526 | 517 | 942 |
| 2 | 108 | 117 | 885 |
| 4 | 341 | 350 | 962 |
| 6 | 162 | 161 | 884 |
| 8 | 133 | 133 | 967 |
| 10 | 102 | 108 | 901 |
| 12 | 58 | 40 | 941 |
| H,4,5 | | | |
| 0 | 304 | 306 | 47 |
| 2 | 798 | 815 | 62 |
| 4 | 356 | 360 | 59 |
| 6 | 382 | 401 | 47 |
| 8 | 319 | 321 | 61 |
| 10 | 157 | 169 | 34 |
| H,4,6 | | | |
| 0 | 170 | 183 | 831 |
| 2 | 102 | 105 | 984 |
| 4 | 135 | 136 | 901 |
| 6 | 59 | 83 | 831 |
| 8 | 92 | 83 | 992 |
| 10 | 62 | 65 | 811 |
| H,4,7 | | | |
| 0 | 388 | 377 | 15 |
| 2 | 322 | 320 | 13 |
| 4 | 297 | 309 | 21 |
| 6 | 240 | 247 | 11 |
| 8 | 213 | 195 | 25 |
| 10 | 158 | 155 | 11 |
| H,4,8 | | | |
| 0 | 191 | 221 | 877 |
| 2 | 125 | 134 | 915 |
| 4 | 164 | 165 | 899 |
| 6 | 96 | 110 | 865 |
| 8 | 90 | 89 | 941 |
| H,4,9 | | | |
| 0 | 203 | 209 | 1 |
| 2 | 429 | 413 | 42 |
| 4 | 227 | 229 | 23 |
| 6 | 249 | 242 | 25 |
| 8 | 209 | 204 | 39 |
| H,4,10 | | | |
| 0 | 104 | 99 | 971 |
| 2 | 36* | 30 | 48 |
| 4 | 83 | 81 | 989 |
| 6 | 37* | 30 | 927 |
| H,4,11 | | | |
| 0 | 169 | 172 | 36 |
| 2 | 168 | 166 | 37 |
| 4 | 155 | 153 | 37 |
| 6 | 137 | 133 | 28 |
| H,4,12 | | | |
| 0 | 84 | 71 | 809 |
| 2 | 40* | 56 | 949 |
| H,5,0 | | | |
| 1 | 114 | 119 | 169 |
| 3 | 302 | 281 | 953 |
| 5 | 114 | 93 | 107 |
| 7 | 214 | 206 | 960 |
| 9 | 133 | 127 | 20 |
| 11 | 63 | 69 | 924 |
| H,5,1 | | | |
| 1 | 371 | 362 | 41 |
| 3 | 605 | 576 | 50 |
| 5 | 206 | 200 | 10 |
| 7 | 330 | 324 | 43 |
| 9 | 147 | 146 | 33 |
| 11 | 132 | 128 | 39 |
| H,5,2 | | | |
| 1 | 743 | 728 | 939 |
| 3 | 538 | 524 | 18 |
| 5 | 528 | 555 | 919 |
| 7 | 247 | 247 | 22 |
| 9 | 286 | 287 | 944 |
| 11 | 124 | 114 | 957 |
| H,5,3 | | | |
| 1 | 526 | 526 | 5 |
| 3 | 662 | 666 | 994 |
| 5 | 234 | 251 | 38 |
| 7 | 375 | 392 | 990 |
| 9 | 163 | 164 | 35 |
| 11 | 135 | 147 | 6 |
| H,5,4 | | | |
| 1 | 237 | 239 | 968 |
| 3 | 307 | 314 | 971 |
| 5 | 153 | 157 | 984 |
| 7 | 189 | 194 | 959 |
| 9 | 138 | 147 | 984 |
| 11 | 71 | 79 | 930 |
| H,5,5 | | | |
| 1 | 202 | 215 | 68 |
| 3 | 297 | 302 | 109 |
| 5 | 120 | 131 | 997 |
| 7 | 210 | 213 | 102 |
| 9 | 104 | 95 | 34 |
| 11 | 88 | 87 | 83 |
| H,5,6 | | | |
| 1 | 300 | 297 | 964 |
| 3 | 289 | 286 | 9 |
| 5 | 255 | 259 | 939 |
| 7 | 161 | 162 | 5 |
| 9 | 185 | 170 | 960 |
| 11 | 58 | 80 | 955 |
| H,5,7 | | | |
| 1 | 296 | 290 | 21 |
| 3 | 378 | 384 | 993 |
| 5 | 168 | 167 | 59 |
| 7 | 248 | 255 | 992 |
| 9 | 122 | 112 | 57 |
| H,5,8 | | | |
| 1 | 261 | 256 | 948 |
| 3 | 237 | 240 | 968 |
| 5 | 202 | 207 | 933 |
| 7 | 142 | 156 | 969 |
| 9 | 152 | 147 | 949 |
| H,5,9 | | | |
| 1 | 131 | 127 | 46 |
| 3 | 166 | 161 | 97 |
| 5 | 92 | 85 | 999 |
| 7 | 127 | 118 | 103 |
| H,5,10 | | | |
| 1 | 135 | 131 | 976 |
| 3 | 143 | 141 | 983 |
| 5 | 106 | 103 | 971 |
| 7 | 105 | 100 | 974 |
| H,5,11 | | | |
| 1 | 124 | 113 | 67 |
| 3 | 157 | 146 | 32 |
| 5 | 98 | 75 | 112 |
| H,5,12 | | | |
| 1 | 163 | 151 | 941 |
| 3 | 143 | 132 | 972 |
| H,6,0 | | | |
| 0 | 476 | 450 | 71 |
| 2 | 1077 | 950 | 101 |
| 4 | 526 | 484 | 71 |
| 6 | 423 | 400 | 101 |
| 8 | 397 | 395 | 80 |
| 10 | 164 | 161 | 84 |
| 12 | 203 | 193 | 97 |
| H,6,1 | | | |
| 0 | 360 | 336 | 755 |
| 2 | 611 | 557 | 891 |
| 4 | 310 | 293 | 837 |
| 6 | 258 | 250 | 872 |
| 8 | 217 | 232 | 873 |
| 10 | 116 | 116 | 847 |
| 12 | 122 | 119 | 878 |
| H,6,2 | | | |
| 0 | 941 | 885 | 84 |
| 2 | 410 | 397 | 70 |
| 4 | 664 | 634 | 75 |
| 6 | 342 | 330 | 83 |
| 8 | 319 | 319 | 68 |
| 10 | 235 | 208 | 85 |
| 12 | 131 | 139 | 86 |
| H,6,3 | | | |
| 0 | 389 | 387 | 228 |
| 2 | 606 | 615 | 934 |
| 4 | 293 | 315 | 816 |
| 6 | 264 | 277 | 888 |
| 8 | 229 | 232 | 889 |
| 10 | 106 | 123 | 829 |
| 12 | 127 | 124 | 904 |
| H,6,4 | | | |
| 0 | 441 | 440 | 71 |
| 2 | 657 | 674 | 85 |
| 4 | 442 | 454 | 64 |
| 6 | 339 | 337 | 85 |
| 8 | 329 | 336 | 77 |
| 10 | 173 | 157 | 79 |
| H,6,5 | | | |
| 0 | 208 | 204 | 911 |
| 2 | 333 | 336 | 860 |
| 4 | 218 | 218 | 880 |
| 6 | 171 | 184 | 876 |
| 8 | 175 | 175 | 867 |
| 10 | 80 | 92 | 878 |
| H,6,6 | | | |
| 0 | 391 | 389 | 85 |
| 2 | 309 | 311 | 95 |
| 4 | 328 | 345 | 85 |
| 6 | 223 | 220 | 104 |
| 8 | 218 | 220 | 81 |
| 10 | 137 | 134 | 96 |
| H,6,7 | | | |
| 0 | 219 | 247 | 752 |
| 2 | 329 | 329 | 937 |
| 4 | 178 | 197 | 810 |
| 6 | 160 | 173 | 880 |
| 8 | 150 | 159 | 889 |
| 10 | 93 | 90 | 818 |
| H,6,8 | | | |
| 0 | 343 | 338 | 64 |
| 2 | 327 | 321 | 67 |
| 4 | 309 | 302 | 62 |
| 6 | 221 | 214 | 75 |
| 8 | 212 | 211 | 67 |
| H,6,9 | | | |
| 0 | 161 | 160 | 929 |
| 2 | 215 | 212 | 884 |
| 4 | 164 | 157 | 910 |
| 6 | 143 | 136 | 898 |
| 8 | 129 | 123 | 889 |
| H,6,10 | | | |
| 0 | 152 | 160 | 103 |
| 2 | 203 | 201 | 104 |
| 4 | 154 | 159 | 95 |
| 6 | 135 | 130 | 112 |
| H,6,11 | | | |
| 0 | 105 | 106 | 248 |
| 2 | 122 | 128 | 913 |
| 4 | 99 | 91 | 801 |
| H,6,12 | | | |
| 0 | 183 | 163 | 73 |
| 2 | 110 | 119 | 68 |
| H,7,0 | | | |
| 1 | 418 | 358 | 784 |
| 3 | 270 | 233 | 763 |
| 5 | 360 | 357 | 835 |
| 7 | 110 | 105 | 789 |
| 9 | 195 | 202 | 853 |
| 11 | 59 | 66 | 782 |
| H,7,1 | | | |
| 1 | 509 | 500 | 114 |
| 3 | 632 | 574 | 47 |
| 5 | 334 | 335 | 141 |
| 7 | 366 | 362 | 49 |
| 9 | 197 | 193 | 106 |
| 11 | 172 | 176 | 82 |
| H,7,2 | | | |
| 1 | 509 | 509 | 931 |
| 3 | 611 | 626 | 913 |
| 5 | 248 | 252 | 945 |
| 7 | 341 | 350 | 908 |
| 9 | 184 | 185 | 922 |
| 11 | 119 | 118 | 893 |
| H,7,3 | | | |
| 1 | 627 | 636 | 71 |
| 3 | 607 | 613 | 64 |
| 5 | 396 | 408 | 79 |
| 7 | 380 | 387 | 69 |
| 9 | 234 | 229 | 65 |
| 11 | 187 | 192 | 82 |
| H,7,4 | | | |
| 1 | 283 | 295 | 849 |
| 3 | 222 | 214 | 866 |
| 5 | 250 | 263 | 864 |
| 7 | 133 | 118 | 852 |
| 9 | 164 | 169 | 872 |
| 11 | 38* | 61 | 829 |
| H,7,5 | | | |
| 1 | 280 | 292 | 131 |
| 3 | 350 | 351 | 30 |
| 5 | 224 | 233 | 190 |
| 7 | 254 | 262 | 33 |
| 9 | 128 | 133 | 140 |
| 11 | 123 | 129 | 76 |
| H,7,6 | | | |
| 1 | 244 | 252 | 888 |
| 3 | 286 | 290 | 888 |
| 5 | 164 | 170 | 885 |
| 7 | 177 | 181 | 880 |
| 9 | 124 | 127 | 889 |
| H,7,7 | | | |
| 1 | 390 | 394 | 59 |
| 3 | 373 | 376 | 64 |
| 5 | 284 | 292 | 53 |
| 7 | 260 | 263 | 71 |
| 9 | 181 | 177 | 49 |
| H,7,8 | | | |
| 1 | 185 | 192 | 913 |
| 3 | 187 | 198 | 908 |
| 5 | 143 | 146 | 910 |
| 7 | 140 | 125 | 903 |
| 9 | 130 | 105 | 909 |
| H,7,9 | | | |
| 1 | 206 | 191 | 106 |
| 3 | 243 | 226 | 40 |
| 5 | 149 | 150 | 160 |
| 7 | 175 | 174 | 34 |
| H,7,10 | | | |
| 1 | 94 | 109 | 844 |
| 3 | 85 | 97 | 846 |
| 5 | 100 | 95 | 844 |
| H,7,11 | | | |
| 1 | 177 | 172 | 54 |
| 3 | 180 | 170 | 55 |
| 5 | 149 | 136 | 52 |
| H,7,12 | | | |
| 1 | 89 | 94 | 918 |
| H,8,0 | | | |
| 0 | 727 | 644 | 43 |
| 2 | 443 | 379 | 872 |
| 4 | 493 | 441 | 12 |
| 6 | 269 | 241 | 984 |
| 8 | 239 | 229 | 956 |
| 10 | 167 | 158 | 15 |
| H,8,1 | | | |
| 0 | 163 | 160 | 30 |
| 2 | 534 | 496 | 981 |
| 4 | 221 | 206 | 993 |
| 6 | 259 | 250 | 17 |
| 8 | 169 | 181 | 958 |
| 10 | 88 | 99 | 47 |
| H,8,2 | | | |
| 0 | 303 | 294 | 987 |
| 2 | 428 | 433 | 42 |
| 4 | 312 | 296 | 987 |
| 6 | 239 | 232 | 28 |
| 8 | 217 | 230 | 10 |
| 10 | 99 | 113 | 995 |
| H,8,3 | | | |
| 0 | 363 | 380 | 108 |
| 2 | 363 | 359 | 967 |
| 4 | 267 | 261 | 43 |
| 6 | 235 | 231 | 36 |
| 8 | 158 | 162 | 973 |
| 10 | 124 | 118 | 81 |
| H,8,4 | | | |
| 0 | 479 | 484 | 39 |
| 2 | 311 | 303 | 940 |
| 4 | 377 | 379 | 15 |
| 6 | 223 | 221 | 997 |
| 8 | 213 | 209 | 976 |
| 10 | 146 | 144 | 20 |
| H,8,5 | | | |
| 0 | 117 | 105 | 899 |
| 2 | 360 | 371 | 999 |
| 4 | 134 | 140 | 930 |
| 6 | 183 | 185 | 8 |
| 8 | 147 | 139 | 957 |
| 10 | 67 | 62 | 10 |
| H,8,6 | | | |
| 0 | 218 | 238 | 984 |
| 2 | 231 | 243 | 986 |
| 4 | 227 | 219 | 983 |
| 6 | 150 | 160 | 995 |
| 8 | 156 | 164 | 983 |
| 10 | 99 | 96 | 987 |
| H,8,7 | | | |
| 0 | 221 | 219 | 98 |
| 2 | 177 | 183 | 945 |
| 4 | 154 | 152 | 56 |
| 6 | 128 | 130 | 36 |
| 8 | 83 | 94 | 958 |
| H,8,8 | | | |
| 0 | 280 | 265 | 26 |
| 2 | 231 | 237 | 3 |
| 4 | 247 | 232 | 14 |
| 6 | 168 | 173 | 20 |
| 8 | 164 | 160 | 999 |
| H,8,9 | | | |
| 0 | 37* | 69 | 970 |
| 2 | 212 | 197 | 18 |
| 4 | 108 | 85 | 979 |
| 6 | 116 | 109 | 26 |
| H,8,10 | | | |
| 0 | 169 | 169 | 9 |
| 2 | 134 | 131 | 945 |
| 4 | 150 | 147 | 990 |
| 6 | 101 | 103 | 980 |
| H,8,11 | | | |
| 0 | 74 | 58 | 90 |
| 2 | 71 | 71 | 905 |
| 4 | 61 | 44 | 17 |
| H,9,0 | | | |
| 1 | 294 | 274 | 142 |
| 3 | 252 | 245 | 25 |
| 5 | 283 | 242 | 177 |
| 7 | 177 | 179 | 43 |
| 9 | 144 | 132 | 139 |
| 11 | 94 | 93 | 119 |
| H,9,1 | | | |
| 1 | 455 | 439 | 905 |
| 3 | 498 | 464 | 885 |
| 5 | 341 | 296 | 921 |
| 7 | 312 | 309 | 896 |
| 9 | 170 | 176 | 893 |
| 11 | 146 | 156 | 930 |
| H,9,2 | | | |
| 1 | 523 | 541 | 95 |
| 3 | 356 | 370 | 127 |
| 5 | 471 | 442 | 75 |
| 7 | 214 | 232 | 140 |
| 9 | 231 | 222 | 75 |
| 11 | 124 | 135 | 141 |
| H,9,3 | | | |
| 1 | 394 | 400 | 955 |
| 3 | 493 | 496 | 921 |
| 5 | 251 | 229 | 964 |
| 7 | 330 | 342 | 924 |
| 9 | 143 | 142 | 932 |
| 11 | 159 | 163 | 950 |
| H,9,4 | | | |
| 1 | 259 | 269 | 129 |
| 3 | 221 | 235 | 78 |
| 5 | 245 | 240 | 160 |
| 7 | 145 | 157 | 78 |
| 9 | 132 | 131 | 132 |
| 11 | 96 | 91 | 132 |
| H,9,5 | | | |
| 1 | 322 | 335 | 885 |
| 3 | 294 | 298 | 859 |
| 5 | 266 | 268 | 897 |
| 7 | 201 | 204 | 877 |
| 9 | 156 | 162 | 877 |
| H,9,6 | | | |
| 1 | 256 | 272 | 85 |
| 3 | 195 | 202 | 88 |
| 5 | 235 | 237 | 80 |
| 7 | 124 | 133 | 109 |
| 9 | 147 | 133 | 76 |
| H,9,7 | | | |
| 1 | 261 | 275 | 958 |
| 3 | 345 | 352 | 927 |
| 5 | 148 | 164 | 982 |
| 7 | 263 | 263 | 929 |
| 9 | 110 | 108 | 947 |
| H,9,8 | | | |
| 1 | 201 | 214 | 126 |
| 3 | 166 | 172 | 122 |
| 5 | 182 | 183 | 128 |
| 7 | 114 | 120 | 130 |
| H,9,9 | | | |
| 1 | 185 | 179 | 908 |
| 3 | 139 | 152 | 887 |
| 5 | 156 | 155 | 920 |
| 7 | 105 | 115 | 900 |
| H,9,10 | | | |
| 1 | 105 | 102 | 96 |
| 3 | 103 | 86 | 55 |
| 5 | 86 | 93 | 118 |
| H,9,11 | | | |
| 1 | 160 | 157 | 930 |
| 3 | 192 | 188 | 914 |
| H,10,0 | | | |
| 0 | 716 | 657 | 890 |
| 2 | 528 | 491 | 921 |
| 4 | 543 | 485 | 894 |
| 6 | 380 | 356 | 911 |
| 8 | 278 | 269 | 908 |
| 10 | 216 | 204 | 891 |
| H,10,1 | | | |
| 0 | 415 | 420 | 137 |
| 2 | 312 | 312 | 64 |
| 4 | 300 | 296 | 128 |
| 6 | 291 | 276 | 103 |
| 8 | 133 | 139 | 91 |
| 10 | 180 | 171 | 133 |
| H,10,2 | | | |
| 0 | 459 | 450 | 3 |
| 2 | 355 | 351 | 833 |
| 4 | 344 | 337 | 960 |
| 6 | 242 | 238 | 911 |
| 8 | 189 | 196 | 888 |
| 10 | 147 | 147 | 949 |
| H,10,3 | | | |
| 0 | 296 | 301 | 174 |
| 2 | 354 | 378 | 128 |
| 4 | 249 | 230 | 160 |
| 6 | 259 | 274 | 134 |
| 8 | 146 | 145 | 139 |
| 10 | 147 | 150 | 150 |
| H,10,4 | | | |
| 0 | 449 | 462 | 908 |
| 2 | 341 | 357 | 923 |
| 4 | 346 | 363 | 907 |
| 6 | 264 | 277 | 914 |
| 8 | 193 | 212 | 911 |
| 10 | 150 | 163 | 904 |
| H,10,5 | | | |
| 0 | 356 | 380 | 119 |
| 2 | 220 | 218 | 10 |
| 4 | 254 | 251 | 104 |
| 6 | 210 | 216 | 91 |
| 8 | 123 | 114 | 54 |
| 10 | 148 | 150 | 117 |
| H,10,6 | | | |
| 0 | 307 | 322 | 940 |
| 2 | 275 | 280 | 862 |
| 4 | 266 | 264 | 923 |
| 6 | 192 | 205 | 898 |
| 8 | 160 | 168 | 885 |
| H,10,7 | | | |
| 0 | 136 | 161 | 156 |
| 2 | 260 | 257 | 131 |
| 4 | 144 | 149 | 154 |
| 6 | 182 | 185 | 133 |
| 8 | 101 | 109 | 136 |
| H,10,8 | | | |
| 0 | 232 | 232 | 953 |
| 2 | 174 | 180 | 904 |
| 4 | 195 | 189 | 939 |
| 6 | 130 | 147 | 925 |
| 8 | 105 | 119 | 917 |
| H,10,9 | | | |
| 0 | 234 | 225 | 127 |
| 2 | 133 | 133 | 45 |
| 4 | 169 | 162 | 115 |
| 6 | 138 | 140 | 93 |
| H,10,10 | | | |
| 0 | 189 | 185 | 896 |
| 2 | 164 | 161 | 897 |
| 4 | 165 | 159 | 891 |
| H,10,11 | | | |
| 0 | 101 | 88 | 102 |
| 2 | 129 | 120 | 95 |
| H,11,0 | | | |
| 1 | 390 | 339 | 998 |
| 3 | 132 | 123 | 1 |
| 5 | 408 | 357 | 989 |
| 7 | 76 | 81 | 48 |
| 9 | 190 | 185 | 998 |
| 11 | 86 | 88 | 25 |
| H,11,1 | | | |
| 1 | 310 | 307 | 974 |
| 3 | 283 | 287 | 942 |
| 5 | 250 | 220 | 994 |
| 7 | 212 | 209 | 940 |
| 9 | 98 | 100 | 976 |
| 11 | 117 | 123 | 967 |
| H,11,2 | | | |
| 1 | 323 | 325 | 52 |
| 3 | 297 | 303 | 31 |
| 5 | 274 | 249 | 71 |
| 7 | 199 | 204 | 22 |
| 9 | 140 | 147 | 63 |
| H,11,3 | | | |
| 1 | 269 | 283 | 999 |
| 3 | 179 | 182 | 979 |
| 5 | 253 | 248 | 8 |
| 7 | 133 | 132 | 970 |
| 9 | 113 | 109 | 990 |
| H,11,4 | | | |
| 1 | 249 | 261 | 14 |
| 3 | 115 | 127 | 46 |
| 5 | 273 | 273 | 11 |
| 7 | 73 | 84 | 56 |
| 9 | 160 | 150 | 16 |
| H,11,5 | | | |
| 1 | 210 | 212 | 949 |
| 3 | 278 | 256 | 920 |
| 5 | 127 | 125 | 975 |
| 7 | 196 | 195 | 924 |
| 9 | 80 | 63 | 946 |
| H,11,6 | | | |
| 1 | 263 | 256 | 21 |
| 3 | 205 | 214 | 16 |
| 5 | 245 | 217 | 27 |
| 7 | 159 | 140 | 14 |
| 9 | 122 | 133 | 28 |
| H,11,7 | | | |
| 1 | 197 | 196 | 995 |
| 3 | 104 | 114 | 982 |
| 5 | 183 | 186 | 996 |
| 7 | 67 | 82 | 973 |
| H,11,8 | | | |
| 1 | 163 | 168 | 59 |
| 3 | 118 | 123 | 62 |
| 5 | 159 | 158 | 55 |
| 7 | 74 | 91 | 59 |
| H,11,9 | | | |
| 1 | 86 | 88 | 936 |
| 3 | 119 | 118 | 913 |
| 5 | 44* | 48 | 970 |
| H,11,10 | | | |
| 1 | 163 | 154 | 4 |
| 3 | 105 | 112 | 10 |
| H,12,0 | | | |
| 0 | 459 | 435 | 77 |
| 2 | 161 | 154 | 982 |
| 4 | 321 | 301 | 71 |
| 6 | 165 | 167 | 44 |
| 8 | 116 | 113 | 64 |
| 10 | 121 | 120 | 64 |
| H,12,1 | | | |
| 0 | 441 | 432 | 948 |
| 2 | 399 | 404 | 960 |
| 4 | 374 | 335 | 952 |
| 6 | 336 | 320 | 962 |
| 8 | 212 | 199 | 943 |
| 10 | 185 | 184 | 972 |
| H,12,2 | | | |
| 0 | 138 | 138 | 22 |
| 2 | 185 | 211 | 227 |
| 4 | 99 | 110 | 109 |
| 6 | 86 | 99 | 145 |
| 8 | 82 | 100 | 199 |
| 10 | 77 | 52 | 57 |
| H,12,3 | | | |
| 0 | 322 | 318 | 1 |
| 2 | 273 | 297 | 920 |
| 4 | 251 | 243 | 975 |
| 6 | 252 | 243 | 958 |
| 8 | 138 | 151 | 933 |
| 10 | 146 | 150 | 992 |
| H,12,4 | | | |
| 0 | 293 | 293 | 91 |
| 2 | 98 | 100 | 34 |
| 4 | 204 | 208 | 82 |
| 6 | 115 | 117 | 54 |
| 8 | 71 | 84 | 89 |
| H,12,5 | | | |
| 0 | 377 | 382 | 932 |
| 2 | 347 | 363 | 981 |
| 4 | 293 | 307 | 939 |
| 6 | 277 | 287 | 966 |
| 8 | 179 | 185 | 956 |
| H,12,6 | | | |
| 0 | 154 | 160 | 34 |
| 2 | 95 | 110 | 152 |
| 4 | 122 | 122 | 73 |
| 6 | 84 | 85 | 80 |
| 8 | 59 | 71 | 132 |
| H,12,7 | | | |
| 0 | 213 | 218 | 17 |
| 2 | 184 | 197 | 917 |
| 4 | 161 | 170 | 995 |
| 6 | 160 | 166 | 967 |
| 8 | 116 | 109 | 940 |
| H,12,8 | | | |
| 0 | 103 | 105 | 87 |
| 2 | 39* | 62 | 176 |
| 4 | 85 | 81 | 106 |
| 6 | 39* | 55 | 110 |
| H,12,9 | | | |
| 0 | 221 | 215 | 935 |
| 2 | 205 | 205 | 987 |
| 4 | 177 | 177 | 947 |
| H,12,10 | | | |
| 0 | 124 | 114 | 48 |
| 2 | 40* | 49 | 24 |
| H,13,0 | | | |
| 1 | 445 | 410 | 945 |
| 3 | 402 | 402 | 957 |
| 5 | 343 | 312 | 936 |
| 7 | 282 | 274 | 952 |
| 9 | 201 | 192 | 950 |
| H,13,1 | | | |
| 1 | 173 | 181 | 121 |
| 3 | 137 | 149 | 163 |
| 5 | 149 | 152 | 113 |
| 7 | 105 | 96 | 148 |
| 9 | 82 | 88 | 159 |
| H,13,2 | | | |
| 1 | 415 | 423 | 950 |
| 3 | 246 | 255 | 949 |
| 5 | 439 | 411 | 950 |
| 7 | 159 | 160 | 941 |
| 9 | 234 | 232 | 955 |
| H,13,3 | | | |
| 1 | 109 | 136 | 162 |
| 3 | 114 | 140 | 139 |
| 5 | 78 | 108 | 192 |
| 7 | 93 | 101 | 116 |
| 9 | 67 | 74 | 220 |
| H,13,4 | | | |
| 1 | 333 | 331 | 937 |
| 3 | 283 | 303 | 954 |
| 5 | 279 | 268 | 933 |
| 7 | 206 | 212 | 946 |
| 9 | 190 | 167 | 946 |
| H,13,5 | | | |
| 1 | 166 | 155 | 103 |
| 3 | 109 | 108 | 181 |
| 5 | 160 | 152 | 79 |
| 7 | 79 | 72 | 182 |
| H,13,6 | | | |
| 1 | 304 | 319 | 955 |
| 3 | 242 | 236 | 958 |
| 5 | 308 | 292 | 952 |
| 7 | 147 | 160 | 951 |
| H,13,7 | | | |
| 1 | 87 | 109 | 158 |
| 3 | 97 | 117 | 119 |
| 5 | 42* | 80 | 203 |
| 7 | 91 | 90 | 94 |
| H,13,8 | | | |
| 1 | 178 | 196 | 935 |
| 3 | 149 | 154 | 943 |
| 5 | 181 | 182 | 933 |
| H,13,9 | | | |
| 1 | 74 | 75 | 112 |
| 3 | 67 | 55 | 213 |
| H,13,10 | | | |
| 1 | 175 | 180 | 949 |
| H,14,0 | | | |
| 0 | 323 | 298 | 968 |
| 2 | 272 | 273 | 111 |
| 4 | 256 | 235 | 15 |
| 6 | 172 | 173 | 41 |
| 8 | 162 | 157 | 92 |
| H,14,1 | | | |
| 0 | 291 | 285 | 973 |
| 2 | 291 | 280 | 975 |
| 4 | 239 | 233 | 978 |
| 6 | 225 | 216 | 967 |
| 8 | 140 | 142 | 970 |
| H,14,2 | | | |
| 0 | 170 | 182 | 84 |
| 2 | 56 | 68 | 977 |
| 4 | 145 | 146 | 77 |
| 6 | 70 | 71 | 18 |
| 8 | 82 | 82 | 83 |
| H,14,3 | | | |
| 0 | 251 | 238 | 903 |
| 2 | 195 | 199 | 991 |
| 4 | 184 | 185 | 920 |
| 6 | 163 | 166 | 948 |
| 8 | 110 | 105 | 954 |
| H,14,4 | | | |
| 0 | 229 | 231 | 975 |
| 2 | 184 | 190 | 104 |
| 4 | 194 | 182 | 17 |
| 6 | 109 | 130 | 31 |
| 8 | 131 | 123 | 88 |
| H,14,5 | | | |
| 0 | 256 | 256 | 9 |
| 2 | 260 | 255 | 955 |
| 4 | 215 | 213 | 997 |
| 6 | 210 | 193 | 970 |
| 8 | 135 | 134 | 968 |
| H,14,6 | | | |
| 0 | 151 | 163 | 57 |
| 2 | 107 | 115 | 78 |
| 4 | 151 | 143 | 69 |
| 6 | 82 | 94 | 54 |
| H,14,7 | | | |
| 0 | 167 | 163 | 874 |
| 2 | 111 | 121 | 5 |
| 4 | 142 | 122 | 900 |
| 6 | 129 | 108 | 942 |
| H,14,8 | | | |
| 0 | 126 | 118 | 10 |
| 2 | 71 | 78 | 76 |
| 4 | 77 | 101 | 41 |
| H,14,9 | | | |
| 0 | 141 | 143 | 984 |
| 2 | 153 | 152 | 929 |
| H,15,0 | | | |
| 1 | 138 | 136 | 39 |
| 3 | 68 | 72 | 157 |
| 5 | 168 | 153 | 999 |
| 7 | 37* | 41 | 231 |
| 9 | 102 | 97 | 13 |
| H,15,1 | | | |
| 1 | 274 | 282 | 995 |
| 3 | 288 | 283 | 9 |
| 5 | 220 | 212 | 989 |
| 7 | 204 | 204 | 6 |
| 9 | 142 | 136 | 7 |
| H,15,2 | | | |
| 1 | 107 | 99 | 958 |
| 3 | 133 | 144 | 27 |
| 5 | 111 | 69 | 886 |
| 7 | 88 | 91 | 25 |
| H,15,3 | | | |
| 1 | 263 | 270 | 978 |
| 3 | 212 | 225 | 988 |
| 5 | 243 | 237 | 978 |
| 7 | 146 | 157 | 988 |
| H,15,4 | | | |
| 1 | 91 | 100 | 998 |
| 3 | 53 | 53 | 97 |
| 5 | 114 | 115 | 974 |
| 7 | 34* | 24 | 139 |
| H,15,5 | | | |
| 1 | 193 | 218 | 11 |
| 3 | 234 | 255 | 20 |
| 5 | 154 | 147 | 5 |
| 7 | 174 | 192 | 17 |
| H,15,6 | | | |
| 1 | 82 | 85 | 4 |
| 3 | 87 | 96 | 58 |
| 5 | 74 | 69 | 958 |
| H,15,7 | | | |
| 1 | 185 | 196 | 991 |
| 3 | 146 | 150 | 999 |
| 5 | 185 | 182 | 990 |
| H,15,8 | | | |
| 1 | 80 | 58 | 918 |
| 3 | 57 | 44 | 972 |
| H,15,9 | | | |
| 1 | 130 | 132 | 2 |
| H,16,0 | | | |
| 0 | 341 | 343 | 29 |
| 2 | 338 | 336 | 985 |
| 4 | 325 | 314 | 18 |
| 6 | 232 | 232 | 993 |
| 8 | 244 | 217 | 9 |
| H,16,1 | | | |
| 0 | 33* | 27 | 6 |
| 2 | 80 | 88 | 120 |
| 4 | 52 | 36 | 78 |
| 6 | 54 | 44 | 99 |
| 8 | 38* | 39 | 111 |
| H,16,2 | | | |
| 0 | 312 | 329 | 928 |
| 2 | 252 | 254 | 18 |
| 4 | 272 | 272 | 954 |
| 6 | 183 | 195 | 968 |
| 8 | 175 | 176 | 2 |
| H,16,3 | | | |
| 0 | 31* | 18 | 230 |
| 2 | 64 | 59 | 931 |
| 4 | 57 | 15 | 84 |
| 6 | 48 | 24 | 955 |
| H,16,4 | | | |
| 0 | 287 | 290 | 4 |
| 2 | 280 | 287 | 983 |
| 4 | 250 | 264 | 1 |
| 6 | 194 | 202 | 983 |
| H,16,5 | | | |
| 0 | 38* | 46 | 958 |
| 2 | 104 | 115 | 159 |
| 4 | 36* | 45 | 44 |
| 6 | 38* | 56 | 116 |
| H,16,6 | | | |
| 0 | 215 | 227 | 970 |
| 2 | 175 | 198 | 18 |
| 4 | 207 | 201 | 987 |
| H,16,7 | | | |
| 0 | 31* | 30 | 799 |
| 2 | 55 | 43 | 871 |
| 4 | 38* | 14 | 205 |
| H,16,8 | | | |
| 0 | 178 | 189 | 958 |
| 2 | 185 | 176 | 983 |
| H,17,0 | | | |
| 1 | 53 | 58 | 105 |
| 3 | 132 | 131 | 87 |
| 5 | 33* | 6 | 142 |
| 7 | 86 | 98 | 100 |
| H,17,1 | | | |
| 1 | 216 | 216 | 992 |
| 3 | 227 | 215 | 992 |
| 5 | 183 | 167 | 988 |
| 7 | 177 | 156 | 990 |
| H,17,2 | | | |
| 1 | 120 | 124 | 997 |
| 3 | 79 | 81 | 4 |
| 5 | 119 | 124 | 995 |
| 7 | 64 | 43 | 36 |
| H,17,3 | | | |
| 1 | 223 | 217 | 969 |
| 3 | 268 | 251 | 982 |
| 5 | 170 | 151 | 955 |
| 7 | 199 | 186 | 983 |
| H,17,4 | | | |
| 1 | 55 | 62 | 50 |
| 3 | 104 | 110 | 71 |
| 5 | 33* | 29 | 998 |
| H,17,5 | | | |
| 1 | 154 | 167 | 4 |
| 3 | 131 | 144 | 994 |
| 5 | 142 | 149 | 4 |
| H,17,6 | | | |
| 1 | 68 | 75 | 53 |
| 3 | 91 | 70 | 72 |
| H,17,7 | | | |
| 1 | 158 | 153 | 958 |
| 3 | 190 | 187 | 978 |
| H,18,0 | | | |
| 0 | 144 | 140 | 912 |
| 2 | 102 | 98 | 72 |
| 4 | 121 | 116 | 942 |
| 6 | 41* | 67 | 986 |
| H,18,1 | | | |
| 0 | 125 | 154 | 48 |
| 2 | 195 | 199 | 20 |
| 4 | 142 | 146 | 36 |
| 6 | 124 | 137 | 39 |
| H,18,2 | | | |
| 0 | 78 | 76 | 999 |
| 2 | 151 | 146 | 907 |
| 4 | 96 | 91 | 963 |
| 6 | 85 | 77 | 915 |
| H,18,3 | | | |
| 0 | 140 | 166 | 990 |
| 2 | 194 | 188 | 35 |
| 4 | 142 | 150 | 997 |
| 6 | 137 | 135 | 29 |
| H,18,4 | | | |
| 0 | 113 | 129 | 925 |
| 2 | 116 | 94 | 18 |
| 4 | 103 | 110 | 944 |
| H,18,5 | | | |
| 0 | 115 | 135 | 106 |
| 2 | 172 | 166 | 13 |
| 4 | 122 | 123 | 74 |
| H,18,6 | | | |
| 0 | 79 | 58 | 948 |
| 2 | 77 | 82 | 935 |
| H,19,0 | | | |
| 1 | 200 | 195 | 42 |
| 3 | 157 | 151 | 24 |
| 5 | 172 | 183 | 47 |
| H,19,1 | | | |
| 1 | 62 | 46 | 863 |
| 3 | 84 | 67 | 992 |
| 5 | 35* | 29 | 807 |
| H,19,2 | | | |
| 1 | 210 | 224 | 20 |
| 3 | 250 | 256 | 27 |
| 5 | 166 | 158 | 9 |
| H,19,3 | | | |
| 1 | 81 | 74 | 932 |
| 3 | 90 | 79 | 856 |
| H,19,4 | | | |
| 1 | 164 | 183 | 39 |
| 3 | 153 | 156 | 25 |
| H,19,5 | | | |
| 1 | 42* | 28 | 771 |
| H,20,0 | | | |
| 0 | 35* | 34 | 134 |
| 2 | 108 | 95 | 894 |
| 4 | 49 | 36 | 7 |
| H,20,1 | | | |
| 0 | 163 | 163 | 19 |
| 2 | 170 | 173 | 13 |
| 4 | 136 | 144 | 11 |
| H,20,2 | | | |
| 0 | 72 | 97 | 926 |
| 2 | 37* | 43 | 34 |
| H,20,3 | | | |
| 0 | 142 | 157 | 53 |
| 2 | 184 | 190 | 994 |
| H,20,4 | | | |
| 0 | 45* | 40 | 71 |
| H,21,0 | | | |
| 1 | 96 | 90 | 925 |
| H,21,1 | | | |
| 1 | 92 | 100 | 42 |

Columns are h, $10F_o$, $10F_c$ and phase in millicycles. "Unobserved" reflections are marked by *. $F_c$ does not include corrections for extinction or anomalous dispersion. $F_o$ and $F_c$ are on an absolute scale.

Table 3. Probable positions of the hydrogen atoms in $CaKAsO_4 \cdot 8H_2O$

| | Difference synthesis | | | Least squares refinements | | | Calculated | | |
|---|---|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | *x* | *y* | *z* | *x* | *y* | *z* |
| H(1) | .39 | -.02 | .14 | .395(7) | .001(6) | .150(7) | .394 | -.023 | .153 |
| H(2) | .14 | .00 | .43 | .139(7) | -.009(6) | .416(7) | .152 | .025 | .393 |
| H(3) | .25 | .31 | .21 | .236(7) | .320(5) | .192(8) | .235 | .316 | .174 |
| H(4) | .14 | .21 | .25 | .150(9) | .246(6) | .239(10) | .138 | .207 | .237 |

The calculated hydrogen positions were used to obtain distances mentioned in the tables and the text.

Table 4. The cation environments in $CaKAsO_4 \cdot 8H_2O$

| atoms | Distance, Å |
|---|---|
| Ca, $O(4^{I}, 4^{II})$ | 2.459(5) |
| Ca, $O(3^{I}, 3^{II})$ | 2.469(6) |
| Ca, $O(5^{I}, 5^{II}, 5^{III}, 5^{IV})$ | 2.490(3) |
| K, $O(5^{I}, 5^{II}, 5^{V}, 5^{VI})$ | 2.746(3) |
| K, $O(3^{III}, 3^{IV})$ | 2.918(6) |
| K, $O(4^{III}, 4^{IV})$ | 2.960(7) |

In all tables of interatomic distances and angles, the figures in parentheses are standard deviations in the last digit and were calculated from the standard deviation in the atomic positional parameters. They include terms from the variance-covariance matrix.

Table 5. The $AsO_4$ group and its environment in $CaKAsO_4 \cdot 8H_2O$

| atoms | distance, Å or angle, deg. | | riding$^{(a)}$ |
|---|---|---|---|
| | | lower(a) | |
| As, O(1, 1) | 1.682(4) | 1.684 | 1.690 Å |
| As, O(2, 2) | 1.684(4) | 1.685 | 1.692 |
| O(1), As, O(1) | 113.1(3)° | | |
| O(1), As, O(2) | 107.5(1) | | |
| O(2), As, O(2) | 113.7(3) | | |
| O(1), O(1) | 2.807(7) Å | | |
| O(1), O(2) | 2.715(5) | | |
| O(2), O(2) | 2.820(7) | | |
| O(1), H($2^{I}$, $2^{III}$) | 1.87 | | |
| O(1), H($4^{I}$, $4^{II}$) | 1.81 | | |
| O(1), O($5^{II}$, $5^{IV}$) | 2.759(4)* | | |
| O(1), O($4^{IV}$, $4^{V}$) | 2.830(4)* | | |
| O(2), H($1^{I}$, 1)** | 1.89 | | |
| O(2), H($3^{I}$, 3) | 1.81 | | |
| O(2), O($5^{VII}$) | 2.755(4)* | | |
| O(2), O($3^{III}$) | 2.848(4)* | | |

(a) lower bound and riding model corrections for thermal motion(10)

* hydrogen bond between these two oxygens.

** These hydrogen bonds may be seen in Figure 1 if the environments of O(2) and O($2^{I}$) in the right hand side of the $AsO_4$ ion in the center of the figure are combined. O(2) and O($2^{I}$) are related by the c translation.

Table 6. The environments of the water molecules in $CaKAsO_4 \cdot 8H_2O$

| water molecule | atoms | Distance, or angle deg. |
|---|---|---|
| H(1),O(3),H(1) | $O(3^{III}), Ca^{II}$ | 2.469(6) Å |
| | $O(3^{III}), K^{I}$ | 2.918(6) |
| | $O(3^{II}), O(2I, 2)$ | 2.848(4)* |
| | $H(1), O(2^{I})$ | 1.89 |
| | O(3), H(1), O(2) | 175.7° |
| | O(2), O(3), O(2) | 98.8(2) |
| H(2), O(4), H(2) | $O(4^{IV}), Ca^{II}$ | 2.459(5) |
| | $O(4^{IV}), K^{I}$ | 2.960(7) |
| | $O(4^{IV}), O(1,1)$ | 2.830(4)* |
| | H(2), O(1) | 1.87 |
| | O(4), H(2), O(1) | 175.6° |
| | O(1), O(4), O(1) | 98.7(2) |
| H(3), O(5), H(4) | $O(5^{I}), Ca^{I}$ | 2.490(3) |
| | $O(5^{I}), K^{I}$ | 2.746(3) |
| | $O(5^{I}), O(2^{V})$ | 2.755(4)* |
| | $O(5^{I}), O(1)$ | 2.759(4)* |
| | $H(3), O(2^{V})$ | 1.81 |
| | $H(4^{I}), O(1)$ | 1.81 |
| | O(5), H(3), O(2) | 168.7° |
| | O(5), H(4), O(1) | 168.7 |
| | O(1), O(5), O(2) | 119.4(1) |

* hydrogen bond between these two oxygens.

Table 7. Some members of the struvite series

| | $MgNH_4PO_4 \cdot 6H_2O$ | $MgNH_4AsO_4 \cdot 6H_2O$ | $CaNH_4PO_4 \cdot 7H_2O$ | $CaNH_4AsO_4 \cdot 7H_2O$ | $MgKPO_4 \cdot 6H_2O$ | $MgKAsO_4 \cdot 6H_2O$ | $CaKAsO_4 \cdot 8H_2O$ |
|---|---|---|---|---|---|---|---|
| nit-cell dimensions, Å | | | | | | | |
| $a$ | 6.09 | 6.14 | 6.30 | 6.38 | 6.21 | 6.23 | 7.146(1) |
| $b$ | 11.18 | 11.14 | 11.96 | 12.07 | 11.10 | 11.26 | 11.696(2) |
| $c$ | 6.97 | 7.00 | 7.18 | 7.27 | 6.91 | 7.03 | 7.100(2) |
| ngle beta | 90° | 90° | 90.83° | 91.47° | 90° | 90° | 90° |
| , formula weights per unit cell | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| ensity, calculated, $g \cdot cm^{-3}$ | | | | | | | |
| X-ray | 1.71 | 1.99 | 1.70 | 1.91 | 1.85 | 2.08 | 1.933 |
| Optical | 1.72 | 1.95 | 1.71 | 1.86 | 1.91 | 2.15 | 2.10 |
| rystal system | Orthorh. | Orthorh. | Monocl. | Monocl. | Orthorh. | Orthorh. | Orthorh. |
| lass | (mm) | (mm) | (2) | (2) | (mm) | (mm) | (mm) |
| efractive indices: $N_x$ | 1.496 | $1.518_4$ | 1.495 | 1.514 | 1.477 | 1.503 | 1.497 |
| $N_y$ | $1.497_3$ | 1.519 | $1.497_5$ | 1.516 | 1.481 | 1.509 | 1.516 |
| $N_z$ | 1.505 | 1.528 | 1.514 | 1.535 | 1.487 | $1.509_4$ | $1.519_5$ |
| ptic sign | (+) | (+) | (+) | (+) | (+) | (-) | (-) |
| ptic angle 2$V$: measured | 41° | 25° | 41.5° | 34° | - | 22.5° | 46-47° |
| calculated | - | - | - | - | 77.5° | - | 46-47° |
| ispersion | r<v weak | none | none | none | r<v weak | r>v moderate | r>v moderate |
| ptio axial plane | (010) | (001) | ~(001) | ~(001) | (001) | (001) | (100) |
| xtinction angle $z \wedge a$ (in obtuse beta) | - | - | 6° | 6.5° | - | - | - |
| rientation: $N_x$ | $b$ | $b$ | $b$ | $b$ | $b$ | $b$ | $b$ |
| $N_y$ | $b$ | $c$ | ~$c$ | ~$c$ | $c$ | $c$ | $a$ |
| $N_z$ | $a$ | $a$ | ~$a$ | ~$a$ | $a$ | $a$ | $c$ |

Table 8. Other probable members of the struvite series

| | | $Mg_2KH(PO_4)_2 \cdot 15H_2O$ | $MgKAsO_4 \cdot 5H_2O$ | $MgHPO_4 \cdot 7H_2O$ |
|---|---|---|---|---|
| unit cell dimensions, Å | | | | |
| | a | 6.30 | 10.79 | 11.35 |
| | b | 12.29 | 10.79 | 25.36 |
| | c | 6.55 | 12.39 | 6.60 |
| angles, deg. | | | | |
| | α | 93.6° | 90° | 90° |
| | β | 89.7° | 90° | 95° |
| | γ | 95.3° | 120° | 90° |
| formula weights per unit cell | | | | |
| | z | 1 | 6 | 8 |
| crystal system | | tricl. | hexagonal | monocl. |

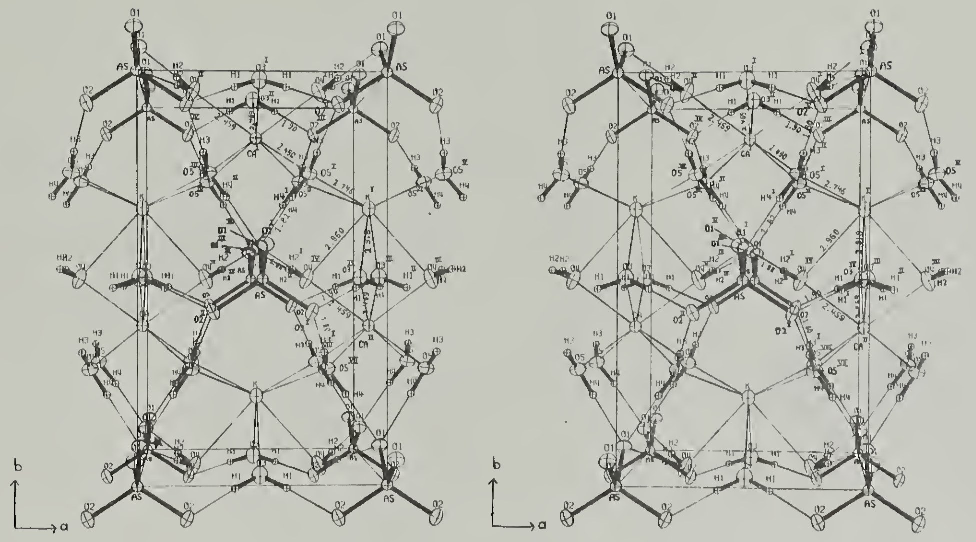

Figure 1: A stereoscopic illustration of the crystal structure of $CaKAsO_4 \cdot 8H_2O$. The origin of the crystallographic coordinate system is marked by *. The atoms with Roman numerals are referred to in the tables of interatomic distances.

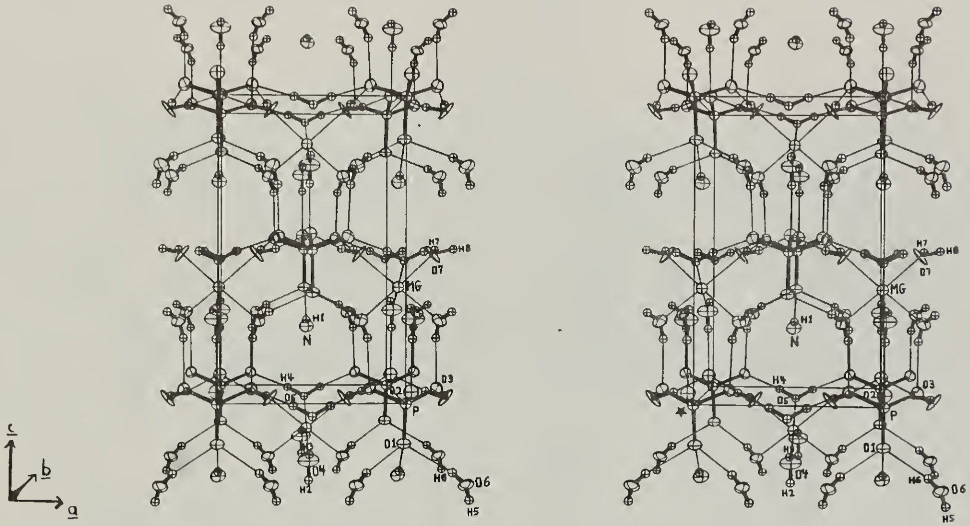

Figure 2: The crystal structure of $MgNH_4PO_4 \cdot 6H_2O$ in an orientation similar to that of $CaKAsO_4 \cdot 8H_2O$ in Figure 1. The atomic parameters for $MgNH_4PO_4 \cdot 6H_2O$ were taken from Whitaker and Jeffrey[17], with the exception of the thermal parameters of O(5), which were non-positive definite as given. O(5) is designated here by a sphere.


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