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Crystal structure refinement of akaganéite

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ABSTRACT

Powder X-ray diffraction data and the Rietveld method have been used to refine the crystal structure of akaganéite, $Fe_{7.6}Ni_{0.4}O_{6.35}(OH)_{9.65}Cl_{1.25}$, that formed as a corrosion crust on the Camp del Cielo meteorite. The study confirms the hollandite-like structure. The symmetry, however, is not tetragonal as previously reported, but is monoclinic ($I2/m$) with: $a = 10.600(2)$ Å, $b = 3.0339(5)$ Å, $c = 10.513(2)$ Å, $\beta = 90.24(2)°$. The monoclinic symmetry explains previous Mössbauer results showing two distinct Fe octahedral sites. The Cl^- ions partially fill the tunnels and probably are essential for the formation of the phase. Structure-energy calculations were used to determine likely H positions.

INTRODUCTION

Akaganéite from the Akagané mine in Japan was first described as the naturally occurring form of β-FeOOH by Nambu in 1961 (Mackay, 1962). It has since been recognized as a major Fe-oxide component in soils and geothermal brines (Holm et al., 1983) and as a corrosion product of some steels. A recent study by Buchwald and Clarke (1989) showed that akaganéite is an important corrosion product of iron meteorites, and also suggests that akaganéite might act as a catalyst promoting the breakdown of the meteorites. Both natural and synthetic akaganéite typically occur as fine-grained masses, and to date no crystals have been found that are suitable for single-crystal diffraction studies. Consequently, the details of the akaganéite crystal structure are poorly understood. We have used the Rietveld method and powder X-ray diffraction (XRD) data collected for akaganéite from the Campo del Cielo meteorite to refine the akaganéite crystal structure for the first time.

On the basis of the unit-cell parameters and powder XRD pattern, Bernal et al. (1959) noted that the structure of β-FeOOH must be similar to that of hollandite. XRD and infrared (IR) spectroscopic studies by Keller (1970) confirmed that β-FeOOH is isostructural with hollandite. The hollandite structure consists of double chains of edge-linked Mn^{4+}-O octahedra that share corners to form a framework containing large tunnels with square cross sections that measure two octahedra on a side (Fig. 1). The tunnels are partially filled with Ba^{2+} and minor amounts of other uni- or divalent cations such as K^+, Na^+, Pb^{2+}, and charge balance is maintained by substitution of lower valence cations (e.g., Al^{3+}, Mn^{3+}, and Mg^{2+}) in the octahedral sites. In akaganéite the octahedral sites are occupied by Fe^{3+}, and Cl (and perhaps H_2O) is presumably located in the tunnels. Charges are balanced by substituting OH^- for O^{2-}. Phases with the hollandite structure typically have monoclinic or tetragonal symmetry, depending on composition (Post et al., 1982). Bernal et al. (1959) and Keller (1970) assumed that β-FeOOH is tetragonal, space group $I4/m$, but as will be discussed below, the results of our Rietveld refinements of akaganéite indicate monoclinic symmetry.

DATA COLLECTION AND REFINEMENT

The akaganéite used in this study formed as a corrosion crust on the Campo del Cielo (USNM 347) iron-nickel meteorite. The sample is very finely crystalline, and powder XRD patterns showed it to be pure akaganéite. Transmission electron microscope images show blade- or spindle-shaped crystallites, ranging from approximately 0.1 to 1.0 μm in size.

Powder X-ray diffraction data used in the Rietveld refinements were obtained from samples that had been hand ground under acetone in an agate mortar and then (1) smeared onto a low-background quartz slide, or (2) sieved onto a glass-fiber filter. The latter technique minimizes preferred orientation effects, although the similarity of the XRD patterns from the two samples suggests that any such effects are minimal. The data were obtained on a Scintag computer-automated powder X-ray diffractometer using Cu$K\alpha$ radiation and an intrinsic-Ge solid-state detector. A counting time of 15 s per 0.03° step was used for the 2θ range 10–90°.

A small amount of the sample powder used in the XRD study was embedded in epoxy and prepared for electron microprobe analysis. The wt% Fe_2O_3 for 14 analyses ranged from 69 to 76%; NiO ranged from 0.4 to 5.6% and Cl from 3.6 to 6.3%. The summations were between 80 and 85%, which are low despite allowing for 12–14 wt% H_2O (Keller, 1970). The low totals are not surprising considering the powdered nature of the samples, and it follows that the composition ranges listed above probably

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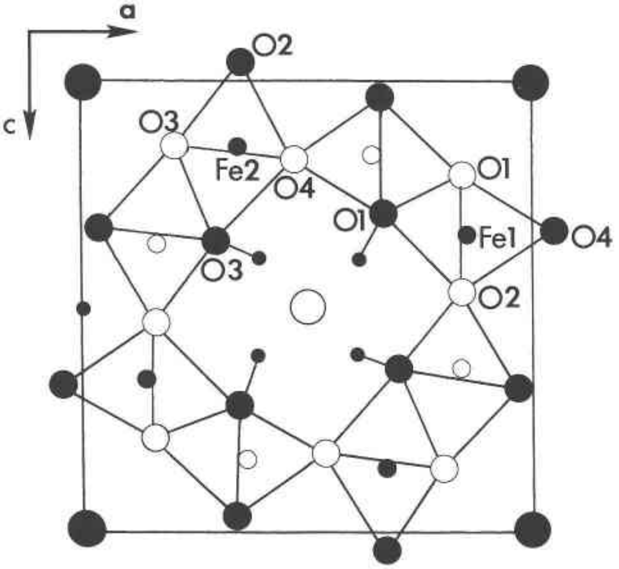

Fig. 1. Projection of the akaganéite structure, as determined by Rietveld refinement, down **b**. The solid circles represent atoms at $y = 0$ and the open circles represent atoms at $y = 0.5$. The smallest circles indicate H atom positions from structure-energy calculations.

Table 2. Akaganéite atom positions

	x	y	z	occ*
Fe1	0.858	0	0.341	
Fe2	0.339	0	0.141	
O1	0.663	0	0.290	
O2	0.657	0	0.030	
O3	0.293	0	0.357	
O4	0.039	0	0.332	
Cl	0	0	0	1.35(7)

Note: Estimated standard deviations determined by refinement are 0.001 Å for Fe and 0.003 Å for O. Isotropic temperature factors were fixed to B = 0.5 (Fe), 0.8 (O), and 2.0 (Cl).

* Occupancy; atoms per unit cell (refined only for Cl).

are also slightly low. The average of all the analyses yields the values $Fe_{7.6}Ni_{0.4}Cl_{1.25}$, assuming eight cations per unit cell. Adding O^{2-} and OH^- in the proportion necessary for charge balance yields the formula $Fe^{3+}_{7.6}Ni^{2+}_{0.40}O_{6.35}(OH)_{9.65}Cl_{1.25}$. Unfortunately, there was not sufficient pure sample to perform an H_2O analysis. The above formula indicates about 10.0 wt% H_2O (as OH^-), which compares well with the values reported by Keller (1970) for crystallographic H_2O (given off above 110 °C) in $(Cl,OH)_{<2}Fe_8(O,OH)_{16}$.

The Rietveld refinements were carried out using the computer program DBW3.2 (Wiles and Young, 1981) as modified by S. Howard (personal communication). The low-angle data ($<30°\ 2\theta$) were not used in the refinements because in this range not all of the X-ray beam was intercepted by the sample. The starting structure model was that of hollandite determined by Post et al. (1982) from a single-crystal X-ray refinement, but with the tunnel cations (i.e., Ba and Pb) omitted and Fe substituted for Mn. In the initial cycles of refinement, only the scale factor and unit-cell, background, peak-width, and peak-shape parameters were refined. The peak shapes were modeled using a pseudo-Voigt profile function, and the background was fit with a third-order polynomial.

When the refinement converged, the observed Bragg intensities determined by the Rietveld program were corrected for Lorentz polarization and multiplicity effects and converted into structure factors. These observed structure factors and the starting hollandite structure model (i.e., the octahedral framework) were used by the XTAL (Stewart and Hall, 1985) crystallographic computing package to calculate a difference Fourier map. The only significant electron density peak on the map was in the tunnel region centered at (0,0,0) and it was assigned to Cl. The Cl was added to the hollandite structure model, and atom positions and occupancy factors were refined. Individual atom temperature factors were fixed at the comparable values determined in the single-crystal study of hollandite (Post et al., 1982), and an overall thermal parameter was refined. The refinements from the two data sets did not yield significantly different results, and therefore only the results for the sample on the quartz plate are reported here. The refinement converged to an

Table 1. Rietveld refinement results

a (Å)	10.600(2)
b (Å)	3.0339(5)
c (Å)	10.513(2)
β (°)	90.24
Pseudo-Voigt coefficient	1.05(4)
Overall B	−1.3(1)
Parameters	29
Bragg reflections	147
R_p	0.101
R_{wp}	0.132
R_{wp} (expected)	0.106
R_{Bragg}	0.062

Note: In Table 1 and subsequent tables, numbers in parentheses represent estimated standard deviations.

Table 3. Selected akaganéite bond lengths (Å)

Fe1-O4	1.92	O2-O3 (×2)	2.78
-O2 (×2)	2.04	-O4 (×2)	2.86
-O1 (×2)	2.06	-O4′ (×2)	2.96
-O1′	2.13	-O2 (×2)	3.03
⟨Fe-O⟩	2.04	-Cl	3.65
Fe2-O2	1.80	O3-O4	2.70
-O4 (×2)	2.01	-O3 (×2)	2.86
-O3 (×2)	2.06	-O3′ (×2)	3.03
-O3′	2.32	-Cl (×2)	3.06
⟨Fe-O⟩	2.04	-O4 (×2)	3.07
O1-O1 (×2)	2.53	O4-O4 (×2)	3.03
-O2	2.73	-Cl	3.51
-O4 (×2)	2.92		
-O1 (×2)	3.03	Cl-Cl (×2)	3.03
-O2 (×2)	3.08		
-Cl (×2)	3.19		

Note: Estimated errors range from 0.02 to 0.05 Å for Fe-O and O-O distances, respectively.

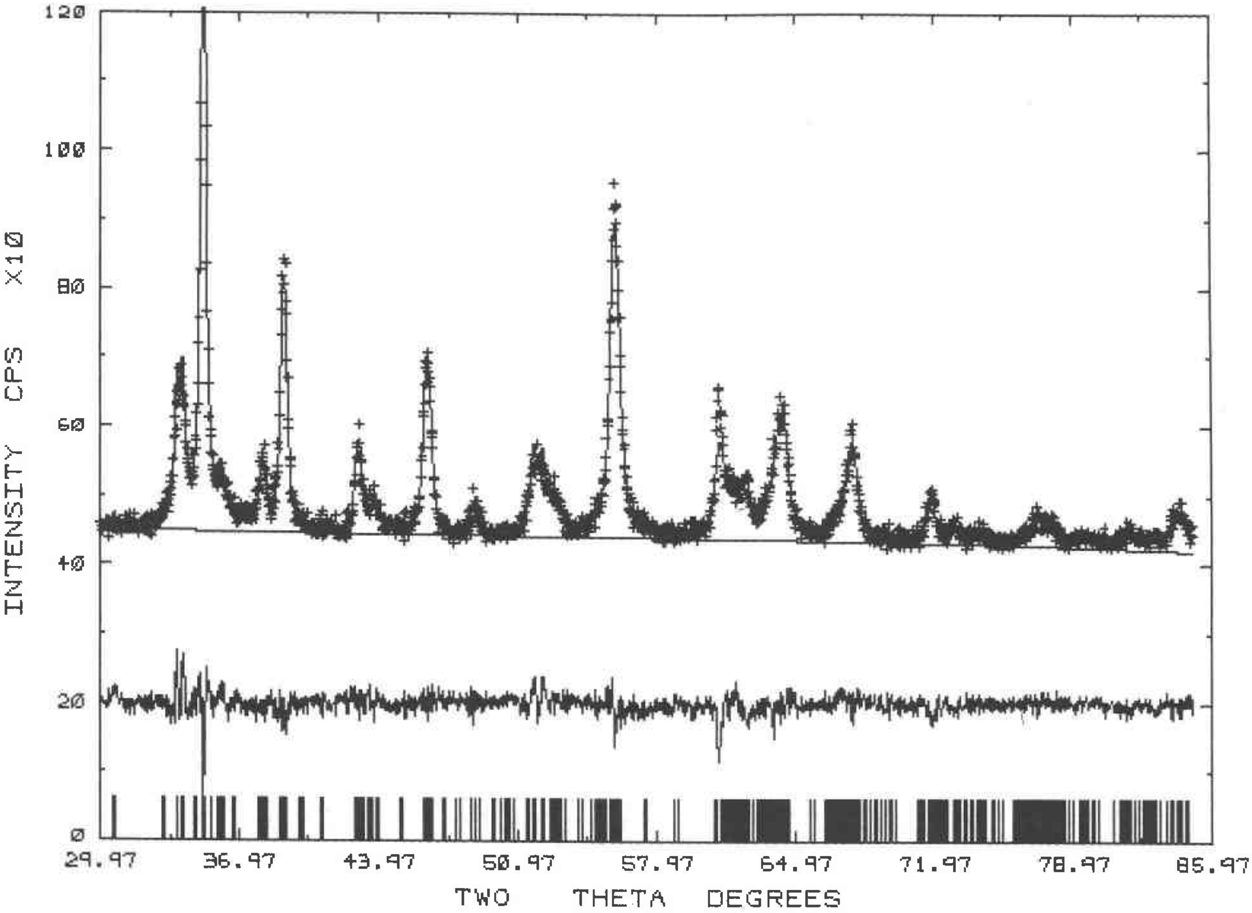

Fig. 2. Final observed (crosses) and calculated powder XRD patterns for akaganéite. The background is indicated by the horizontal line, and the vertical lines mark the positions of the Bragg reflections ($K\alpha_1$ and $K\alpha_2$) for akaganéite and goethite. The plot near the bottom of the figure shows the difference between the observed and calculated patterns.

R_{wp} of 0.135 (R_{exp} = 0.106) and R_{Bragg} of 0.072. At this point in the refinement, the plot of the difference between the observed and calculated diffraction patterns revealed the presence of a small amount of goethite. Addition of goethite to the refinement, varying only the scale factor and peak-width parameters for that phase, caused R_{wp} to decrease to 0.132 and R_{Bragg} to decrease to 0.062. Results of the refinement show that there is approximately 6.0 wt% goethite in the sample. The final Rietveld refinement parameters are listed in Table 1, atom positions are in Table 2, and selected bond distances are in Table 3. The final observed and calculated powder diffraction patterns are plotted in Figure 2.

The unit-cell parameters determined by the Rietveld refinements (Table 1) confirm that akaganéite is monoclinic, and not tetragonal as previously reported. In the refinements, we assumed space group $I2/m$, which is the same as that determined by Post et al. (1982) for hollandite. Attempts to refine the akaganéite structure in space group $I4/m$ yielded R_{wp} and R_{Bragg} factors that were more than 0.03 larger than those calculated for the monoclinic refinement. Refinement of unit-cell parameters using the Rietveld method for akaganéite from the type locality in Japan (NMNH 142657) also yielded a monoclinic unit cell [a = 10.561(4) Å, b = 3.031(1) Å, c = 10.483(4) Å, β = 90.63(4)°].

DISCUSSION

The results of the refinements confirm a hollandite-like structure for akaganéite (Fig. 1). Akaganéite is a unique and particularly interesting hollandite-like phase for two reasons: (1) the octahedral cations are predominately Fe^{3+}, whereas in virtually all other known hollandite-type compounds the octahedra primarily contain tetravalent cations (typically Mn^{4+} or Ti^{4+}), and (2) Cl^- is the major tunnel species, as opposed to large univalent or divalent cations such as Ba^{2+} or K^+ that are typical in most hollandite-type phases. A consequence of Fe^{3+} in the octahedral sites, as opposed to the typical tetravalent cations, is that at least one-half of the O anions must be replaced by OH^- in order to maintain charge balance. Additional OH^- anions are required to offset the Cl^- and any Ni^{2+} substituting for Fe^{3+}.

Octahedral sites

There are two distinct Fe-O octahedra in the akaganéite structure. The bond distances in Table 3 reveal that both octahedra are distorted, particularly that of Fe2. The octahedral Fe-O distances for Fe1 range from 1.92 to 2.13 Å (mean = 2.04 Å) and for Fe2 from 1.80 to 2.32 Å (mean = 2.04 Å). Using IR spectra, Keller (1970) derived Fe-O distances for akaganéite that range from 2.0 to 2.19 Å with a mean of 2.09 Å. For comparison, the Fe^{3+}-(O,OH) distances in goethite (α-FeOOH) range from 1.95 to 2.09 Å (mean = 2.02 Å) (Szytuta et al., 1968). One of the drawbacks of Rietveld refinements, especially for powder X-ray diffraction data, is that it is difficult to assess the reliability of the estimated errors determined by the refinement. If the data are affected by systematic errors, such as preferred orientation, then the estimated standard deviations might be considerably smaller than the actual errors [see, for example, review by Post and Bish (1989)]. Consequently, the errors in the bond distances for akaganéite might be significantly larger than indicated in Table 3. With this caveat, some general observations about the distortions of the Fe octahedra are appropriate. In both octahedra, the Fe cations are displaced off center, probably at least in part due to cation-cation repulsions between adjacent octahedra. Similar displacements are observed in other phases with the hollandite structure (e.g., Post et al., 1982). The octahedral distortions are undoubtedly enhanced because at least three of the O atoms coordinating each Fe are actually OH^-. In both octahedra, the longest Fe-O bonds are to O1 and O3, which are located in the middle of the tunnel edges and, as is discussed below, are the most likely OH^- sites. The reduced effective charge for O in OH^- gives rise to longer Fe-O bonds. Weak H bonding between O1 or O3 and Cl also probably affects the Fe-O octahedral bonds.

It is not obvious why the Fe2 octahedron shows a larger range of Fe-O distances than that of Fe1. One possibility is that in some unit cells Cl is on the O3 site, giving rise to the longer Fe-O3 bonds in Table 3. The refined value of the occupancy factor for O3, however, does not indicate a significant amount of Cl. The possibility also must be considered, of course, that the long Fe-O3 distance is somehow an artifact of the refinement. It is interesting, however, that refinements of both samples yielded comparable atom positions.

The electron microprobe analyses indicate an average of about 3.6 wt% NiO in the akaganéite samples studied here. It seems most likely that the Ni (presumably Ni^{2+}) substitutes for Fe^{3+} on the octahedral sites, and this is supported by the electron microprobe analyses that show that the amount of Fe decreases in linear proportion to increasing Ni. On the average, approximately one out of every 20 octahedral sites is occupied by Ni. In order to maintain charge balance, for every Ni^{2+} an additional OH^- must substitute for an O^{2-}, or one Cl^- must be removed. The chemical analyses do not, however, show any correlation between Cl and Ni contents.

Mössbauer studies of akaganéite have concluded that two doublets are necessary to fit the spectrum (Johnston and Logan, 1979; Murad, 1979). This observation posed a perplexing problem, considering the previous assumption of a tetragonal unit cell for akaganéite and, therefore, only a single, unique Fe site. Johnston and Logan (1979) proposed that the two doublets resulted from Fe^{3+} in both the octahedral chains and in the tunnels. Murad (1979), however, concluded that Fe^{3+} in the tunnels was not consistent with spectra he had obtained at 135 and 4 K. He suggested the possibility that the role of the Cl^- anions is somehow responsible for the complex Mössbauer spectra of this phase. The Mössbauer results are entirely consistent, of course, with the monoclinic structure, and consequently with the two nonequivalent Fe sites determined for akaganéite by our Rietveld refinements.

Tunnel sites

The difference Fourier map and refinement results confirm that the Cl^- anion is in the tunnels at (0,0,0) where it is at the center of a prism formed by eight H atoms, four at $y = 0.5$ and four at $y = -0.5$ (Fig. 1). These H atoms form hydroxyl groups with O1 and O3 anions. The map does not show any additional significant electron density in the tunnel region. The Cl electron density peak appears spherical, suggesting that there is little if any anisotropic thermal motion or positional disorder associated with the site. The refined occupancy of 1.35 Cl per unit cell is not significantly different from the value of about 1.25 determined from the electron microprobe analysis, and is consistent with the tunnel sites being approximately two-thirds occupied. The separation distance between Cl sites within a given tunnel, 3.03 Å, is less than typical Cl-Cl distances of about 3.3–3.4 Å. Therefore, if adjacent tunnel sites are occupied, it is likely that the Cl anions are displaced slightly from (0,0,0) away from each other toward vacant tunnel positions. Such displacements would be similar to those observed for tunnel cations in other hollandite phases (e.g., Post et al., 1982). Some previous investigators have suggested that molecular H_2O might occur in the tunnels of akaganéite, but our results are consistent with IR spectroscopy studies of Keller (1970) that show little if any H_2O in the tunnels.

Several studies have shown that a portion of the Cl can be removed from synthetic akaganéite by repeated washing with H_2O (Mackay, 1960; Keller, 1970; Johnston and Logan, 1979). Johnston and Logan (1979), for example, report that the Cl content decreased from an initial value of 6.9 to 3.5 wt% after eight days of washing. Keller (1970) measured Cl amounts ranging from 2.2 to 6.4 wt%. As mentioned above, the Cl contents for the akaganéite used here ranged from 3.6 to 6.3 wt%. Weiser and Milligan (1935) and Mackay (1960) observed that synthetic akaganéite always contains Cl. The chemical analysis for akaganéite from the type locality (by M. Nambu, reported by Mackay, 1960), however, does not include Cl. Unfortunately, no indication is given as to whether an analysis

TABLE 4. H atom positions determined by structure-energy calculations

	x	y	z
H1	0.586	0.001	0.353
H2	0.371	−0.001	0.403
H3	0.407	0.002	0.642
H4	0.623	−0.001	0.603
H5	0.144	0.661	0.866
H6	0.870	0.400	0.881
H7	0.858	0.616	0.127
H8	0.134	0.390	0.113
H9	0.953	0.500	0.479

Note: Calculations performed on $P1$ cell with Cl at (½,½,½). Only H positions were allowed to refine.

was actually made for Cl. Furthermore, the analysis includes 3.1% Si and 1.21% Al, suggesting that the sample of akaganéite was impure. Our XRD study of akaganéite from the type locality shows it to be intimately mixed with goethite, which if present in the analyzed sample also would affect the validity of the result. Energy dispersive X-ray analyses of akaganéite from the type locality do in fact show a significant amount of Cl. It is possible, of course, that the akaganéite from Japan exhibits a range of Cl contents and that the sample originally analyzed did not contain Cl. It seems more likely, however, that the original analysis is incorrect, and that the akaganéite does contain Cl. The analytical results support the conclusion that Cl (or a similar anion such as F^-) is essential for the formation of synthetic or natural akaganéite.

Structure-energy modeling of OH^-

Structure-energy calculation methods were used to model the positions of the H^+ cations in the akaganéite structure. The calculations were performed using the computer program WMIN (Busing, 1981) and modified electron gas (MEG) short-range pair potentials (Post and Burnham, 1986). The O-H short-range interactions were approximated using potentials determined by Abbott et al. (1989), which have been used successfully to model H positions in a variety of structures. During the energy-minimization calculations, the non-H atoms were held fixed at the positions determined by the Rietveld refinement. Formal charges were assigned to all ions. For the purpose of the calculations, space group $P1$ was assumed, and only one of the two Cl sites was occupied [at (0.5,0.5,0.5)]. Minimum-energy positions were determined simultaneously for the nine independent H atoms required for charge balance (one for each Fe^{3+} and one for Cl^-). The final H positions are listed in Table 4 and plotted in Figure 1. The calculations confirm that O1 and O3 are the hydroxyl sites. The calculated O-H distances of approximately 0.93–1.03 Å compare well with typical O-H bond lengths observed in other structures. In the tunnel containing the Cl atom, the O-H vectors point almost directly toward the Cl site at the center of the tunnel. Weak H bonds are likely formed between O1 or O3 and Cl. In the tunnel with the vacant Cl site, the O-H vector points about 30° away from the line connecting O1, O3 and the center of the tunnel. The ninth H atom, initially placed in the tunnel near O2, shifted during the minimization to a site 1.15 Å from O2, inside one of the small tunnels that are one octahedron × one octahedron wide (1 × 1) and that run parallel to the large 2 × 2 tunnels.

SUMMARY

We have used the Rietveld refinement method and powder X-ray diffraction data to refine the crystal structure of akaganéite for the first time. Our results confirm the hollandite-type structure but reveal that the unit cell is monoclinic rather than tetragonal as had previously been assumed. The two nonequivalent Fe sites in the monoclinic structure explain, and are consistent with, results of previous Mössbauer studies. Structure-energy calculations show that O1 and O3 are the OH^- sites and that the O-H vectors are directed toward the centers of the tunnels. Chemical analyses combined with the structure refinements suggest that Cl probably is essential to the formation of synthetic and natural akaganéite.

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