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HILLITE, A NEW MEMBER OF THE FAIRFIELDITE GROUP: ITS DESCRIPTION AND CRYSTAL STRUCTURE

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ABSTRACT

Hillite (хиллит *in Russian)*, ideally $Ca_2(Zn,Mg)[PO_4]_2{\bullet}2H_2O$, is a new zinc-dominant analogue of collinsite, isostructural with fairfieldite. It occurs in unmetamorphosed sediments of the Lower Cambrian Parachilna Formation, Reaphook Hill, South Australia, Australia, in association with zincian collinsite and scholzite. Hillite is triclinic, a 5.736(1), b 6.767(2), c 5.462(1) Å, α 97.41(2), β 108.59(2), γ 107.19(2)°, V 186.05(8) Å^3, space group $P1$, $Z = 1$. The average result of fifteen electron-microprobe analyses of relatively homogeneous crystals of the latest generation is: Na_2O 0.11, CaO 30.36, MgO 4.34, ZnO 14.79, FeO 0.04, P_2O_5 40.85, H_2O_{calc} 10.23 (calculated to give 2 H_2O), total 100.72 wt.%. The single crystals of hillite do not exceed 50 μm in length; larger aggregates are rather inhomogeneous in terms of Zn:Mg ratio. Chemical analyses show that hillite contains as much as 64 mol.% of the Zn end-member, and there is perfect solid-solution toward collinsite. The mineral is colorless or grey with greenish or bluish tint, and shows weak greenish yellow fluorescence in short-wave ultraviolet light. It has a perfect cleavage along {010} and {001}; the Mohs hardness is 3½. Hillite is biaxial positive with $2V_z$ (calc.) = 83.4°, α 1.635(3), β 1.650(5), γ 1.669(3); D_{meas} = 3.16(2) g/cm^3 . The six strongest X-ray powder-diffraction lines [d_{meas} in Å(I)(hkl)]: 6.24(34)(010), 3.230(22)(110), 3.130(37)(020), 3.038(40)(101), 2.690(100)(121), 2.230(14)(130). The crystal structure of hillite has been determined [automated single-crystal diffractometer, Mo$K\alpha$, graphite monochromator, image-plate area-detector system, T = 293 K, 2928 reflections, $wR_2 = 0.0998$ for all 1078 unique reflections, $R = 0.0378$ for 993 observed reflections with $I \geq 2\sigma(I)$]. The refinement of site occupancies showed that Zn and Mg are in the octahedral position at the center of symmetry in the proportion 0.623(5) : 0.377(5), in agreement with an empirical formula based on the electron-microprobe data. The positions of two independent H atoms were obtained from difference-Fourier syntheses and were refined under isotropic approximation. The structure of hillite consists of isolated $MO_4(H_2O)_2$ octahedra, which are connected by orthophosphate tetrahedra to form chains parallel to the c axis. In the a and b directions, these chains are held together by Ca atoms and hydrogen bonds.

Keywords: new mineral species, hillite, fairfieldite, collinsite, crystal structure, Reaphook, South Australia.

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SOMMAIRE

La hillite (хиллит en Russe), dont la composition idéale est $Ca_2(Zn,Mg)[PO_4]_2 \bullet 2H_2O$, est l'analogue à dominance de zinc de la collinsite, isostructurale par rapport à la fairfieldite. Nous l'avons découverte dans des sédiments non métamorphisés de la Formation Parachilna (âge cambrien inférieur) à Reaphook Hill, Australie du Sud, Australie, en association avec la collinsite zincifère et la scholzite. La hillite est triclinique, *a* 5.736(1), *b* 6.767(2), *c* 5.462(1) Å, α 97.41(2), β 108.59(2), γ 107.19(2)°, *V* 186.05(8) $Å^3$, groupe spatial *P*1, *Z* = 1. La composition moyenne, d'après quinze déterminations à la microsonde électronique effectuées sur des cristaux relativement homogènes de la dernière génération, est: Na_2O 0.11, CaO 30.36, MgO 4.34, ZnO 14.79, FeO 0.04, P_2O_5 40.85, H_2O_{calc} 10.23 (calculé pour donner 2 H_2O), total 100.72% (poids). Les cristaux de hillite ne dépassent pas 50 μm en longueur. Les agglomérations plus grosses sont plutôt hétérogènes en termes du rapport Zn:Mg. Les analyses chimiques montrent que la hillite contient jusqu'à 64% du pôle Zn (base molaire), et que la solution solide vers le pôle collinsite est parfaite. Il s'agit d'un minéral incolore, ou gris avec une teinte verdâtre ou bleuâtre, qui possède une faible fluorescence jaune verdâtre en lumière ultra-violette. Le clivage est parfait le long de {010} et de {001}; la dureté de Mohs est 3½. La hillite est biaxe positive, avec $2V_z$ (calc.) = 83.4°, α 1.635(3), β 1.650(5), γ 1.669(3); D_{mes} = 3.16(2) g/cm^3 . Les six raies les plus intenses du spectre de diffraction X [d_{mes} en Å(I)(*hkl*)] sont: 6.24(34)(010), 3.230(22)(110), 3.130(37)(020), 3.038(40)(101), 2.690(100)(121), et 2.230(14)(130). Nous avons déterminé la structure avec un diffractomètre automatisé sur monocristal, rayonnement Mo*K*α, monochromatisation au graphite, et un détecteur à aire (CCD), T = 293 K, en utilisant 2928 réflexions; wR_2 est égal à 0.0998 en considérant toutes les 1078 réflexions uniques, *R* est égal à 0.0378 pour les 993 réflexions observées, $I \geq 2\sigma(I)$]. L'affinement des occupations des sites montre que le Zn et le Mg sont en coordinence octaédrique au centre de symétrie dans la proportion 0.623(5) : 0.377(5), ce qui concorde avec la formule empirique dérivée des résultats analytiques.Nous avons trouvé les positions des deux atomes independants de H sur les synthèses de la difference de Fourier, et nous les avons affinées en les considerant isotropes. La structure cristalline de la hillite contient des octaèdres $MO_4(H_2O)_2$ isolés qui sont liés par les tétraèdres d'orthophosphate, formant des chaines parallèles à l'axe *c.* Le long de *a et b*, ces axes sont rattachés par les atomes de Ca et des liaisons hydrogène.

(Traduit par la Rédaction)

Mot-clés: nouvelle espèce minérale, hillite, fairfieldite, collinsite, structure cristalline, Reaphook, Australie du Sud.

INTRODUCTION

A hydrated phosphate of Ca, Mg and Zn, related to collinsite (fairfieldite group), was originally described by Hill *et al.* (1973) and Hill & Milnes (1974) as potentially a new mineral species, zincian collinsite. The mineral occurs in a small "gossanous" mass covering unmetamorphosed, poorly sorted argillaceous siltstones of the Lower Cambrian Parachilna Formation, Reaphook Hill, South Australia, Australia, where it is associated with other phosphates: scholzite, tarbuttite, parahopeite, collinsite (zincian variety), switzerite and phosphophyllite. For a geological outline of the occurrence, readers are referred to the above-mentioned publications. Aggregates of zincian collinsite were described as grossly heterogeneous in terms of Zn:Mg ratio (mostly concentric aggregates). Hill & Milnes (1974) considered this chemical heterogeneity to be "not desirable in X-ray study of the crystal structure".

On behalf of Museum Victoria, Melbourne, Australia, Mr. Dermot Henry, the Senior Manager of the Mineralogical Collections, kindly donated to us several representative samples of collinsite from the Reaphook Hill occurrence. The samples were used primarily as reference material during a study of a rare strontian variety of collinsite, found to occur in hydrothermal mineral assemblages of the Kovdor carbonatite complex (Liferovich *et al.* 2001, Yakubovich *et al.* 2003). Systematic electron-microprobe analyses of the zincian collinsite led to the discovery of the latest collinsite-like phase with a Zn-dominant composition in the South Australian samples. Consequently, this species was subjected to a structural investigation and description as a new mineral species, considered and approved by the Committee on New Minerals and Mineral Names (IMA #2003–05). We have named this mineral hillite (хиллит in Russian) in honor of Dr. Roderick Hill (*b.* 1949), Chief of Mineral Research Division, CSIRO, Melbourne, Australia, who first described this mineral and recognized it as a potentially new species. The holotype sample of hillite is housed in the collection of Museum Victoria, Melbourne, Australia, under catalogue number M46032.

Hillite is a member of the fairfieldite group of minerals, which includes triclinic species, with the general formula $A_2M(TO_4)_2 \bullet 2H_2O$, where *A* = Ca and Sr, *M* = Mg, Fe, Zn, Ni, Co and Mn, and *T* = P and As. Table 1 shows a comparison of the characteristics available for minerals isostructural with fairfieldite and collinsite; of the fairfieldite group, the crystal structures of fairfieldite, collinsite, strontian collinsite and talmessite have been studied so far.

In this paper, we provide a short description of hillite on the basis of the available samples, and report on results of its characterization by single-crystal X-ray study.

PHYSICAL, OPTICAL AND X-RAY POWDER-DIFFRACTION DATA

Hillite occurs as euhedral doubly terminated crystals and clusters of crystals (Figs. 1a, b); single crystals observed in the samples available do not exceed 50 μm in length. The euhedral crystals of hillite occur in the latest phosphate assemblages subjected to incipient dissolution and regeneration. Crystals of hillite occur mostly on prismatic faces of scholzite crystals and form clusters on the surface of the previously formed crusts of zincian collinsite. Spatial relationships of the euhedral hillite to associated minerals argue in favor of nucleation and growth of hillite microcrystals mostly in a free-floating state. In addition, hillite forms concentric zones up to 200 μm in thickness within kidney-like aggregates and crusts of zincian collinsite. Hillite is greenish and bluish to colorless, transparent in crystals and translucent in aggregates, with a vitreous luster (silky in aggregates) and weak greenish yellow fluorescence in short-wave ultraviolet light. The mineral has a

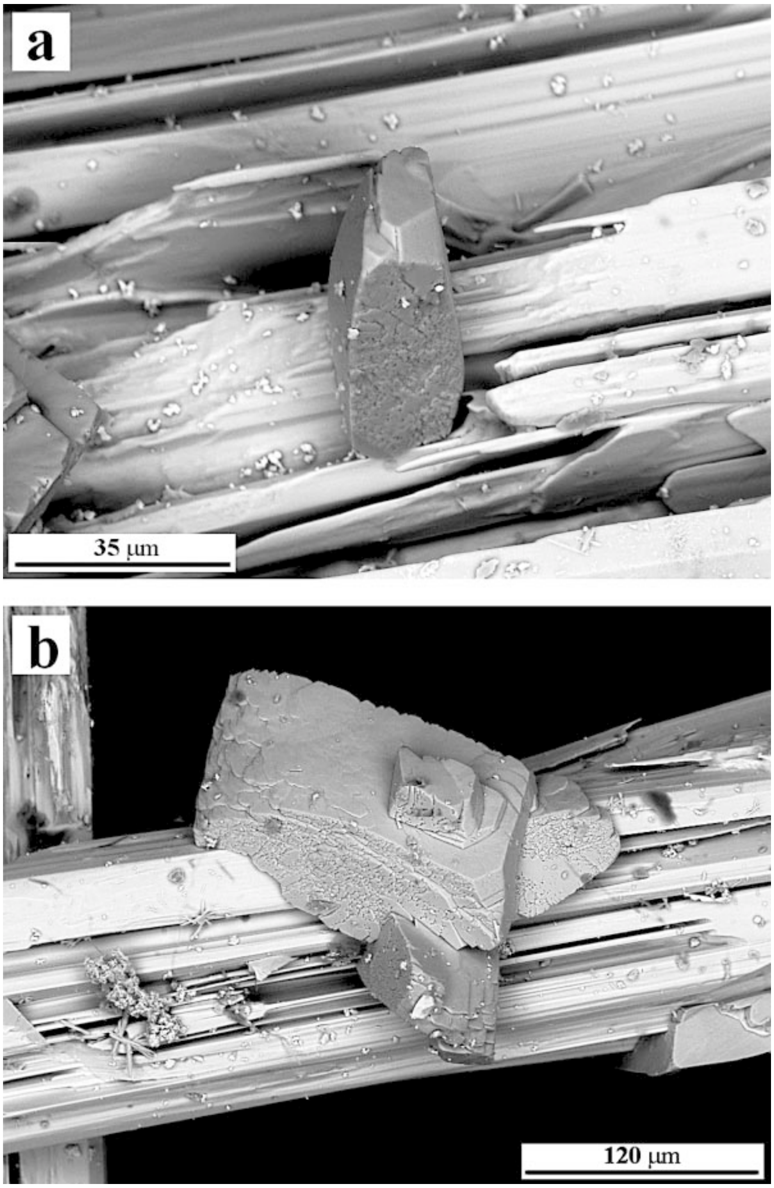

FIG. 1. Morphology of tiny single crystal of hillite (a) and less homogeneous larger cluster (b), growing on an acicular crystal of scholzite. SEM back-scattered electron images.

perfect cleavage along {010} and {001}; the Mohs hardness is 3½. Hillite is soluble in hydrochloric acid (after some hours at room temperature).

The density of a relatively homogeneous single crystal of hillite, measured by microflotation in Clerici–H_2O solutions at 20°C, is 3.16(2) g/cm^3; this value is in agreement with the calculated density (Table 1). Homogeneous crystals of hillite are optically biaxial, positive; indices of refraction for Na-light are: α 1.635(3), β 1.650(5), γ 1.667(3), $2V_Z$(calc.) 83.4°. A Gladstone–Dale calculation gave a compatibility index of –0.007, superior (Mandarino 1981).

The powder-diffraction data for the zinc-dominant analogue of collinsite was reported by Hill & Milnes (1974). Taking into consideration variations in Zn:Mg ratio in zincian collinsite and hillite from the Reaphook Hill occurrence, as described by Hill & Milnes, we re-collected these data (DRON–2.0 diffractometer, Cu$K\alpha$ radiation, graphite monochromator) for the holotype hillite, also subjected to a refinement of crystal structure. The unit-cell parameters, a 5.736(1), b 6.767(2), c 5.462(1) Å, α 97.41(2), β 108.59(2), γ 107.19(2)°, V 186.05(8) Å^3, space group $P1$, $Z = 1$, were refined from X-ray powder-diffraction data using the indices derived from the single-crystal determination of the structure (Table 2).

TABLE 1. CRYSTAL DATA FOR FAIRFIELDITE-GROUP MINERALS¶

Mineral, formula	Unit-cell parameters, a, b, c (Å), α, β, γ (°)	D_{calc}* g/cm^3	R
Cassidyite $Ca_2(Ni,Mg)[PO_4]_2 \cdot 2H_2O$ White *et al.* (1967)	5.71(1), 6.73(1), 5.43(1), 96.7(2), 107.3(3), 104.7(2)	3.15	
Collinsite $Ca_2(Mg,Fe)[PO_4]_2 \cdot 2H_2O$ Brotherton *et al.* (1974)	5.7344(8), 6.780(1), 5.4413(9), 97.29(1), 108.56(1), 107.28(1)	2.93	0.033
Gaitite $Ca_2(Zn,Mg)[AsO_4]_2 \cdot 2H_2O$ Sturman *et al.* (1980)	5.90, 7.61, 5.57, 111.67, 109.17, 119.42	3.81	
Fairfieldite $Ca_2(Mn,Fe)[PO_4]_2 \cdot 2H_2O$ Fanfani *et al.* (1970)	5.79(1), 6.57(1), 5.51(1), 102.3(3), 108.7(3), 90.3(3)	3.10	0.075
Hillite $Ca_2(Zn,Mg)[PO_4]_2 \cdot 2H_2O$ our data	5.736(1), 6.767(2), 5.462(1), 97.41(2), 108.59(2), 107.19(2)	3.18	0.038
Messelite $Ca_2(Fe,Mn)[PO_4]_2 \cdot 2H_2O$ Frondel (1955)	5.95(2), 6.52(2), 5.45(2), 102.3(4), 107.5(4), 90.8(2)	3.16	
Parabrandtite $Ca_2Mn[AsO_4]_2 \cdot 2H_2O$ Dunn *et al.* (1987)	5.89(1), 7.031(7), 5.64(1), 96.77(10), 109.32(10), 108.47(8)	3.55	
Talmessite $Ca_2(Mg,Co)[AsO_4]_2 \cdot 2H_2O$ Catti *et al.* (1977)	5.874(7), 6.943(11), 5.537(6), 97.3(1), 108.7(1), 108.1(2)	3.42	0.081
Roselite-beta $Ca_2(Co,Mg)[AsO_4]_2 \cdot 2H_2O$ Bariand *et al.* (1960), Pierrot (1964)	5.884(6), 6.963(8), 5.581(9), 97.72(8), 109.24(9), 107.53(10)	3.60	

* calculated on the basis of data derived from the crystal-structure refinement.
¶ $P\bar{1}$, $Z = 1$.

Chemical Composition

As a result of back-scattered electron (BSE) scanning and quantitative analyses of several polished and carbon-coated sections of crystals and aggregates of zinc-rich collinsite (using a JEOL JSM–6400 SEM equipped with a Link eXL energy-dispersion spectrometer), we were able to find tiny single crystals of zinc-dominant composition showing minimal chemical heterogeneity, *i.e.*, composed principally of hillite. The chemical composition of these crystals was cross-checked using a wavelength-dispersion (WDS) technique, employing a Cameca Camebax Microbeam electron microprobe, operated at an acceleration potential of 15 kV, and a current of 15 nA. A ZAF correction was applied to all the raw data. Jadeite (Na), sphalerite (Zn), periclase (Mg), apatite (P, F) and metallic Fe were employed as standards.

The thermal instability of hillite under the focused electron beam places restrictions on the accuracy of the electron-microprobe data. This is in accordance with the thermal properties known for its Mg-dominant analogue, collinsite (Rimskaya-Korsakova 1965). We have previously observed similar instability in all hydrous phosphates isostructural with hillite, *i.e.*, for those from the Kovdor Complex (collinsite, strontian collinsite), from British Columbia, from Rapid Creek, Yukon Territory, Canada (collinsite) and from Messel, Germany (messelite) (Liferovich *et al.* 2001). Hill & Milnes (1974) noted the same problem during their electron-microprobe analysis of zincian collinsite from Reaphook Hill, and defocused the beam to 50 μm to minimize the decomposition of the mineral. In addition to defocusing, our routine for analyses of the fairfieldite-group minerals included the regular micro-movement of a sample under the electron beam during the counting period (in cases where samples were homogeneous and large enough). Unfortunately, both of these approaches cannot be applied to the small crystals of hillite, nor to the larger but heterogeneous clusters. This problem resulted

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR HILLITE

I_{obs}	$d_{obs.}$	$d_{calc.}$	$h\,k\,l$	I_{obs}	d_{obs}	$d_{calc.}$	$h\,k\,l$
34	6.24	6.2653	0 1 0	14	2.230	2.2332	$1\,\bar{3}\,0$
4	5.01	5.0173	0 0 1	7	2.192	2.1948	$\bar{2}\,1\,2$
6	4.49	4.4938	$0\,\bar{1}\,1$	6	2.151	2.1530	0 1 2
16	3.512	3.5162	0 1 1	6	2.118	2.1188	$\bar{1}\,\bar{2}\,2$
		3.5078	$\bar{1}\,\bar{1}\,1$			2.1187	$1\,\bar{3}\,1$
22	3.230	3.2332	$1\,\bar{2}\,0$	14	2.089	2.0884	0 3 0
37	3.130	3.1326	0 2 0	11	2.062	2.0630	$\bar{2}\,\bar{1}\,2$
40	3.038	3.0412	1 0 1	9	1.996	1.9960	$1\,\bar{2}\,2$
9	3.008	3.0115	$0\,\bar{2}\,1$	11	1.969	1.9699	$\bar{1}\,3\,1$
		2.7137	$\bar{2}\,0\,1$	5	1.918	1.9233	$\bar{2}\,2\,2$
100	2.690	2.7001	$\bar{1}\,2\,1$	6	1.870	1.8685	1 2 1
		2.6867	$\bar{1}\,0\,2$	5	1.830	1.8307	$\bar{3}\,2\,1$
7	2.554	2.5565	$0\,\bar{1}\,2$	10	1.801	1.8003	$\bar{1}\,\bar{1}\,3$
6	2.465	2.4653	$\bar{1}\,\bar{2}\,1$	10	1.778	1.7788	0 3 1
6	2.403	2.4043	0 2 1				$3\,\bar{2}\,0$
3	2.363	2.3202	1 2 0	14	1.757	1.7581	0 2 2
10	2.289	2.2903	$\bar{2}\,\bar{1}\,1$	7	1.694	1.6920	3 0 0
				22	1.668	1.6696	$\bar{2}\,\bar{1}\,3$

DRON-2.0 diffractometer, graphite-monochromatized Cu$K\alpha$ radiation.

in some deviation of the analytical data from the theoretical stoichiometry.

The hillite crystals analyzed with the electron microprobe do not exceed 25–30 μm in length. As a result, the electron beam employed for wavelength-dispersion (WDS) electron-microprobe analyses had to be focussed to 10–15 μm. Back-scattered electron images show the presence of an external zone in the hillite crystals, as thin as 1–3 μm, in which the proportion of Zn is less than that of Mg. Although this zone is relatively depleted in Zn, it comprises a fairly insignificant proportion of the volume of the crystals. The mean of 15 WDS determinations of the chemical composition of hillite is given in Table 3. The empirical formula of the new mineral species, calculated on the basis of O = 8 and with H_2O calculated to give $2H_2O$, is as follow: $(Ca_{1.91}Na_{0.01})_{\Sigma 1.92}(Zn_{0.64}Mg_{0.38})_{\Sigma 1.02}P_{2.03}O_8 \bullet 2.00H_2O$. This finding is close to the idealized formula, $Ca_2(Zn_{0.62}Mg_{0.38})[PO_4]_2 \bullet 2H_2O$, based on the results of the structure determination. The chemical analyses show that hillite contains as much as 64 mol.% of the Zn end-member; our data and the previously published chemical compositions reveal the existence of a perfect solid-solution of hillite toward the isostructural collinsite and fairfieldite (Hill *et al.* 1973, Hill & Milnes 1974). Similar solid-solutions could be expected between hillite and fairfieldite and between hillite and messelite joins ($^{VI}Zn \rightarrow {}^{VI}Mn$ and $^{VI}Zn \rightarrow {}^{VI}Fe$ isovalent substitutions, respectively).

A quantitative determination of H_2O in hillite was not possible because of the scarcity of the material available for study. However, the presence of H_2O molecules was clearly shown in the infrared absorption spectrum, which consisted of the following lines (the strongest are underlined, in cm^{-1}): $\underline{3020}$, 2680, 2450, 2230, 1900, 1603, $\underline{1513}$, $\underline{1103}$, $\underline{996}$, 940, 915, $\underline{771}$, 585, $\underline{578}$ and $\underline{559}$ (courtesy of Dr. N.V. Chukanov). The infrared absorption data also indicate the absence of carbonate groups in hillite.

The Crystal Structure of Hillite

A tiny, colorless single crystal of hillite, with dimensions 5 × 15 μm, was selected for the collection of the X-ray data. The unit-cell parameters were determined and refined with an IPDS II area-detector system (Stoe & Cie 1997) using Mo*K*α radiation (graphite monochromator). The intensities were corrected for Lorentz and polarization effects, and a numerical absorption-correction, based on the shape of the crystal, was applied. In Table 4, we report the crystallographic characteristics and the experimental conditions of data collection and refinement.

All calculations were performed with the SHELXL-97 program (Sheldrick 1997). Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography (Hahn 1995). Starting with the atom coordinates of collinsite (Brotherton *et al.* 1974), we refined the structure of hillite using the F^2 data to residuals $wR_2 = 0.0998$ (for all 1078 reflections) and $R = 0.0378$ [for 993 reflections $> 2\sigma(I)$], with anisotropic displacement parameters for all non-H atoms.

Refinement of site occupancies showed that Zn and Mg atoms share one octahedral position in the structure, in the proportion of 0.623(5) : 0.377(5). During the refinement, the displacement parameters of Zn and Mg were constrained to be equal. These inferred occupancies correspond to the formula: $Ca_2(Zn_{0.62}Mg_{0.38})[PO_4]_2 \bullet 2H_2O$ ($Z = 2$, $D_{calc} = 3.178$ g/cm^3).

The positions of two independent H atoms were obtained from difference-Fourier syntheses and were refined under isotropic approximation. The final atom-coordinates and interatomic distances are given in Tables 5 and 6. Table 7 presents the geometric charac-

TABLE 3. CHEMICAL COMPOSITION AND UNIT FORMULA OF HILLITE

Hillite	Mean*	Range	$CaZn(PO_4)_2 \bullet 2H_2O$		
Na_2O wt.%	0.11	0.10-0.12	Na *apfu*	0.01	
CaO	30.36	30.17-30.54	Ca	1.91	30.19
MgO	4.34	4.08-4.59	Mg	0.38	
ZnO	14.79	14.37-15.21	Zn	0.64	21.90
FeO	0.04	0.03-0.05	Fe	-	
P_2O_5	40.85	40.63-41.06	P	2.03	38.21
$H_2O^†$	10.23		H_2O	2.00	9.70
Total	100.72		Σ	3.97	100.0

* mean of 15 determinations; † calculated to give $2H_2O$. *apfu*: atoms per formula unit.

TABLE 4. CRYSTAL DATA AND DETAILS OF THE X-RAY DATA COLLECTION AND REFINEMENT FOR HILLITE

Crystal data					
Formula		$Ca_2(Zn_{0.62}Mg_{0.38})[PO_4]_2 \bullet 2H_2O$			
Absorption μ [mm^{-1}]		4.000			
Space group		$P\bar{1}$, $Z = 1$			
Lattice constants					
a (Å)	5.736(1)	*b* (Å)	6.767(2)	*c* (Å)	5.462(1)
α (°)	97.41(2)	β (°)	108.59(2)	γ (°)	107.19(2)
V (Å^3)	186.03(8)				
Density [g/cm^{-3}]		D_{calc}	3.178	D_{meas}	3.16
Data collection					
Diffractometer		IPDS – II area detector system (Stoe)			
Radiation		Mo*K*α, graphite monochromator			
Temperature [K]		293			
Scanning mode		Φ = 0–200°, δΦ = 1°, 3 min/rec			
Measurement range		max θ = 30.0°			
Reflections (total)		2928			
R_{int}		0.0788			
R_σ		0.0565			
Refinement					
Reflections unique/observed [I>2σ (I)]		1078/993			
Parameters		79			
Absorption correction		numerical			
T_{max}, T_{min}		0.123, 0.069			
Extinction coefficient		0.035(13)			
Residuals					
R (observed reflections)		0.0378			
R, wR_2 (all reflections)		0.0411, 0.0998			
Goodness of fit S		0.804			
δρ (max)		0.7594			
δρ (min)		-0.599			

teristics of hydrogen bonds. The results of a bond-valence analysis (Pyatenko 1972, Brown 1976) are given in Table 8. The tables of structure factors and anisotropic displacement parameters are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

INTERATOMIC DISTANCES IN HILLITE

Four of the vertices of the (Zn,Mg)-octahedron are occupied by O atoms of phosphate groups (henceforth O_P) and two vertices by *trans*-positioned O atoms of H_2O molecules (henceforth O_W). The interatomic distances M–O_W [1.990(2) Å] are shorter than the distances M–O_P [2.140(2) and 2.164(2) Å]. In collinsite, $Ca_2Mg[PO_4]_2 \cdot 2H_2O$ (Brotherton *et al.* 1974), a similar distribution of distances can be found: the interatomic distances M–O_W [1.997(5) Å] also are shorter than the M–O_P distances [2.107(4), 2.144(5) Å]. As can be seen, the distortion of the (Zn,Mg) octahedron and the average M–O distance (2.098 Å) are somewhat larger than those of the Mg octahedron in collinsite (2.083 Å); this is in agreement with the larger size of the Zn^{2+} ion (radius 0.74 Å) compared with Mg^{2+} (0.72 Å). The dilution of Mg octahedra by Co, as in the structure of talmessite, $Ca_2(Mg,Co)[AsO_4]_2 \cdot 2H_2O$ (Catti *et al.* 1977), also leads to an increase in the average M–O distance (2.097 Å). A still higher value of the average cation–anion distance M^{2+}–O (2.197 Å) among these isostructural minerals can be found in the structure of fairfieldite $Ca_2Mn[PO_4]_2 \cdot 2H_2O$ (Fanfani *et al.* 1970), where the octahedra are occupied by the rather large Mn^{2+} ion (${}^{VI}Mn^{2+}$ = 0.83 Å). In this case, the distance Mn–O_W [2.180(7) Å] is not the shortest in the octahedron, as it is in the structures discussed above, but lies between 2.142(9) and 2.269(7) Å. When considering the unit-cell parameters of the triclinic members of the fairfieldite group of minerals (Table 1), Catti *et al.* (1977) distinguished two subgroups on the basis of the α and γ values, with fairfieldite and messelite in one subgroup, and collinsite, talmessite, roselite-beta, and cassidyite in the other. The same authors showed that the x coordinate of two oxygen atoms and of the H_2O molecule in collinsite and talmessite differ from those found in fairfieldite. The conclusion of Catti *et al.* (1977) is confirmed by our data on the unit-cell parameters and atomic coordinates of hillite, as well as on the type of octahedron distortion.

The P–O distances in the orthophosphate tetrahedron are in the range 1.518(2)–1.560(2) Å (average 1.546 Å) and correlate well with similar bond-lengths in the structure of fairfieldite, where they vary from 1.514(7) to 1.563(7) Å (average 1.546 Å) (Table 1). In the structure of collinsite, the orthophosphate tetrahedron is more regular, with the distribution of P–O distances in the interval 1.527(6)–1.559(5) Å (average 1.543 Å).

The Ca–O bond lengths in the $[CaO_8]$ eight-vertex polyhedron are between 2.375(2) Å and 2.662(2) Å. A similar spread of cation–anion distances is observed for the eight-vertex Ca polyhedra in the other isostructural minerals. In collinsite, these distances vary from

TABLE 5. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å^2) FOR HILLITE

Atom	*x*	*y*	*z*	U(eq)
Zn¶	0.0	0.0	0.0	0.0159(3)
Mg¶	0.0	0.0	0. 0	0.0159(3)
Ca	0.3026(1)	0.7605(1)	0.6536(1)	0.0165(2)
P	0.3353(1)	0.2447(1)	0.6655(1)	0.0145(2)
O(1)	0.3375(4)	0.1298(4)	0.8947(4)	0.0172(4)
O(2)	0.2572(4)	0.0702(4)	0.4078(4)	0.0182(4)
O(3)	0.1563(4)	0.3738(3)	0.6344(4)	0.0173(4)
O(4)	0.6222(4)	0.3874(3)	0.7202(4)	0.0176(4)
O(5)	0.9493(4)	0.2773(3)	0.0692(5)	0.0170(4)
H(1)	0.105(12)	0.380(10)	0.118(12)	0.045(11)*
H(2)	0.857(12)	0.314(10)	-0.053(12)	0.045(11)*

¶ occupancy of the Zn site: 0.623(5), and of the Mg site: 0.377(5). * isotropic approximation. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 6. BOND LENGTHS (Å) IN HILLITE

(Zn,Mg) octahedron		Ca polyhedron		P tetrahedron	
(Zn,Mg) – O5	1.990(2) 2×	Ca – O4	2.375(2)	P – O3	1.518(2)
O2	2.140(2) 2×	O5	2.392(2)	O4	1.550(2)
O1	2.164(2) 2×	O3	2.410(2)	O1	1.555(2)
average	2.098	O3	2.477(2)	O2	1.560(2)
		O1	2.505(2)	average	1.546
		O1	2.590(2)		
		O2	2.594(2)		
		O2	2.662(2)		
		average	2.501		

TABLE 7. H-BONDING IN HILLITE

D – H ····· *A*	*D* – H, Å	H ····· *A*, Å	*D* ····· *A*, Å	*D* – H ····· *A*, °
O5 – H1 ····· O4	0.89(7)	1.74(7)	2.596(3)	163(7)
O5 – H2 ····· O4	0.83(7)	1.76(7)	2.573(3)	169(7)

D: donor, *A*: acceptor.

TABLE 8. BOND-VALENCE ANALYSIS FOR HILLITE

	Zn,Mg	P	Ca	H1	H2	Σ	|Δ|
O(1)	$0.28^{\times 2\downarrow}$	1.19	0.25 0.22			1.94	0.06
O(2)	$0.29^{\times 2\downarrow}$	1.17	0.22 0.21			1.89	0.11
O(3)		1.41	0.28 0.25			1.94	0.06
O(4)		1.22	0.29	0.31	0.33	2.15	0.15
O(5)	$0.43^{\times 2\downarrow}$		0.28	0.69	0.67	2.07	0.07
Σ	2.00	4.99	2.00	1.00	1.00		

2.384(6) to 2.702(6) Å, in fairfieldite, from 2.336(10) to 2.724 Å, and in talmessite, from 2.361(15) to 2.769(15) Å.

DESCRIPTION OF THE STRUCTURE

The crystal structure of hillite (Fig. 2) consists of isolated $MO_4(H_2O)_2$ octahedra (Brotherton *et al.* 1974), which are connected by orthophosphate tetrahedra to form chains parallel to the *c* axis. Each tetrahedron shares two vertices with neighboring octahedra along the chain, whereas the other two oxygen vertices coordinate a Ca^{2+} ion. In the *a* and *b* directions, these chains are held together by Ca atoms and hydrogen bonds (Table 7).

Two oxygen atoms are involved in the system of hydrogen bonds in the structure. The oxygen atom O5 of the H_2O molecule plays the role of donor of two hydrogen bonds, and the O4 atom acts as their acceptor. A similar geometry of the hydrogen bonds was found in the collinsite and talmessite structures, unlike the hydrogen bonding in the fairfieldite structure, where an-

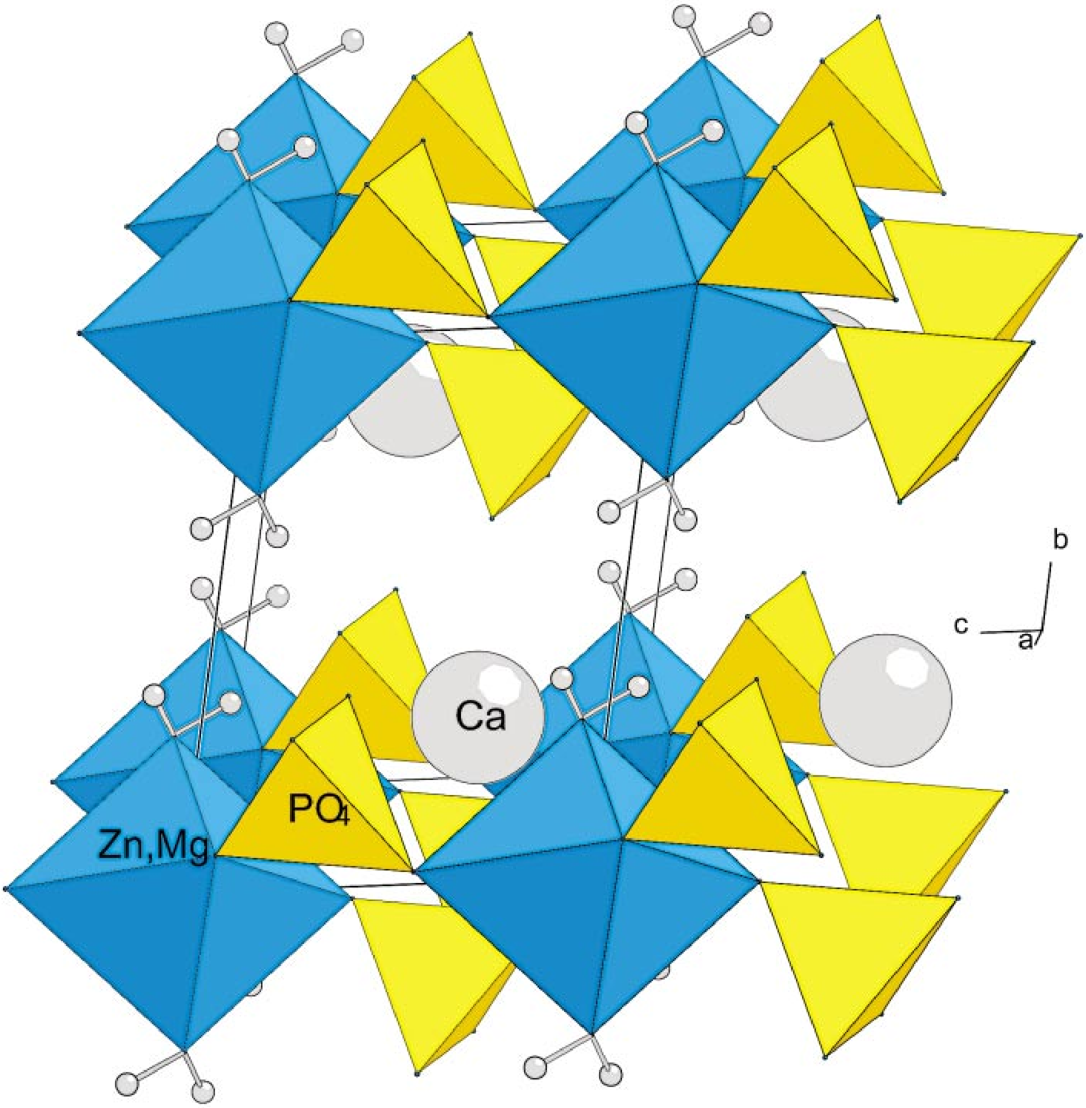

FIG. 2. Crystal structure of hillite. Clinographic projection.

other O atom was suggested to be the hydrogen bond acceptor by Fanfani *et al.* (1970). The possibility of a different pattern of hydrogen bonding in fairfieldite is one more argument in favor of the hypothesis made by Catti *et al.* (1977), that the triclinic minerals of the fairfieldite group should be considered isostructural to a first approximation only. We agree with their suggestion of two subgroups (fairfieldite and collinsite), and we consider the new mineral hillite as a member of the collinsite subgroup.

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