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CADWALADERITE, $Al_2(H_2O)(OH)_4{\cdot}n(Cl,OH^-,H_2O)$, FROM CERROS PINTADOS, CHILE, DEFINED AS A VALID MINERAL SPECIES AND THE DISCREDITATION OF LESUKITE

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Abstract

Cadwaladerite, described in 1941 as $Al(OH)_2Cl{\cdot}4H_2O$, and lesukite, described in 1997 as $Al_2(OH)_5Cl{\cdot}2H_2O$, are very closely related chemically and structurally, but are found in very different environments. Cadwaladerite was found at the edge of a salar in Chile. Lesukite has been described from a volcanic fumarole and from burning coal seams. Both materials have cubic symmetry with $a = 19.788$ to 19.859Å. The crystal structure, common to both, consists of a rigid three-dimensional framework of edge- and corner-sharing $Al(OH,H_2O)_6$ octahedra that contains large interconnected cavities where loosely held Cl, OH, and H_2O are located. The fact that Cl is loosely held within the structure is demonstrated by a dramatic reduction in Cl content after washing the material in distilled water, while the structural integrity is maintained. Herein, cadwaladerite is confirmed as a valid mineral species and lesukite is discredited because the only difference between the two materials is the loosely held extra-framework Cl, OH, and H_2O. Cadwaladerite, $Al_2(H_2O)(OH)_4{\cdot}n(Cl,OH,H_2O)$ ($Z = 48$) takes precedence over lesukite based on the date of description. Material similar to cadwaladerite is found as a corrosion product on some types of nuclear fuel elements and is also closely related to the molecular species used in antiperspirant and water filtration.

Keywords: cadwaladerite, lesukite, crystal structure, aluminum chlorohydrate, nuclear fuel corrosion, new mineral, FTIR, Raman.

Introduction

Cadwaladerite was discovered in 1938 in a small epithermal sulfate outcrop at Cerro (*sic*) Pintados, in the El Tamarugal Province, Chile (Gordon 1941). Gordon (1941) gave the mineral formula of cadwaladerite as $Al(OH)_2Cl{\cdot}4H_2O$. The International Mineralogical Association's Commission on New Minerals, Nomencla-

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[§] *Corresponding author e-mail address*: peterson@queensu.ca ture and Classification (IMA-CNMNC) has previously listed the status of cadwaladerite as questionable/doubtful. Material from the type locality and matching the description of cadwaladerite in Gordon (1941) was collected in 2015 and was initially identified as lesukite based on X-ray diffraction analysis and comparison with ICDD data. Lesukite was first described in 1997 (Vergasova *et al*. 1997) from the site of the Tolbachik fissure eruption (55° 50′ N 160° 20′ E) on the Kamchatka Peninsula, Russia, which lasted from 1975 to 1976. The mineral formula was given by Vergasova *et al*. (1997) as $Al_2(OH)_5Cl\cdot 2H_2O$.

In order to explore, in detail, the relationship of cadwaladerite and lesukite, five samples were examined. These are: (1) recently collected samples from the Chilean epithermal deposit location of Cerros Pintados; (2) the type material of cadwaladerite described in Gordon (1941); (3) material from the Barranca del Sulfato, Chile; (4) material from the Maria mine, Chile; and (5) material from the type locality of the Tolbachik fissure locality in Russia. Efforts to obtain deposited type material for lesukite were unsuccessful.

Aluminum chlorohydrate is used extensively in cosmetics as an antiperspirant (Darbre 2005), as a flocculating agent in water purification systems (Bratby 2006), and as a catalyst in the petroleum refining industry. The antiperspirant mechanism is thought to involve the interaction of $Al_2(OH)_5Cl\cdot 2H_2O$ with perspiration to block sweat ducts (Teagarden *et al*. 1981). In water filtration, the aluminum chlorohydrate molecules are thought to cause flocculation because the net positive charge or "basicity" of the molecules attracts other material from solution and then the larger assemblage settles more readily. Material similar to lesukite has been identified as a corrosion product on UAl_x-Al fuel rods used in research reactors that have been exposed to $MgCl_2$ brines to simulate alteration by possible brines associated with salt-based long-term repositories (Klinkenberg *et al*. 2014).

Location Descriptions

The type locality of cadwaladerite is the Cerros Pintados locality (20° 37′ 27″ S 69° 38′ 45″ W), which is adjacent to the nitrate fields within Pampa del Tamarugal, Tamarugal Province, Chile (Rich 1941). The locality is an inactive epithermal hot spring deposit fed by SO_4-rich waters from the intravolcanic basins of the Western Cordillera (Risacher *et al*. 2003). The locality is along a steep hillside, termed "Cerro", separated from the Salar de Pintados by a fault. There are nitrate deposits that have been worked up to the base of the Cerros (see Figure 1 of Gordon 1941). The Cerros Pintados locality is also the type locality for pickeringite, $MgAl_2(SO_4)_4\cdot 22(H_2O)$ (Bandy 1938), tamarugite, $NaAl(SO_4)_2\cdot 6H_2O$ (Bandy 1938), and the discredited "trudellite". Gordon collected the cadwaladerite sample in 1938 from a nearby dump site and the relationship to these other minerals remains unknown (Gordon 1941). The samples collected in 2015 (sample CP2015) were from the cut on the west side of the road seen in Figure 1. Associated minerals are halite, anhydrite, and jarosite.

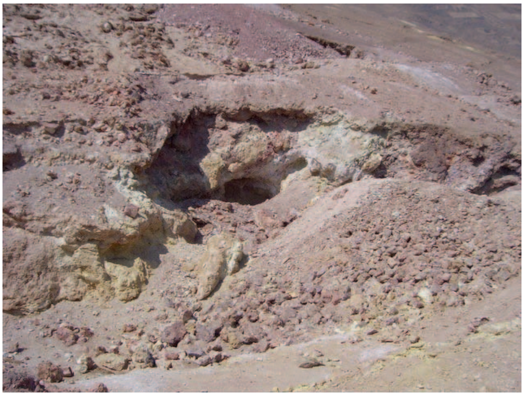

FIG. 1. The type locality of cadwaladerite, which is a small pit on the side of the hill at Cerros Pintados, Chile. The site is protected by The Council of National Monuments of Chile and includes the nearby painted geoglyphs.

"Barranca del Sulfato" is the unofficial name of a small, poorly described epithermal deposit located proximal to the Pacific coast on the Mejillones Peninsula, Antofagasta Province, Chile (23°5′44″S 70°30′54″W). The material studied from this locality (BDS) was collected in 2015.

The Maria mine (18°45′51″S 70°18′15″W) is in the Caleta Vitor district of Arica Province, Chile. Minerals related to cadwaladerite also found at this location are tondiite, atacamite, paratacamite, and anhydrite. Samples used in this study were collected from this locality by Arturo Molina (sample MM).

Lesukite was first described in 1997 (Vergasova *et al*. 1997) from the site of the Tolbachik fissure eruption (55°50′N 160°20′E) on the Kamchatka Peninsula, Russia. The mineral grains are found as accumulations in hot (50–300 °C) ash and lava within zones of metasomatic transformation (Vergasova *et al*. 1997). Lesukite is associated with menyailovite, chlorartinite, pauflerite, sofiite, and halite at the first cone of the northern breakout, along the Tolbachik fissure; see Vergasova & Filatov (2012) for a summary of the complex mineralogy of these fissures. Lesukite has also been identified from burning coal seems in Germany (Witzke 1997), Poland (Kruszewski 2012),

FIG. 2. Cadwaladerite and lesukite images. (a) the sample of cadwaladerite described in Gordon (1941) from the Harvard museum. (b) Type specimen of lesukite from the Tolbachik fissure, Russia (Photo by A.A. EBCEEB). (c) Cadwaladerite collected in 2015 from Cerros Pintados (CP2015) (FOV 30 cm) with a sample of associated columnar halite. (d) Maria mine sample from which the crystal used to determine the crystal structure was taken (MM) (FOV 3 mm).

and the Czech Republic (Zacek & Ondrus 2000), as well as at a Sb-Hg deposit in Kyrgyzstan (Belousov 2002). Powder X-ray diffraction data for synthetic lesukite were reported by Belton (1980).

PHYSICAL AND OPTICAL PROPERTIES

Figure 2 shows the various samples studied. The type sample of cadwaladerite from Cerros Pintados (Harvard Museum 134143) was described by Gordon (1941) as lemon-yellow and transparent to translucent. It occurs within masses of colorless granular and columnar halite crystals. Gordon (1941) observed halite as the only associated mineral. Cadwaladerite was described by Gordon (1941) as amorphous, although no X-ray diffraction measurements are reported, and the material is optically isotropic with a refractive index of n = 1.513 (variable). Gordon (1941) made no mention of crystal habit, but we observed small euhedral crystals with cubic habit in

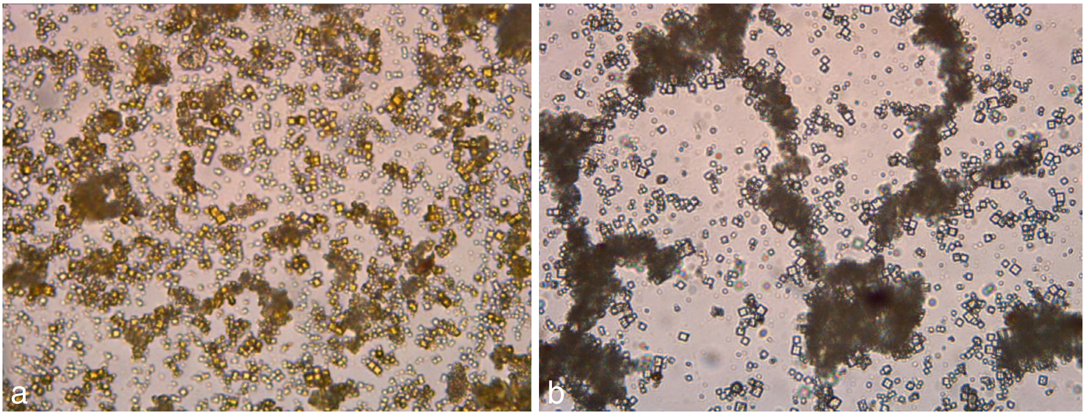

FIG. 3. Cubic crystals of the Cerros Pintados 2015 cadwaladerite viewed in plane polarized light. (a) Crystals are yellow on initial immersion in distilled water. (b) After being washed twice with deionized water the crystals become clear. Field of view is 200 μm.

this sample with the SEM. Frondel & Fleischer (1942) speculated that upon further investigation cadwaladerite "will prove to be crystalline".

Gordon (1941) described the material as lemon-yellow, however, we described the type material obtained from the Harvard museum (sample 134143) as pale yellow, similar to the pale-yellow material from Barranca del Sulfato. The samples of lesukite from Russia, from Cerros Pintados (CP2015), and from the Maria mine are all lemon-yellow in color.

The refractive indices for the CP2015 material were determined to be 1.55 in white light at 20 °C by oil immersion technique. Gordon (1941) described the refractive index of cadwaladerite to be 1.513, Vergasova *et al*. (1997) found the refractive index for lesukite from Kamchatka to be 1.53–1.55, and Witzke (1997) reported the material from Germany to have a refractive index of 1.563. Figure 3 shows the CP2015 crystals immersed in water in transmitted light. After washing in deionized water, the color of the crystals changes from yellow to almost colorless and the refractive index decreases from 1.55 to 1.53. This reduction in refractive index is consistent with the loss of Cl from within the crystal structure when the material is washed, and this is supported by EDS analysis (see below).

SEM ANALYSIS AND CHEMICAL COMPOSITION

The chemical compositions of cadwaladerite and lesukite are difficult to determine accurately. These minerals always occur as very small crystals in limited amounts and are intimately mixed with other minerals. Both contain significant amounts of hydroxyl and/or water and suffer from rapid damage under an electron beam. The chemical formula of cadwaladerite calculated from wet-chemical analysis by Gordon (1941) was $Al(OH)_2Cl{\cdot}4H_2O$. The chemical formula of lesukite determined by wet-chemical analysis was given as $Al_2(OH)_5Cl{\cdot}2H_2O$ by Vergasova *et al*. (1997). Lesukite is described as being soluble in warm, dilute acids (Vergasova *et al*. 1997). Our attempts to measure the chemical composition of the CP2015 sample by wet-chemical methods were not successful because, when left in aqua regia for 5 hr at 90 °C, the sample did not completely dissolve. Microbeam analyses of all materials were performed at Queen's University using a JEOL JXA-8230 electron microprobe. The carbon-coated material was analyzed using EDS analysis *via* the JEOL PC-SEM software. Accelerating potential was 10 kV and the beam was defocused to minimize mineral damage. Replicate analyses were performed in order to assess changes in the Al to Cl ratio over time. All the samples (including the type material with crystals <2 μm) showed cubic morphology (Fig. 4). Only the sample from the Maria mine had crystals large enough for single-crystal X-ray diffraction analysis. No significant amounts of elements other than Al and Cl were observed. The ratio of Al to Cl for all the samples was determined using a standardless approach to the analysis of the EDS spectra. Although the determination of the absolute amount of Al and Cl is based on a series of assumptions, the analysis is quite sensitive to changes in the relative amounts of the two elements. Table 1 shows the amount of measured Cl based on two Al atoms per formula unit. The previously recognized cadwaladerite formula, $Al_2(OH)_4Cl_2{\cdot}8H_2O$, has two Cl atoms per two Al atoms, while the previously recognized lesukite formula, $Al_2(OH)_5Cl{\cdot}2H_2O$, has one Cl atom per two

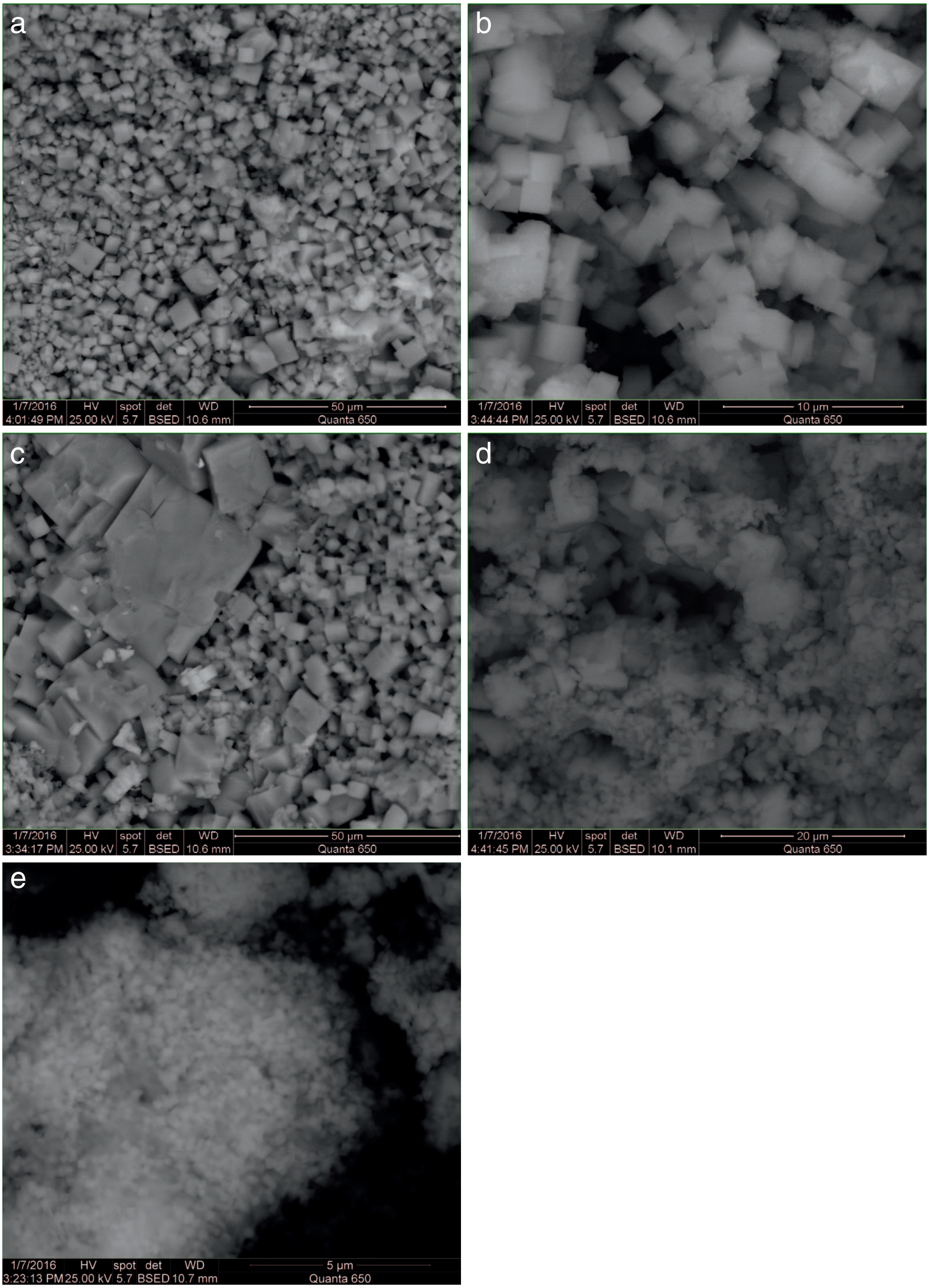

FIG. 4. SEM backscattered electron images of the samples studied. The Maria mine sample showed the largest crystals and the crystal selected for diffraction experiments was taken from this sample. Other samples are seen to be composed of small (<5 µm) cubic crystals. (a) BDS. (b) CP2015. (c) Maria mine. (d) Lesukite from Tolbachik Fissure. (e) 1938 sample described in Gordon (1941).

TABLE 1. NUMBER OF CHLORINE ATOMS PER FORMULA UNIT BASED ON TWO ALUMINUM ATOMS PER FORMULA UNIT

	Cadwaladerite type material	Lesukite	Cerro Pintados 2015 sample 1	Cerro Pintados 2015 sample 2	Cerro Pintados 2015 sample 1 washed
	1.16	1.78	1.56	1.22	1.05
	1.24	2.16	1.43	1.05	1.01
	1.06	1.75	1.49	1.32	0.82
	0.98	1.88	1.59	-	-
	1.27	1.61	1.59	-	-
Average	1.14(11)	1.84(18)	1.53(6)	1.19(11)	0.96(10)

Lesukite has recognised formula $Al_2(OH)_5Cl{\cdot}2H_2O$ with a ratio of Al:Cl of 2:1. Cadwaladerite has the recognised formula $Al(OH)_2Cl{\cdot}4H_2O$ with an Al:Cl ratio of 1:1. The cadwaladerite type material is observed to have an Al:Cl ratio consistent with the lesukite formula and *vice versa*. Material collected from the type locality in 2015 exhibits intermediate Al:Cl ratios. All materials studied have essentially the same powder diffraction spectra.

Al atoms in the formula unit. In Table 1, we show that the sample of lesukite from the Russian locality has significant more Cl than expected for the Al:Cl ratio of 2:1 predicted by the previously recognized formula of Vergasova *et al*. (1997), while the type sample of cadwaladerite has significantly less Cl than predicted by the previously recognized formula of Gordon (1941), which has an Al:Cl ratio of 1:1. We also determined that the ratio of Al to Cl is variable among closely associated samples collected at Cerros Pintados in 2015. We observed that the Cl content of the Cerros Pintados material decreases significantly if the sample is washed in fresh water. All lesukite and cadwaladerite materials studied have the same powder diffraction spectra. All of these observations are consistent with all of these samples having the same crystal structure in which large interconnected cavities formed by Al-containing octahedra contain various amounts of Cl^-, OH^-, and H_2O.

Looking carefully at how Vergasova *et al*. (1997) arrived at the formula for lesukite, it is clear that there is significantly more Cl per Al than predicted by their $Al_2(OH)_5Cl{\cdot}2H_2O$ formula. Vergasova *et al*. (1997) apparently lowered the Cl content in the reported formula calculated from wet-chemical analysis to account for other halides, assumed to be present,

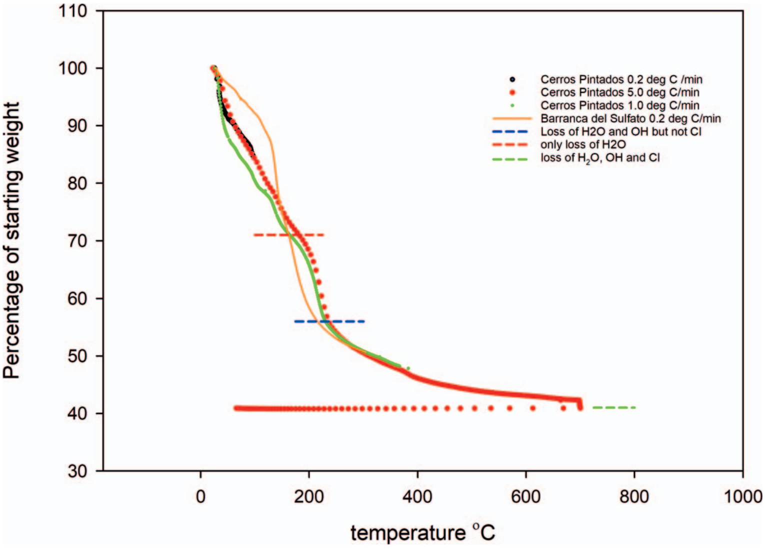

FIG. 5. Weight loss on heating for samples from Cerros Pintados and Barranca del Sulfato. Weight loss begins immediately at the start of heating and the total weight loss for each of the experiments approaches 59% for all samples studied. This weight loss is consistent with the structurally determined formula of $Al_2(H_2O)(OH)_4{\cdot}2Cl{\cdot}5H_2O$ dehydrating to Al_2O_3 by 700 °C. Other possible amounts and ratios of Cl to H_2O will give similar weight losses.

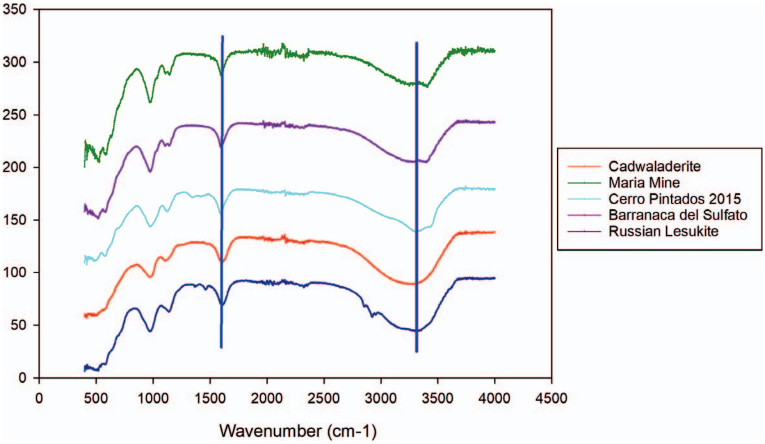

FIG. 6. Infrared absorption spectra of the samples studied. The blue lines at 3400 and 1600 cm^{-1} highlight the absorption features resulting from the bending of H_2O groups. Similar spectra were found for all five locations. The larger broad trough at 3400 cm^{-1} in spectra of the Russian lesukite and cadwaladerite samples may represent a slightly higher degree of hydration.

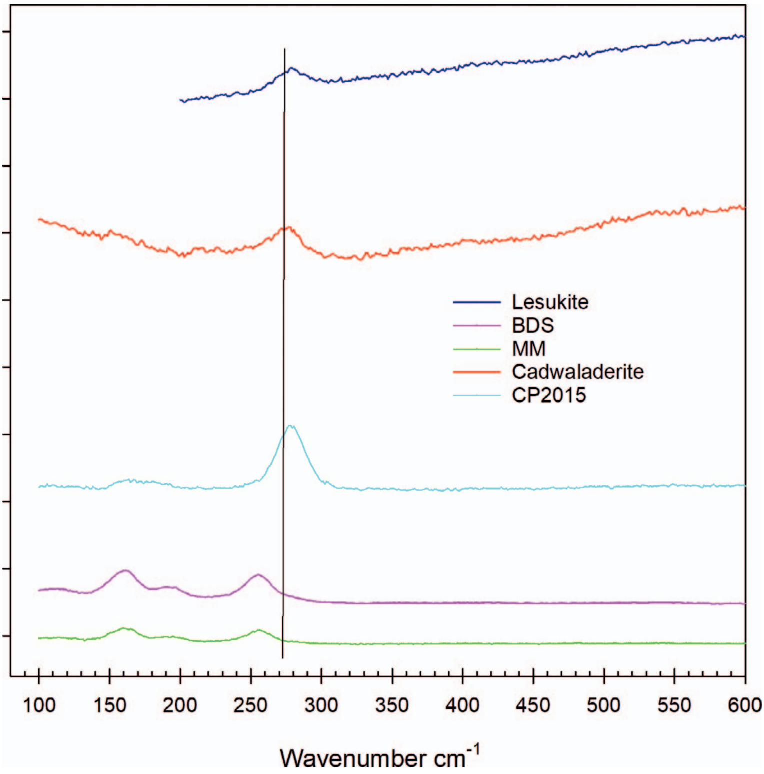

FIG. 7. Raman spectra for samples from all five localities. The black line shows the alignment of peaks at ∼275 cm^{-1} for lesukite, cadwaladerite (Harvard sample #134143), and the CP2015 material. The Raman spectra measured from the Maria mine and Barranca del Sulfato samples have peaks at ∼260, 191, and 160 cm^{-1}.

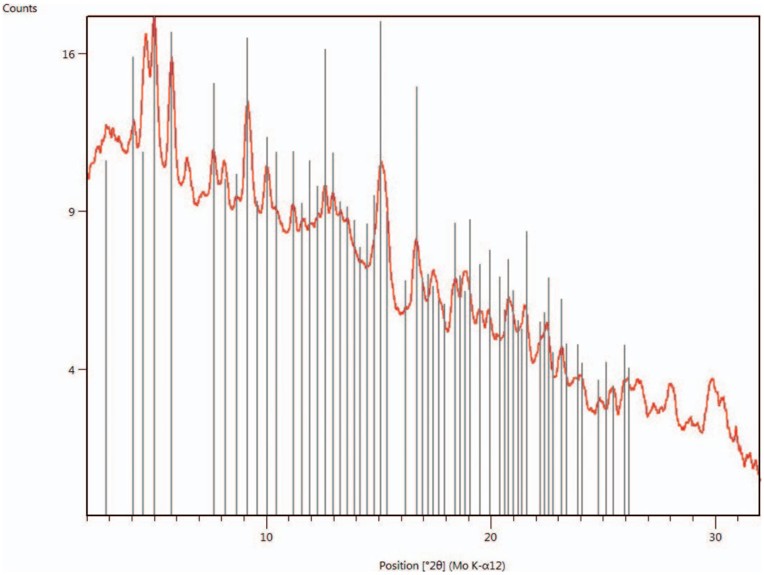

FIG. 8. Powder XRD pattern obtained from the type specimen of cadwaladerite collected by Gordon in 1938 (Harvard sample #134143) with the peak positions of lesukite ICDD 50-1640 Witzke (1997) overlain as vertical lines. All peaks are accounted for except the peaks at ~6.59° 2Θ and perhaps a weak peak at 7.21° 2Θ.

based on the presence of Mg, Ca, Na, and K in the bulk chemical analysis. However, they mentioned the presence of Si in the analysis and attribute this to the admixture of ash. The silica content was ignored, but not the other elements that would also be present in the basic magnesium basalt ash. Vergasova *et al.* (1997) removed the Cl from the lesukite formula that would be associated with NaCl, $MgCl_2$, $CaCl_2$, and KCl. All Al in the analysis was attributed to lesukite with no contribution from the ash. If all the Cl in the analysis of Vergasova *et al.* (1997) is attributed to lesukite, the ratio of Al:Cl based on 2 Al *pfu* is 1.86. We determined this ratio to be 1.84 for lesukite by microprobe analysis. The tendency to assume the ratio of Al:Cl of 2:1 given by Vergasova *et al.* (1997) may result from the JCPDS 31-0006 record, which gives the same unit cell and diffraction pattern, and provides the formula for the synthetic material as $Al_2(OH)_5Cl{\cdot}2H_2O$ (Belton 1980).

THERMO-GRAVIMETRIC ANALYSIS

Samples of CP2015 and BDS material were studied by thermogravimetric analysis using a Shimadzu TGA-50 thermo-gravimetric analyzer. Experiments studying CP2015 material were conducted at various heating rates. The results of the experiment are presented in Figure 5, which shows that weight loss

TABLE 2. COMPARISON OF MEASURED UNIT CELL DIMENSIONS

Sample	Where/how was cell dimension was measured	Cell dimension
Lesukite	Queen's University using Co-tube diffractometer (λ = 1.79 Å)	19.788 Å
BDS (2015)	Queen's University using Co-tube diffractometer (λ = 1.79 Å)	19.841 Å
CP (2015)	Canadian Light Source in Saskatchewan Synchrotron data using λ = 0.688Å	19.8495 Å
CP (2015)	Queen's University using Co-tube diffractometer (λ = 1.79 Å) Calculated using Rietveld analysis	19.842 Å
Maria Mine	Los Angeles County Museum Mo-tube diffractometer (λ = 0.709 Å) Single-crystal X-ray diffraction analysis	19.840(12) Å
Cadwaladerite (Gordon 1941)	Los Angeles County Museum Mo-tube diffractometer (λ = 0.709 Å) Calculated using Rietveld analysis of Gandolfi data	19.859 Å

TABLE 3. COMPARISON OF POWDER DIFFRACTION PATTERNS

			ICDD 50-1640	Witzke (1997)	ICDD 31-0006	Belton (1980)	ICDD 50-1656	Vergasova *et al.* (1997)	cadwaladerite type material #134143	
h	*k*	*l*	*d* (Å)	*I* (rel)	*d* (Å)	*I* (rel)	*d* (Å)	*I* (rel)	*d* (Å)	*I* (rel)
1	1	0	14.19	3					13.96	5
2	0	0	9.99	38	9.925	95	9.94	20	9.98	10
			9.04	5					8.76	80
2	1	1	8.13	100	8.093	100	8.11	70	8.1	100
2	2	0	7.03	52	6.997	5	7.03	50	7.03	60
2	2	2			5.716	19				
3	2	1	5.31	38	5.292	70	5.32	30	5.33	20
4	0	0	4.97	7					5.01	20
4	1	1	4.682	9	4.665	15	4.71	10	4.69	5
4	2	0	4.442	57	4.426	65	4.47	60	4.43	50
3	3	2	4.243	3	4.222	12	4.26	10	4.23	2
4	2	2	4.052	23	4.043	15	4.04	20	4.08	20
5	1	0	3.896	20	3.882	31	3.9	20	3.92	5
5	2	1	3.628	22	3.614	50	3.63	20	3.64	10
4	4	0	3.512	7	3.498	4	3.52	10	3.49	5
5	3	0	3.408	19	3.395	25	3.44	20	3.38	5
6	0	0	3.312	12	3.299	25	3.32	20	3.29	5
6	1	1	3.221	59	3.211	85	3.23	70	3.23	10
6	2	0	3.138	23	3.129	54	3.12	20	3.14	8
5	4	1	3.064	10	3.054	10	3.07	20	3.05	5
6	2	2	2.99	10	2.983	6	2.99	10	3	5
6	3	1	2.927	8						
4	4	4	2.871	3	2.857	4				
5	5	0	2.811	10	2.8	16				
6	4	0	2.753	19	2.7445	20	2.755	20		
7	2	1	2.701	81	2.6932	75	2.706	100	2.69	80
6	4	2	2.652	18	2.6449	25	2.658	30		
7	3	2	2.519	6	2.514	7	2.522	20		
8	0	0			2.4741	9				
8	1	1	2.442	61	2.4359	100	2.446	80	2.44	50
8	2	0	2.406	7	2.3999	30	2.408	20		
6	5	3	2.37	8	2.3651	14	2.388	20		
8	2	2	2.34	6	2.3327	13	2.349	10	2.33	20
7	5	0	2.306	4	2.3004	11				
6	6	2	2.274	4	2.2704	5				
7	5	2			2.2412	4				
8	4	0	2.218	21	2.2122	30	2.224	10	2.21	20
9	1	0	2.192	9	2.1851	9				
8	4	2	2.166	6						

Note: Witzke (1997) material from a burning coal seam in Germany. Belton (1980) synthetic material produce by Dow Chemical Company. Vergasova *et al.* (1997) lesukite from Kamchatka, Russia. Cadwaladerite from the type specimen from Cerros Pintados, Chile.

begins immediately on the start of heating and that the total weight loss for each of the experiments approaches 59% for all samples studied. This weight loss is consistent with the structurally derived formula of $Al_2(H_2O)(OH)_4 \cdot 2Cl \cdot 5H_2O$ ($Z = 48$) dehydrating to Al_2O_3 by 700 °C, but other amounts and ratios of Cl, OH, and H_2O will give similar weight loss.

Infrared Spectroscopy

The infrared spectra were recorded with a Nicolet Avatar 320 FTIR spectrometer using 32 scans over the range of 4000 to 400 cm^{-1} with 4 cm^{-1} resolution. The absorption intensities (Fig. 6) were normalized to the BDS material trough at ~980 cm^{-1} in order to compare samples. The blue arrows at 3400 and 1600

TABLE 4. DATA COLLECTION AND ATOMIC STRUCTURE REFINEMENT DETAILS

Diffractometer	Bruker D8 three-circle; multilayer optics: Apex-II CCD
X-ray source	Mo*K*α (λ = 0.71073 Å)
Temperature	293(2) K
Structural formula	$Al_2(H_2O)(OH)_4 \cdot n(Cl,OH,H_2O)$
Space group	$I2_13$
Unit cell	19.840(12)
V	7810(14)
Z	48
Absorption coefficient (mu)	1.262
F(000)	6936
Crystal size	6 × 6 × 5 μm
Θ	3.247 to 25.242
Index range	$-23 \leq h \leq 21$, $-23 \leq k \leq 13$, $-10 \leq l \leq 22$
Reflections collected/unique	4327/1967 $R_{int} = 0.0937$
Reflections with $I > 2\sigma I$	1323
Refinement method	Full matrix least-squares on F^2
Parameters / restraints	112/0
GoF	1.085
Final R indices $I > 2\sigma I$	$R_1 = 0.129$, $wR_2 = 0.286$
R indices (all data)	$R_1 = 0.175$, $wR_2 = 0.315$

$R_{int} = \sum|F_o^2 - F_o^2(\text{mean})| / \sum[F_o^2]$. GoF = $S = \{\sum[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$. $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum(w(F_o^2)^2]\}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where a is 0.0497 and b is 17.2583 and P is $[2 F_c^2 + \text{Max}(F_o^2,0)] / 3$.

TABLE 5. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS

	x	*y*	*z*	U_{eq}
Al1	0.6289(5)	0.1688(4)	0.7105(4)	0.021(1)
Al2	0.7520(5)	0.2480(5)	0.7480(5)	0.018(2)
Al3	0.5	0.25	0.6282(6)	0.020(2)
Al4	0.6692(5)	0.2889(5)	0.6286(4)	0.028(2)
Al5	0.75	0.3726(7)	0.5	0.029(3)
Cl1	0.4638(6)	0.6015(5)	0.5454(6)	0.074(3)
Cl2	0.5278(8)	0.357(2)	0.4284(9)	0.27(2)
Cl3	0.4990(4)	0.4990(4)	0.4990(4)	0.041(2)
O1	0.659(1)	0.192(1)	0.619(1)	0.031(5)
O2	0.6983(8)	0.3763(8)	0.6547(8)	0.016(4)
O3	0.655(1)	0.264(1)	0.722(1)	0.034(5)
O4	0.7314(9)	0.1581(8)	0.7354(8)	0.017(4)
O5	0.8060(9)	0.374(1)	0.578(1)	0.025(4)
O6	0.540(1)	0.191(1)	0.697(1)	0.034(5)
O7	0.5778(9)	0.3050(9)	0.6241(9)	0.021(4)
O8	0.530(1)	0.195(1)	0.554(1)	0.036(5)
O9	0.6967(8)	0.3086(8)	0.5422(8)	0.014(3)
O10	0.6945(9)	0.444(1)	0.539(1)	0.025(4)
O11	0.564(2)	0.354(2)	0.779(2)	0.08(1)
O12	0.776(10)	0.086(10)	0.615(1)	0.032(4)
O13	0.626(2)	0.454(2)	0.766(3)	0.16(2)
O14	0.792(2)	0.064(2)	0.648(2)	0.074(9)

The Cl and O11, O12, O13, and O14 sites are located in the extra-framework cavities.

cm^{-1} highlight the absorption features resulting from the bending of H_2O groups. Similar spectra were found for all five samples. Minor peaks found at ~2800 cm^{-1} for the Russian lesukite are indicative of a hydrocarbon influence, which is likely a result of minor contamination.

RAMAN SPECTROSCOPY

Raman spectra presented in Figure 7 were measured with a LabRAM ARAMIS instrument. Samples were studied using a laser with a wavelength of 532 nm (yellow-green), an aperture of 400 μm, a 100 μm slit, and a grating of 1200 working under 10× magnification. The scans were conducted using an accumulation number of 2 for all samples except the Russian lesukite (accumulation number of 4). The Russian lesukite also required photo-bleaching for 5 s in order to increase the response produced from the laser. The spectra are similar for lesukite, cadwaladerite type material, and CP2015, which all show the major peak at ~270 cm^{-1}. The strongest lines for material from the Maria mine and BDS are shifted slightly to ~260 cm^{-1}.

X-RAY DIFFRACTION STUDIES

Vergasova *et al*. (1997) observed lesukite to be optically isotropic and the powder diffraction spectra measured by them using a Debye-Scherrer camera is consistent with space group *Im*3*m* (229) and *a* = 19.814 to 19.878 Å. No X-ray diffraction measurements of cadwaladerite were made by Gordon (1941). In the course of our study, an X-ray diffraction study was conducted on a sample of cadwaladerite studied by Gordon (1941) and deposited at the Harvard Mineralogical Museum (sample #134143). The pattern was recorded using a Rigaku R-Axis Rapid II curved imaging plate micro-diffractometer with monochromatized Mo*K*α radiation using Gandolfi-like motion on the φ and ω axes to randomize the sample. The pattern obtained closely matches the diffraction pattern ICDD

TABLE 6. BOND LENGTHS (Å) AND BOND VALENCE SUMMATION VALUES (BVS) CALCULATED USING THE PARAMETERS OF BROWN & ALTERMATT (1985)

Al1	O1	1.96(2)		Al4	O1	1.90(2)	
Al1	O2	1.83(2)		Al4	O2	1.90(2)	
Al1	O3	1.97(2)		Al4	O3	1.95(2)	
Al1	O4	2.10(2)		Al4	O4	2.02(2)	
Al1	O5	1.83(2)		Al4	O7	1.84(2)	
Al1	O6	1.84(2)		Al4	O9	1.84(2)	
average		1.92		average		1.91	
Al2	O3	2.00(2)	×3	Al5	O5	1.85(2)	×2
Al2	O4	1.85(2)	×3	Al5	O9	1.91(2)	×2
average		1.93		Al5	O10	1.97(2)	×2
Al3	O6	1.97(2)	×2	average		1.91	
Al3	O7	1.89(2)	×2				
Al3	O8	1.92(2)	×2	BVS	O1	0.94	
		1.93			O2	1.13	
					O3	1.26	
BVS	Al1	2.99			O4	1.25	
	Al2	2.92			O5	1.20	
	Al3	2.85			O6	1.02	
	Al4	3.03			O7	1.12	
	Al5	3.00			O8	0.48	
					O9	1.09	
					O10	0.42	

50-1640 of the material measured by Witzke (1997) (Fig. 8).

Table 2 compares the cell dimensions of the materials of the present study and the cell dimensions published for lesukite. The cell dimensions of this cubic material vary from 19.788 to 19.859 Å. The *d*-values and relative intensities (Table 3) of three published reference spectra of lesukite are compared to the measured powder diffraction spectra of the cadwaladerite type specimen from Cerros Pintados collected by Gordon in 1938. The material described by Witzke (1997) was collected from a burning coal seam in Saxony, Germany. The Belton (1980) powder diffraction data for lesukite was measured from a synthetic material created by the Dow Chemical Company in 1980. The Vergasova *et al.* (1997) powder diffraction data are taken from the new mineral description of lesukite from the Tolbachik Fissure eruption. All the diffraction data are very similar.

SINGLE-CRYSTAL DIFFRACTION

Single-crystal X-ray diffraction data using the material from the Maria mine was obtained and the crystal structure was solved and refined in the acentric space group $I2_13$ (199). Tables 4, 5, and 6 list the experimental conditions, atom coordinates, displacement parameters, and bond lengths. The CIF has been deposited[1]. The Al atoms are coordinated by OH or H_2O groups to form octahedra, and these octahedra are linked by edge- and corner-sharing to form a rigid three-dimensional framework with large interconnected cavities (Fig. 9). The anions at the O3 and O4 sites are each bonded to three Al atoms and at the O1, O2, O5, O6, O7, and O9 sites are each bonded to two Al atoms. These are all assumed to be OH molecules. Anions at the O8 and O10 positions are each bonded to one Al atom and are assumed to be H_2O molecules. Table 6 lists the bond-valence summation calculated using the parameters of Brown & Altermatt (1985). Hydrogen positions were not determined. The electron density within the cavities was modelled using a combination of O and Cl, but the location and occupancies of these extra-framework sites are poorly constrained.

Seichter *et al.* (1998) described the structure of $Al_{13}(OH)_{24}(H_2O)_{24}Cl_{15}\cdot 13H_2O$ in which discreet clusters have the composition $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$ (Fig. 10). Chlorine and H_2O groups are located between the clusters and serve to bind the structure together. In the structure of cadwaladerite, these clusters are linked in three dimensions by corner

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[1] Supplementary Data are available from the Depository of Unpublished data on the MAC website (http://mineralogical association.ca/), document "Cadwaladerite, CM57, 19-00040".

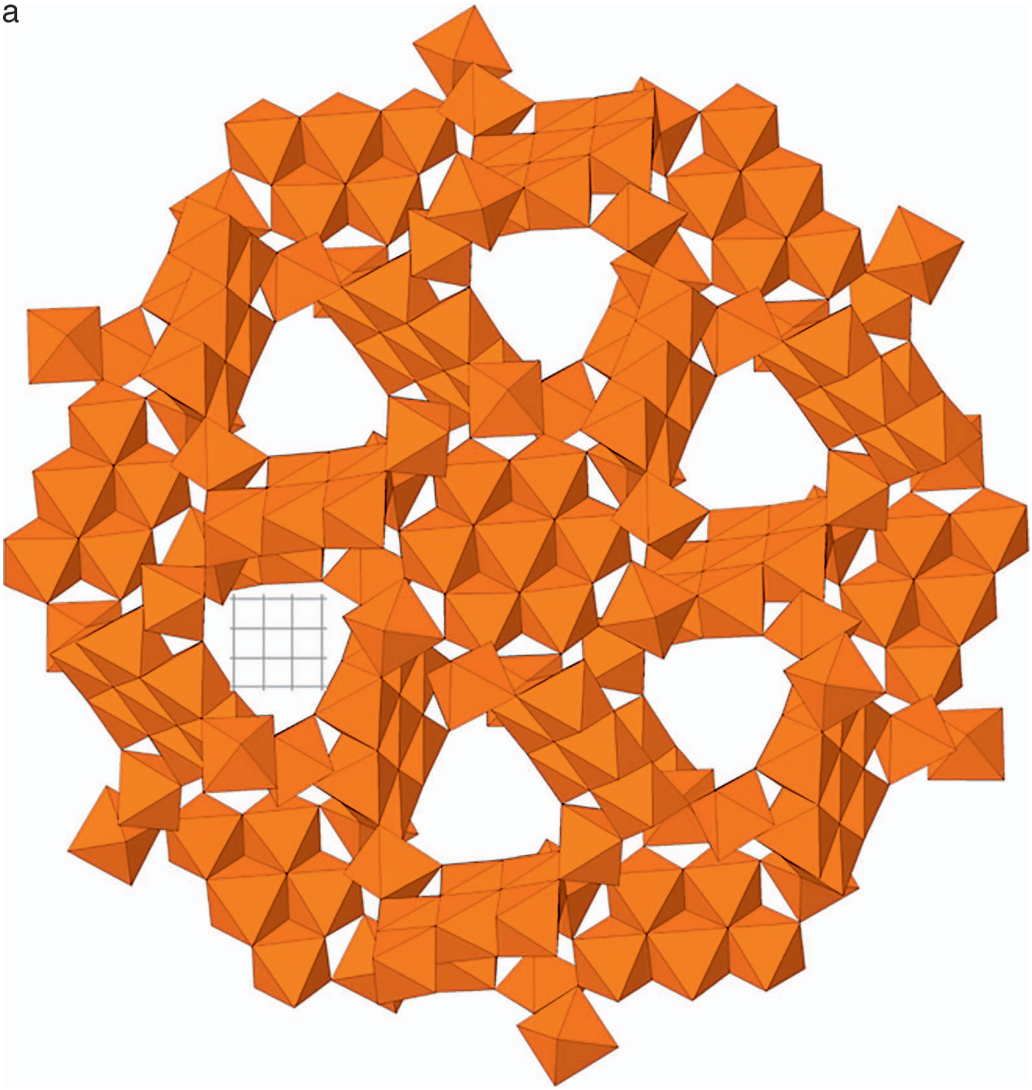

FIG. 9. The structure of cadwaladerite consists of a framework formed by corner-sharing and edge-sharing $Al(O,OH)_6$ octahedra. Viewed looking down (a) [111] and (b) [100] (see next page). Varying amounts of H_2O and Cl occupy the large extra-framework cavities and are not shown. Chlorine is readily exchanged with the surrounding fluid, as seen by the reduction of the Cl content of the solid after washing in distilled water. The grid dimension is 1 × 1 Å. Chlorine has an ionic radius of 1.67 Å and moves easily through these channels.

sharing to form an open structure with cavities, where the Cl, OH, and H_2O are located. The composition of the framework is $Al_{10}O_{25}$. Considering octahedral linkages and bond-valence summations (Table 6), there are H_2O groups and OH groups. The resulting formula $Al_2(H_2O)(OH)_4$ is a three-dimensional framework with a net positive charge. Cl^-, OH^-, and H_2O contained in the cavities may be in the form of hypochlorous acid (HOCl) or hypochlorite (ClO^-), depending on the pH.

CONCLUSIONS

The material collected by Gordon in 1938 and named cadwaladerite (Gordon 1941) produces an X-ray powder diffraction pattern that is the same as the material described by Vergasova *et al.* (1997) and

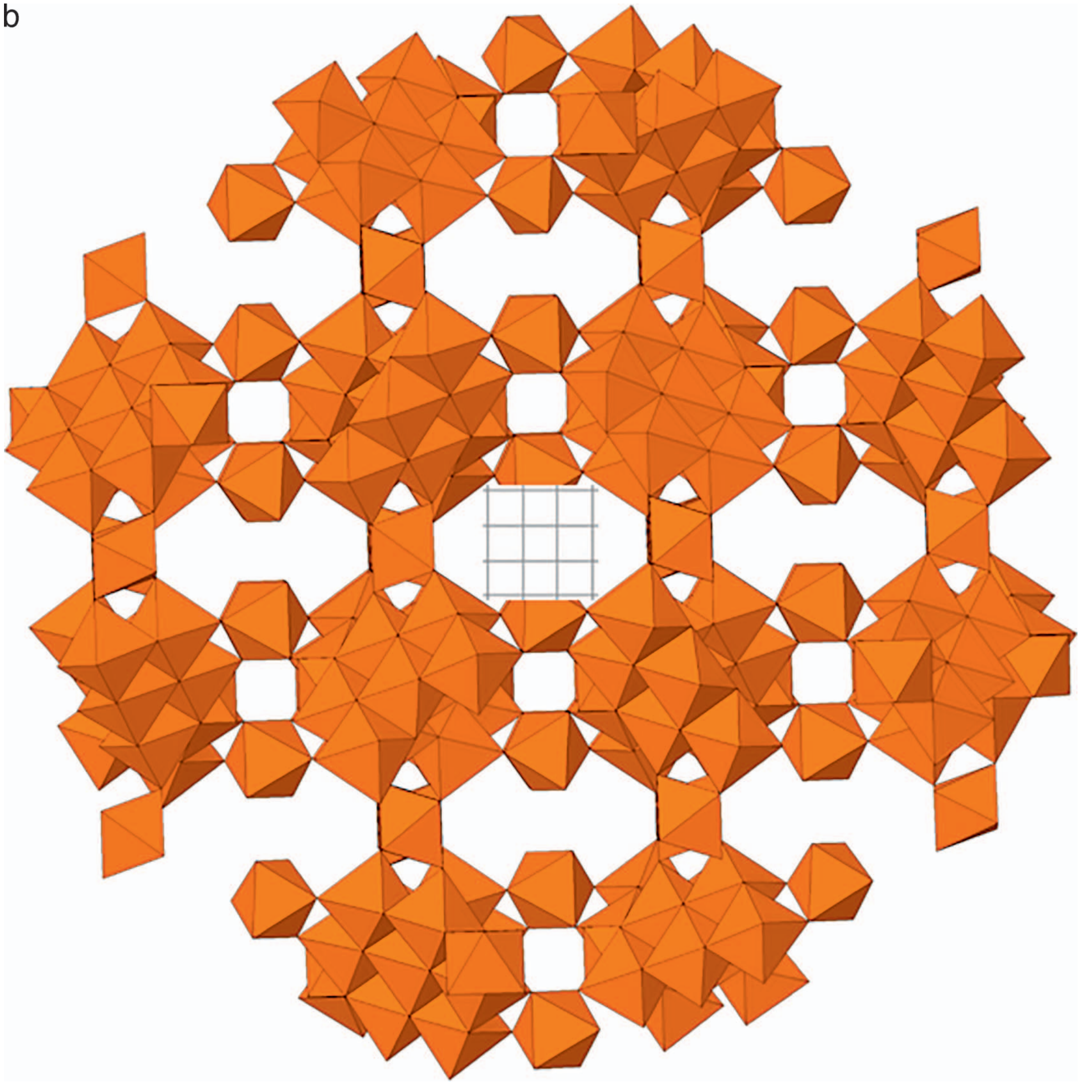

FIG. 9. (continued)

named lesukite. The crystal structure, determined by studying material from the Maria mine with the same powder diffraction pattern and physical properties, is an open-framework structure created by edge- and corner-sharing Al(OH,H_2O)$_6$ octahedra. Cl, OH, and H_2O are loosely held within this open framework, which leads to Cl and H_2O loss during TGA and SEM analysis. The variable Al:Cl ratio is a result of the Cl being easily exchanged within the open cavities. The loss of Cl after washing the sample in water with no change in the powder diffraction pattern shows the octahedral framework to be stable and to allow exchange of the extra-framework anions. This stable framework may prove valuable in industrial or agricultural applications, in the same way as zeolite minerals.

Cadwaladerite versus lesukite

Lesukite and cadwaladerite have the same crystal structure which is composed of edge- and corner-sharing Al-centered octahedra. The difference between the two described materials is the amount of exchangeable Cl and H_2O that are included within the open cavities in the mineral structure. Chlorine and H_2O may be exchanged with no change in the

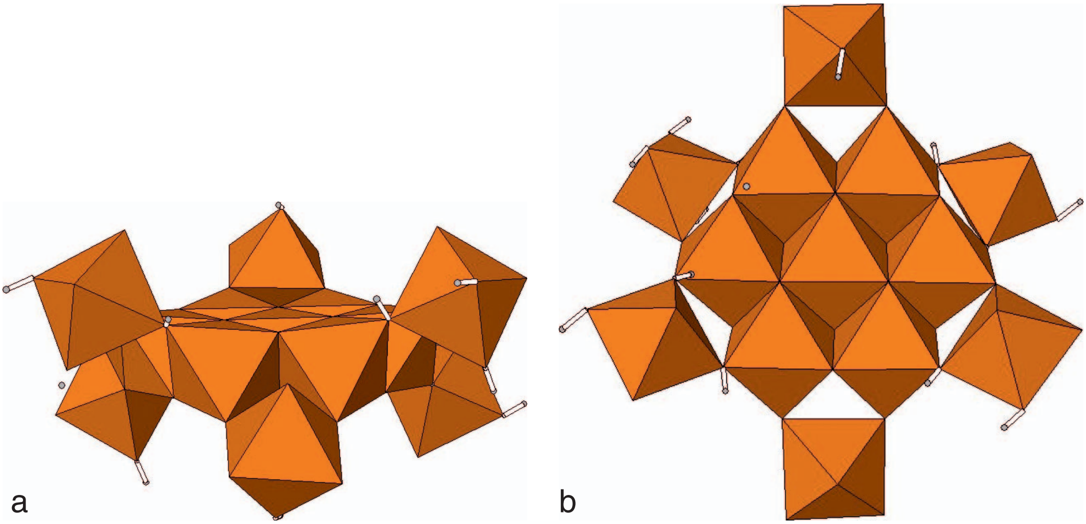

FIG. 10. Seichter *et al.* (1998) describe the structure of $Al_{13}(OH)_{24}(H_2O)_{24}]Cl_{15}\cdot 13H_2O$ in which discreet clusters have the composition $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$ and are held together by Cl and H_2O. These clusters share corners in cadwaladerite to form an open framework.

framework of Al-centered octahedra. By analogy with the rules for defining zeolite minerals (Coombs *et al.* 1997), cadwaladerite and lesukite are the same mineral species because they contain the same dominant extra-framework ionic entity (Cl) and because varying amounts of extra-framework H_2O are not considered species-determining. Cadwaladerite has historical precedence and is recognized as a valid mineral species while lesukite is discredited. Furthermore, the formula of cadwaladerite is redefined as $Al_2(H_2O)(OH)_4\cdot n(Cl,OH,H_2O)$. The foregoing has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (proposal 18-H).

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