The Canadian Mineralogist
Vol. 38, pp. 1457-1466 (2000)

ADAMSITE-(Y), A NEW SODIUM–YTTRIUM CARBONATE MINERAL SPECIES FROM MONT SAINT-HILAIRE, QUEBEC

JOEL D. GRICE[§] and ROBERT A. GAULT

Research Division, Canadian Museum of Nature, P.O. Box 3443, Station D, Ottawa, Ontario K1P 6P4, Canada

ANDREW C. ROBERTS

Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8, Canada

MARK A. COOPER

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

ABSTRACT

Adamsite-(Y), ideally $NaY(CO_3)_2•6H_2O$, is a newly identified mineral from the Poudrette quarry, Mont Saint-Hilaire, Quebec. It occurs as groups of colorless to white and pale pink, rarely pale purple, flat, acicular to fibrous crystals. These crystals are up to 2.5 cm in length and form spherical radiating aggregates. Associated minerals include aegirine, albite, analcime, ancylite-(Ce), calcite, catapleiite, dawsonite, donnayite-(Y), elpidite, epididymite, eudialyte, eudidymite, fluorite, franconite, gaidonnayite, galena, genthelvite, gmelinite, gonnardite, horváthite-(Y), kupletskite, leifite, microcline, molybdenite, narsarsukite, natrolite, nenadkevichite, petersenite-(Ce), polylithionite, pyrochlore, quartz, rhodochrosite, rutile, sabinaite, sérandite, siderite, sphalerite, thomasclarkite-(Y), zircon and an unidentified Na–*REE* carbonate (UK 91). The transparent to translucent mineral has a vitreous to pearly luster and a white streak. It is soft (Mohs hardness 3) and brittle with perfect {001} and good {100} and {010} cleavages. Adamsite-(Y) is biaxial positive, $\alpha = 1.480(4)$, $\beta = 1.498(2)$, $\gamma = 1.571(4)$, $2V_{\text{meas.}} = 53(3)°$, $2V_{\text{calc.}} = 55°$ and is nonpleochroic. Optical orientation: $X = [001]$, $Y = b$, $Z \wedge a = 14°$ (in β obtuse). It is triclinic, space group $P1$, with unit-cell parameters refined from powder data: a 6.262(2), b 13.047(6), c 13.220(5) Å, α 91.17(4), β 103.70(4), γ 89.99(4)°, V 1049.1(5) $Å^3$ and $Z = 4$. The strongest six X-ray powder-diffraction lines [d in Å(I)(hkl)] are: 12.81(100)(001), 6.45(70)(002), 4.456(60)(121,120), 4.291(60)(003), 2.571(60)(005, 043) and 2.050(50)(125,126). Electron-microprobe and thermogravimetric analyses, supported by crystal-structure analysis and infrared-absorption spectroscopy, yield Na_2O 8.64, CaO 0.05, Y_2O_3 22.88, Ce_2O_3 0.37, Nd_2O_3 1.41, Sm_2O_3 1.02, Gd_2O_3 1.92, Tb_2O_3 0.56, Dy_2O_3 3.28, Ho_2O_3 0.90, Er_2O_3 2.83, Tm_2O_3 0.27, Yb_2O_3 1.04, CO_2 25.10, H_2O 29.90, total 100.17 wt.%. The empirical formula, based on 12 oxygen atoms, is $Na_{1.00}(Y_{0.72}Dy_{0.06}Er_{0.05}Gd_{0.04}Nd_{0.03}Yb_{0.02}Sm_{0.02}Ho_{0.02}Ce_{0.01}Tb_{0.01}Tm_{0.01})_{\Sigma 0.99}C_{2.04}H_{11.87}O_{12}$. The calculated density (from the empirical formula) is 2.27 g/cm^3, and the measured density is 2.27(2) g/cm^3. The structure has been refined to $R = 0.046$. The structure is layered, with two different carbonate groups, one parallel and one perpendicular to the layering. Slabs of $[NaY(CO_3)]$ are separated by $[H_2O]$ layers. Adjacent $[H_2O]$ layers are only H-bonded together, which gives rise to the perfect {001} cleavage. The mineral is named after Frank Dawson Adams (1859–1942), geologist and professor at McGill University, Montreal.

Keywords: adamsite-(Y), new mineral species, sodium yttrium dicarbonate hexahydrate, crystal structure, Mont Saint-Hilaire, Quebec.

SOMMAIRE

La nouvelle espèce minérale adamsite-(Y), de composition idéale $NaY(CO_3)_2•6H_2O$, a été découverte à la carrière Poudrette, au mont Saint-Hilaire, Québec. Elle se présente en groupes de cristaux incolores, blancs ou rose pâle, et plus rarement violacés, plats et aciculaires ou fibreux. Ces cristaux atteignent 2.5 cm en longueur et forment des agrégats fibroradiés. Lui sont associés aegyrine, albite, analcime, ancylite-(Ce), calcite, catapleiite, dawsonite, donnayite-(Y), elpidite, epididymite, eudialyte, eudidymite, fluorite, franconite, gaidonnayite, galène, genthelvite, gmelinite, gonnardite, horváthite-(Y), kupletskite, leifite, microcline, molybdénite, narsarsukite, natrolite, nenadkevichite, petersenite-(Ce), polylithionite, pyrochlore, quartz, rhodochrosite, rutile, sabinaïte, sérandite, sidérite, sphalérite, thomasclarkite-(Y), zircon et un carbonate à Na–*REE* non encore identifié (UK 91). Le minéral est transparent à translucide et possède un éclat vitreux à nacré et une rayure blanche. Il s'agit d'un minéral mou (dureté de Mohs de 3) et cassant, ayant un clivage {001} parfait et des clivages {100} et {010} assez bons.

[§] *E-mail address*: jgrice@mus-nature.ca

L'adamsite-(Y) est biaxe positive, α = 1.480(4), β = 1.498(2), γ = 1.571(4), 2$V_{mes.}$ = 53(3)°, 2$V_{calc.}$ = 55°, et non pléochroïque. Son orientation optique est: *X* = [001], *Y* = *b*, *Z* ∧ *a* = 14° (dans l'angle β obtus). Le minéral est triclinique, groupe spatial *P*1, avec une maille élémentaire affinée à partir des données obtenues sur poudre: *a* 6.262(2), *b* 13.047(6), *c* 13.220(5) Å, α 91.17(4), β 103.70(4), γ 89.99(4)°, *V* 1049.1(5) Å^3 et *Z* = 4. Les six raies les plus intenses du spectre de diffraction X [*d* en Å(*I*)(*hkl*)] sont: 12.81(100)(001), 6.45(70)(002), 4.456(60)(121,120), 4.291(60)(003), 2.571(60)(005, 043) et 2.050(50)(125,126). Les analyses obtenues par microsonde électronique et par thermogravimétrie, supplémentées par une ébauche de la structure cristalline et un spectre d'absorption dans l'infra-rouge, mène à la composition Na_2O 8.64, CaO 0.05, Y_2O_3 22.88, Ce_2O_3 0.37, Nd_2O_3 1.41, Sm_2O_3 1.02, Gd_2O_3 1.92, Tb_2O_3 0.56, Dy_2O_3 3.28, Ho_2O_3 0.90, Er_2O_3 2.83, Tm_2O_3 0.27, Yb_2O_3 1.04, CO_2 25.10, H_2O 29.90, pour un total de 100.17% (poids). La formule empirique, fondée sur une base de 12 atomes d'oxygène, est $Na_{1.00}(Y_{0.72}Dy_{0.06}Er_{0.05}Gd_{0.04}Nd_{0.03}Yb_{0.02}Sm_{0.02}Ho_{0.02}Ce_{0.01}Tb_{0.01}Tm_{0.01})_{\Sigma 0.99}C_{2.04}H_{11.87}O_{12}$. La densité calculée (à partir de la formule empirique) est 2.27 g/cm^3, et la densité mesurée est 2.27(2) g/cm^3. La structure a été affinée jusqu'à un résidu *R* de 0.046. L'adamsite-(Y) est un minéral en couches ayant deux groupes de carbonate distincts, un parallèle aux couches et l'autre perpendiculaire. Les couches de composition $[NaY(CO_3)]$ sont séparées par des couches de $[H_2O]$. Les couches adjacentes de $[H_2O]$ ne sont interliées que par liaisons hydrogènes, ce qui rend compte du clivage {001} parfait. Le minéral honore Frank Dawson Adams (1859–1942), géologue et professeur à l'Université McGill.

(Traduit par la Rédaction)

Mots-clés: adamsite-(Y), nouvelle espèce minérale, bicarbonate de sodium et yttrium hexahydraté, structure cristalline, mont Saint-Hilaire, Québec.

INTRODUCTION

The new mineral species described herein, adamsite-(Y), is the latest in a series of new carbonate minerals recently described from the Poudrette quarry, Mont Saint-Hilaire, Rouville County, Quebec. Fifty-seven carbonate species are known to occur at Mont Saint-Hilaire, many of them containing essential Na and rare-earth elements (*REE*) (Grice & Gault 1998). To date, a total of 333 mineral species have been identified from this locality, a well-known source of rare and exotic minerals (Horváth & Gault 1990).

Adamsite-(Y) was initially recognized as being a new species in 1992 by Dr. G.Y. Chao, Carleton University, on material submitted by a private collector, Gilles Haineault, and was designated as UK 96. In 1998, more material was found, but the chemical and X-ray data were not compared with those of the initial find, and the mineral from this second find was designated UK 106. It has since been determined that these two minerals are identical. Another mineral with similar chemical composition, similar appearance, and found in the same environment as adamsite-(Y), has been designated as UK 91. This material is more finely fibrous than adamsite-(Y), however, and has a significantly different X-ray powder-diffraction pattern.

Adamsite-(Y) is named in honor of Frank Dawson Adams (1859–1942), geologist and professor at McGill University, Montreal. After graduating in chemistry and mineralogy from McGill University, he joined the Geological Survey of Canada in 1879 as "lithologist" and chemist. He studied the new science of petrography at Heidelberg, Germany in 1881 and went on to become the Survey's leading specialist in the study of crystalline rocks. In 1889, he was appointed Logan Professor of Geology at McGill University, where he continued his studies on Precambrian rocks, particularly those of the Laurentian and Grenville regions of Quebec and Ontario. It was during this period that he studied the Cretaceous igneous rocks of the Monteregian Hills, of which Mont Saint-Hilaire is a member, and was the first to describe this group of hills as the Monteregian Hills petrographic province (Adams 1903). As well, he served as president of the Geological Society of America and the Canadian Mining Institute.

The new mineral and mineral name were approved by the Commission on New Minerals and Mineral Names, IMA. Cotype material is housed in the collection of the Canadian Museum of Nature under catalogue numbers CMNMC 82939 and CMNMC 82940.

OCCURRENCE

Adamsite-(Y) occurs as a late-stage, low-temperature hydrothermal phase within cavities in a large alkaline pegmatite dike, informally designated the Poudrette dike, exposed in the southern corner of the Poudrette quarry. The quarry, in turn, is situated on the northeastern flank of Mont Saint-Hilaire, one of a series of plutons aligned along the St. Lawrence Valley for almost 150 km eastward from Oka to Megantic, in the province of Quebec. The pegmatite dike, which pinches and swells from 2 to 4 m across, has been exposed on levels 6, 7, 8 and 9 of the quarry. Five new Na- and *REE*-bearing carbonate mineral species have been described from this dike: lukechangite-(Ce), horváthite-(Y), reederite-(Y), thomasclarkite-(Y) and adamsite-(Y), the subject of this paper. Minerals found in that portion of the dike in which adamsite-(Y) was discovered include aegirine, albite, analcime, ancylite-(Ce), calcite, catapleiite, dawsonite, donnayite-(Y), elpidite, epididymite, eudialyte, eudidymite, fluorite, franconite, gaidonnayite, galena, genthelvite, gmelinite, gonnardite, horváthite-(Y), kupletskite, leifite, microcline, molybdenite, narsarsuk-

FIG. 1. Photograph of adamsite-(Y). Photograph by Harry Taylor. The National History Museum, London, specimen number BM 1998, 172. Scale bar: 1 cm.

ite, natrolite, nenadkevichite, petersenite-(Ce), polylithionite, pyrochlore, quartz, rhodochrosite, rutile, sabinaite, sérandite, siderite, sphalerite, thomasclarkite–(Y), zircon and an unidentified Na–*REE*–carbonate (UK 91). We discuss the genesis of adamsite-(Y) later in this paper.

Physical and Optical Properties

Adamsite-(Y) occurs as flat, acicular to fibrous crystals, up to 2.5 cm in length. They typically form spherical groups of radiating crystals, and rarely form reticulated groups (Fig. 1). The mineral is elongate on [001] and flat on (001). Forms observed are the pinacoids {010} and {001}. It is colorless to white, occasionally pale pink, and rarely pale purple. It is transparent to translucent with a vitreous and occasionally pearly luster, and a white streak. It is brittle with perfect {001} and good {100} and {010} cleavages. Adamsite-(Y) is relatively soft (Mohs hardness 3) and does not fluoresce in either long- or short-wave ultraviolet light. The density, measured by suspension in a solution of bromoform and butyl alcohol, is 2.27(2) g/cm^3, which compares very well to the density of 2.27 g/cm^3 calculated for the empirical formula.

Adamsite-(Y) is biaxial positive, α 1.480(4), β 1.498(2), γ 1.571(4); $2V_{meas.} = 53(3)°$, $2V_{calc.} = 55°$, (for $\lambda = 590$ nm). The optical orientation is $X = [001]$, $Y = b$, $Z \wedge a = 14°$ (in β obtuse). It is nonpleochroic. A Gladstone–Dale calculation gives a compatibility index of –0.009, which is regarded as superior (Mandarino 1981).

Chemical Composition

Chemical analyses were done in wavelength-dispersion (WD) mode on a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. Data reduction was done with a PAP routine in XMAQNT (pers. commun., C. Davidson, CSIRO). The analysis of adamsite-(Y) by electron microprobe was problematic because of decrepitation of the sample and the lifting of the carbon coating due to dehydration under prolonged vacuum. The decrepitation results from the weak H-bonding linking adjacent H_2O groups in the structure. To minimize this effect, calibration of the standards was performed first, and the samples were later introduced into the specimen chamber and analyzed immediately. This method, along with adoption of a rather large diameter of the beam, 50 μm, limited Na migration, volatilization and general burn-up of the sample. The operating voltage of the electron probe was 15 kV, and the beam current was 20 nA. Data for all elements in the samples were collected for 25 s or 0.50% precision, whichever was attained first. A 100 s energy-dispersion scan indicated no elements with $Z > 8$ other than those reported here. Seven analyses were performed on three crystals. The presence of CO_2 and H_2O was confirmed by infrared-absorption spectroscopy, and their concentrations were established by thermogravimetric analysis (TGA). As only one-half of the CO_2 was evolved during TGA, the amount given below consists of two summed portions, one measured (the gas evolved, 12.9 wt.%) and the other, the ideal amount determined by crystal-structure analysis (non-evolved during heating, 12.2 wt.%).

The following standards were used in the electron-microprobe analyses: albite (Na*K*α), calcite (Ca*K*α), synthetic yttrium iron garnet (YIG) (Y*K*α), and a set of synthetic *REE* phosphates (Ce*L*α, Nd*L*α, Sm*L*α, Gd*L*α, Tb*L*α, Dy*L*β, Ho*L*α, Er*L*α, Tm*L*α, Yb*L*α). La, Pr and Eu were sought but not detected. Lu was detected in trace amounts. Data for standards were collected for 50 s or 0.25% precision, whichever was attained first. The *REE* raw data were corrected for overlaps. The chemical composition is Na_2O 8.64, CaO 0.05, Y_2O_3 22.88, Ce_2O_3 0.37, Nd_2O_3 1.41, Sm_2O_3 1.02, Gd_2O_3 1.92, Tb_2O_3 0.56, Dy_2O_3 3.28, Ho_2O_3 0.90, Er_2O_3 2.83, Tm_2O_3 0.27, Yb_2O_3 1.04, CO_2 25.10, H_2O 29.90, total 100.17 wt.%. The empirical formula, based on 12 atoms of oxygen, is $Na_{1.00}(Y_{0.72}Dy_{0.06}Er_{0.05}Gd_{0.04}Nd_{0.03}Yb_{0.02}Sm_{0.02}Ho_{0.02}Ce_{0.01}Tb_{0.01}Tm_{0.01})_{\Sigma 0.99}C_{2.04}H_{11.87}O_{12}$. This simplifies to the ideal formula $NaY(CO_3)_2{\bullet}6H_2O$.

Adamsite-(Y) readily dissolves with strong effervescence in 10% HCl and decrepitates owing to dehydration in acetone (rapid) and alcohol (slow).

Thermogravimetric and Differential Thermal Analysis

Two differential thermogravimetric analyses (DTG) of adamsite-(Y) were done using a Mettler–Toledo TA8000 system (software version 3.0), which uses a Mettler TG50 module linked to a Mettler M3 microbalance. The purge gas was dry nitrogen, with a flow rate of 200 mL/min. Two samples of pure material, weighing 10.196 and 10.847 mg, respectively, were each ground to a fine powder and heated from room temperature to 1000°C at a rate of 5°C/min. The weight losses of 4.334 mg (42.5 wt.%) and 4.670 mg (43.1 wt.%) occurred in two major steps (DTG, Fig. 2): between 80 and 270°C, 27.0 wt.% on average and between 380 and 590°C, 15.8 wt.% on average. The interpretation of the DTG scan is given in Table 1. The first weight-loss step is interpreted as the loss of 10 (H_2O) groups, which ideally should be 25.0 wt.%, making the measured value a

TABLE 1. ADAMSITE-(Y): DTG and DTA INTERPRETATION

STEP	PRODUCT	T°C INTERVAL	WT.% OBS	WT.% CALC	STRUCTURE GROUP
	$Na_2Y_2(CO_3)_4{\bullet}12H_2O$	20 – 80	0.0	0.0	
1a	$Na_2Y_2(CO_3)_4{\bullet}4H_2O$	80 – 120	23.0	20.0	OW17 – OW24
1b	$Na_2Y_2(CO_3)_4{\bullet}2H_2O$	120 – 270	4.0	5.0	OW13, OW15
2a	$Na_2Y_2(CO_3)_4$	380 – 480	2.9	5.0	OW14, OW16
2b	$Na_2Y_2O_2(CO_3)_3$	480 – 540	7.0	6.1	C4 or C2 + O_2
2c	$Na_2Y_2O_4(CO_3)_2$	540 – 590	5.9	6.1	C2 or C4 + O_2
TOTAL		20 – 1000	42.8	42.2	$12(H_2O) + 2(CO_2)$

little high. The second weight-loss step is interpreted as the loss of two additional (H_2O) groups plus the break-up of one of the $(CO_3)^{2-}$ anions and its loss as CO_2 (Mochizuki *et al.* 1974). Ideally, this second weight-loss step should be 12.2 wt.%, making the observed value of 12.9 wt.% a little high. Mochizuki *et al.* (1974) discussed their DTG and differential thermal analysis (DTA) results on synthetic double carbonates similar in composition to adamsite-(Y). The TGA and DTA curves they presented are very similar to those of adamsite-(Y). They proposed that the final product after heating is a *REE* oxycarbonate, *e.g.*, $YNaO(CO_3)$. Although the final product after heating was X-rayed, we found no suitable match to any compound listed in the Powder Diffraction File (PDF), including $NaYO_2$ (PDF 32–1203). It is well established that the production of sodium peroxide, Na_2O_2, takes place at temperatures below 500°C (Cotton & Wilkinson 1980). Thus an alternative explanation is that Na acts as a reducing agent for the entire system and evolves CO, not CO_2, and that the final product is a peroxide, $NaYO_4$. Although two possible end-products of heating have been postulated, there is a preference for the *REE* oxycarbonate based on a chemical test with HCl that produced effervescence.

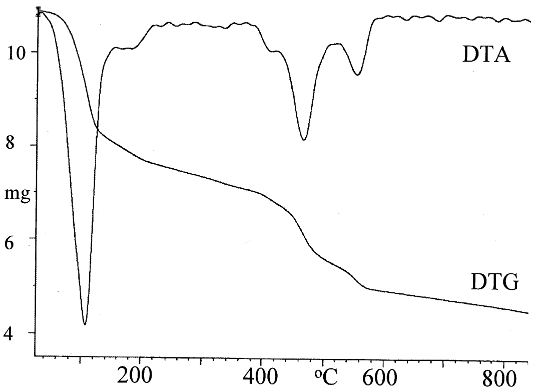

FIG. 2. Differential thermogravimetric analysis (DTG) and differential thermal analysis (DTA) of adamsite-(Y).

The differential thermal analysis curve (DTA, Fig. 2) reveals one smooth endothermic peak for the initial loss in H_2O, followed by a distinct shoulder that corresponds to almost 25% of the weight percent loss in H_2O. This weight loss would be the H_2O groups more strongly bonded to both Na and Y (OW13 and OW15; see below), whereas the other H_2O groups are bonded to Na only (OW17, OW18, OW19, OW20, OW21, OW22, OW23 and OW24). The second weight-loss is trimodal on the DTA curve and is due to the difference in energy required to drive off two additional H_2O groups (OW14 and OW16) and the two less strongly bonded $(CO_3)^{2-}$ groups.

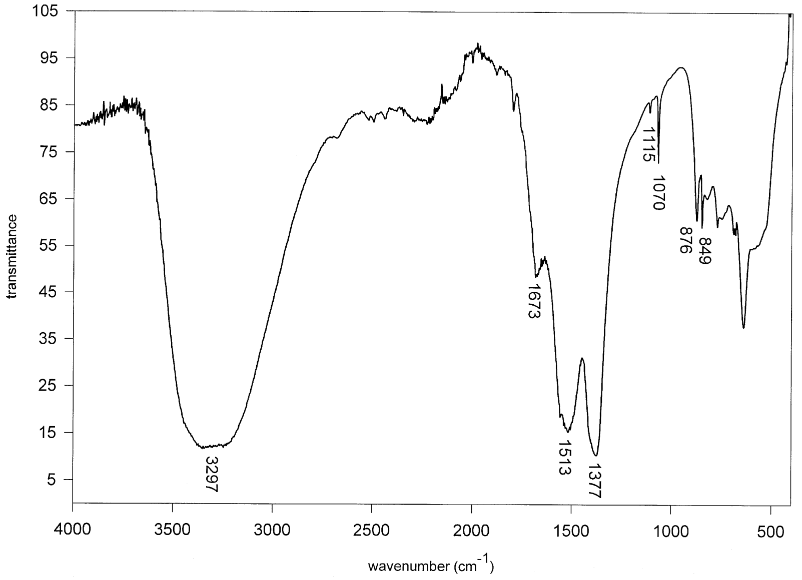

FIG. 3. Infrared-absorption spectrum of adamsite-(Y).

INFRARED SPECTROSCOPY

The infrared-absorption spectrum of adamsite-(Y) (Fig. 3) was obtained using a Bomem Michelson MB–120 Fourier-transform infrared spectrometer equipped with a diamond-anvil cell as a microsampling device. The dominant absorption band is that of the O–H stretching mode (3297 cm^{-1}). The (H_2O) bending band (1673 cm^{-1}) forms a shoulder on the large, split, asymmetric stretching band for $(CO_3)^{2-}$. This splitting (1513 and 1377 cm^{-1}) is explained by the fact that the carbonate groups are very distorted, with distinctly differing C–O bond lengths, as seen in the crystal-structure determination. For this same reason, the $(CO_3)^{2-}$ symmetric band is also split (1115 and 1070 cm^{-1}). The weak intensity of this symmetric band is due to the limited ability of the $(CO_3)^{2-}$ group to undergo this type of stretching mode. The 876 and 849 cm^{-1} bands may be due to out-of-plane bending of $(CO_3)^{2-}$. The remainder of the spectra could not be unequivocally assigned. This infrared-absorption spectrum is very similar in appearance to that of thomasclarkite-(Y) (Grice & Gault 1998). In thomasclarkite-(Y), the splitting of the carbonate peaks is due to the presence of the $(HCO_3)^-$ anion, whereas in adamsite-(Y), the splitting of the carbonate peaks is due to the influence of H-bonding.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

Precession single-crystal photographs initially showed adamsite-(Y) to be pseudo-orthorhombic, with diffraction symmetry *mmm*. These crystals are twinned by reflection on {001}; subsequent more precise work on single crystals using a four-circle diffractometer indicated triclinic symmetry, but metrically close to monoclinic. Much of the problem with the early single-crystal work was the failure to realize that this mineral reacts with the binding agent, amyl acetate, causing dehydration and subsequent almost complete decrepitation of the crystal. This decrepitation reaction was exacerbated by intense X-radiation; crystals subjected to this treatment developed a crazed appearance. The crystal used for the final data-collection was mounted on a glass fiber with non-reacting epoxy. X-ray powder-diffraction data, obtained with a Debye–Scherrer camera having a diameter of 114.6 mm and using Cu*K*α radiation, are given in Table 2. Whereas neither variation in intensity nor shifting of *d*-values was noted in the X-ray powder patterns during this study, other researchers have noted some variability in the patterns, possibly indicating that adamsite-(Y) may not be stable under minor fluctuations in humidity levels (pers. commun., A.M. McDonald, Laurentian Univ.). Indexing the powder data was difficult owing to the previously mentioned pseudosymmetry, but the process was successful with the aid of powder-pattern intensities calculated from the results of the crystal-structure analysis.

In the final stage of data collection, a crystal fragment of adamsite-(Y), measuring 160 × 180 × 40 μm for [100] × [010] × [001], was mounted on a CCD-equipped Bruker *P*4 fully automated four-circle diffractometer operated at 40 kV and 40 mA. With the CCD detector, almost a full sphere of intensity data was collected out to 2θ = 60° using a 15 s frame time and a crystal-to-detector distance of 4 cm. The lowering of the incident radiation power and the high-speed data collection were in anticipation of potential problems with crystal decrepitation. With these operating conditions,

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR ADAMSITE - (Y)

$I_{est.}$	$d_{(obs.)}$	$d_{(calc.)}$	*hkl*	$I_{est.}$	$d_{(obs.)}$	$d_{(calc.)}$	*hkl*
100	12.81	12.841	001	25	2.010	2.013	$\bar{1}45$
70	6.45	6.421	002			2.010	$\bar{2}\bar{4}4$
5	5.51	5.524	$\bar{1}\bar{1}1$			2.010	$2\bar{4}2$
		5.524	$\bar{1}10$			2.006	$\bar{1}\bar{6}2$
		5.503	110			2.006	$1\bar{6}1$
		5.503	$\bar{1}11$			2.005	$\bar{3}\bar{1}3$
60	4.456	4.460	$\bar{1}\bar{2}1$			2.005	$\bar{3}10$
		4.460	$\bar{1}20$			2.004	$\bar{2}\bar{3}5$
		4.438	120			2.004	$2\bar{5}1$
		4.438	$\bar{1}21$			2.004	$2\bar{3}3$
60	4.291	4.280	003			2.004	$\bar{2}51$
10	4.000	4.019	$\bar{1}\bar{2}2$	20	1.983	1.986	$\bar{2}06$
		4.019	$1\bar{2}1$			1.986	204
		3.971	121			1.986	242
		3.971	$\bar{1}22$			1.986	$\bar{2}44$
5	3.622	3.614	$0\bar{2}3$			1.985	$\bar{2}\bar{5}2$
10	3.548	3.545	023			1.985	$\bar{2}50$
25	3.267	3.261	040			1.983	$\bar{3}\bar{2}2$
20	3.181	3.177	$0\bar{4}1$			1.983	$\bar{3}21$
20	3.140	3.145	041			1.981	$\bar{3}\bar{2}1$
		3.131	$\bar{2}01$			1.981	$\bar{3}22$
15	3.035	3.042	$\bar{2}02$	20	1.920	1.920	$\bar{1}\bar{6}3$
		3.042	200			1.915	$1\bar{6}2$
30	2.869	2.868	$\bar{1}\bar{2}4$			1.915	$\bar{3}\bar{1}4$
		2.868	$1\bar{2}3$			1.894	$3\bar{1}\bar{1}$
		2.857	024	10	1.896	1.894	162
15	2.823	2.828	123			1.878	$\bar{1}63$
		2.828	$\bar{1}24$	3	1.875	1.878	$\bar{3}\bar{3}2$
10	2.759	2.756	$\bar{1}\bar{4}2$			1.876	$\bar{3}31$
		2.751	$\bar{2}22$			1.875	$\bar{3}\bar{3}1$
3	2.722	2.725	$1\bar{4}1$			1.858	$\bar{3}32$
15	2.624	2.621	$0\bar{4}3$	3	1.853	1.858	$\bar{3}\bar{2}4$
60	2.571	2.568	005			1.850	$3\bar{2}1$
		2.568	043			1.850	321
5	2.532	2.527	$\bar{2}04$			1.835	$\bar{3}24$
		2.527	202	10	1.834	1.835	243
10	2.368	2.373	025			1.834	$\bar{2}45$
		2.373	$\bar{2}\bar{3}3$			1.834	007
		2.372	$2\bar{3}1$			1.834	330
		2.366	$2\bar{2}2$			1.834	$\bar{3}33$
5	2.312	2.312	$0\bar{4}4$			1.820	$\bar{1}\bar{4}6$
10	2.257	2.264	044	10	1.819	1.820	$\bar{1}\bar{2}7$
		2.259	$\bar{2}\bar{4}1$			1.818	$1\bar{2}6$
		2.258	$\bar{2}41$			1.818	$0\bar{6}4$
		2.251	$\bar{1}43$			1.817	$\bar{2}\bar{3}6$
10	2.242	2.242	$\bar{2}05$			1.807	$2\bar{3}4$
		2.241	203	20	1.800	1.807	$\bar{1}\bar{6}4$
3	2.196	2.197	$\bar{2}\bar{3}4$			1.807	$1\bar{6}3$
		2.197	$2\bar{3}2$			1.804	$0\bar{4}6$
20	2.141	2.140	$\bar{2}\bar{4}3$			1.804	252
		2.140	006			1.800	$\bar{2}54$
		2.140	$2\bar{4}1$			1.800	$\bar{1}27$
10	2.083	2.087	$\bar{1}\bar{2}6$			1.800	126
		2.086	$1\bar{2}5$			1.800	145
50	2.050	2.062	125			1.800	$\bar{3}\bar{1}5$
		2.062	$\bar{1}26$			1.777	$3\bar{1}2$
		2.055	$\bar{3}\bar{1}2$	10	1.773	1.777	163
		2.055	$\bar{3}11$			1.776	$\bar{1}64$
		2.054	$\bar{3}\bar{1}1$			1.772	$0\bar{2}7$
		2.054	$\bar{3}12$			1.772	046
		2.050	$1\bar{4}4$			1.772	$\bar{3}\bar{3}4$
		2.050	$\bar{1}\bar{6}1$			1.767	$3\bar{3}1$
		2.050	$\bar{1}60$			1.767	$\bar{2}07$
							205

114.6 mm Debye-Scherrer powder camera; Cu radiation, Ni filter (λ Cu-*K*α = 1.54178 Å). Intensities visually estimated; not corrected for shrinkage and no internal standard. All reflections used for unit-cell refinement. Indexed with *a* 6.262(2), *b* 13.047(6), *c* 13.220(5) Å, α 91.17(4)°, β 103.70(4)°, γ 89.99(4)°.

TABLE 3. ADAMSITE-(Y): DATA COLLECTION AND STRUCTURE-REFINEMENT INFORMATION

Space Group:	$P\bar{1}$ (No. 2)	Simplified formula: $NaY(CO_3)_2 \cdot 6H_2O$
Radiation:	Mo$K\alpha$	μ 5.3 mm^{-1}
a 6.2592(4) Å	α 91.130(1)°	Reflections collected 8409
b 13.0838(7) Å	β 103.554(1)°	Unique reflections 5500
c 13.2271(5) Å	γ 90.188(1)°	Observed reflections ($F_o > 5\sigma$) 3338
V 1052.8(1) Å^3	$Z = 4$	$R_{int} = 0.025$
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert) / \Sigma\lvert F_o\rvert = 0.046$		$wR = [\Sigma w(F_o - F_c)^2 / \Sigma w(F_o)^2]^{-} = 0.058$, for $w = 1$

no decrepitation was evident in the final analysis of the intensity standards. Information relevant to the data collection and structure determination is given in Table 3. The three-dimensional data were reduced for Lorentz, polarization, and background effects using the Bruker program SAINT. An empirical plate-absorption correction was done on the basis of 3998 reflections and reduced the merging R of this dataset from 3.45% before the absorption correction to 3.10% after the absorption correction with a glancing angle of 7°.

Phasing of a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 0.862. A calculated sharpened Patterson function for space group $P\bar{1}$ located the two Y sites, the two Na sites and six lighter-element sites. This model refined to $R = 0.22$. Additional O and C sites were added following a series of ΔF synthesis maps, which, in turn, reduced the R index to 0.066. In the final least-squares refinement, all atomic positions were refined with anisotropic-displacement factors to a residual of $R = 0.046$. The addition of an isotropic-extinction factor did not improve the results. Although the $|E^2 - 1|$ statistic is low for centrosymmetric structures, lowering the symmetry to $P1$ did not improve the refinement, nor was there any indication that the lower symmetry suggested a better structural model. Use of the program MISSYM (Le Page 1987) suggests the possible presence of a two-fold axis. The Laue merging for monoclinic symmetry is 6.1%. The metric deviation from monoclinic symmetry is only 0.2°, with a 25.72, b 6.260, c 13.085 Å, α 90.19, β 91.21 and γ 89.87. Essentially the same structure can be refined in $C2/c$ ($R = 0.06$) with four of the six H_2O groups coordinated to the Na site split into two half-occupied sites each. We view the 0.2° metric deviation, the 6.1% Laue merging and the site splitting in $C2/c$ as sufficient evidence to rule out monoclinic symmetry.

Table 4 contains the final positional anisotropic-displacement factors and equivalent isotropic-displacement parameters, and Table 5 contains selected interatomic distances and angles. Observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

TABLE 4. ADAMSITE-(Y): ATOMIC COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS (Å^2 X 10^4)

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Y1	0.3114(1)	0.62581(4)	0.00962(6)	114(3)	151(4)	207(5)	0(3)	44(3)	5(2)	156(2)
Y2	0.8016(1)	0.87428(4)	-0.01011(6)	127(4)	153(4)	213(5)	0(3)	60(3)	-9(2)	161(3)
Na1	0.4232(6)	0.6251(3)	0.3243(4)	312(21)	395(22)	376(29)	11(19)	86(18)	36(16)	360(10)
Na2	0.6022(6)	0.8753(3)	-0.3231(3)	327(21)	360(21)	314(27)	-10(18)	84(18)	16(15)	333(10)
C1	0.240(1)	0.8730(6)	-0.0492(7)	170(38)	179(37)	157(50)	-7(32)	12(33)	-18(28)	173(18)
C2	0.872(1)	0.8738(6)	0.2092(8)	269(45)	165(38)	298(59)	-4(38)	146(41)	-16(31)	231(20)
C3	-0.211(1)	0.6269(6)	0.0466(7)	282(44)	168(38)	154(50)	-22(32)	87(37)	22(31)	195(18)
C4	0.169(1)	0.6262(6)	-0.2115(8)	292(47)	138(37)	303(60)	-16(38)	42(41)	3(32)	249(21)
O1	0.1513(9)	0.7890(4)	-0.0331(5)	265(32)	182(29)	254(38)	4(26)	92(28)	-17(22)	229(14)
O2	0.1217(9)	0.9532(4)	-0.0496(5)	228(30)	159(28)	328(42)	-9(27)	92(27)	42(22)	234(14)
O3	0.4350(9)	0.8794(5)	-0.0622(6)	162(29)	326(34)	329(43)	38(30)	45(27)	17(23)	274(15)
O4	0.0296(8)	0.8604(4)	0.1608(5)	149(28)	257(30)	225(36)	-26(26)	71(24)	-0(21)	206(13)
O5	0.6771(9)	0.8886(4)	0.1516(6)	152(29)	279(32)	336(43)	-5(29)	53(27)	3(23)	256(15)
O6	0.909(1)	0.8711(5)	0.3079(6)	360(38)	447(41)	215(44)	-7(33)	135(31)	-14(29)	330(17)
O7	0.3325(8)	0.4531(4)	-0.0506(5)	136(27)	186(28)	311(40)	8(26)	-15(25)	-32(20)	222(14)
O8	0.6827(9)	0.7133(4)	0.0332(5)	207(30)	191(29)	255(39)	6(26)	44(26)	-6(21)	220(14)
O9	-0.0049(9)	0.6204(5)	0.0612(6)	131(28)	324(34)	366(44)	-35(30)	80(27)	-26(23)	270(15)
O10	0.0300(9)	0.6114(4)	-0.1524(6)	171(29)	256(31)	344(44)	33(29)	75(27)	-13(22)	254(15)
O11	0.3732(9)	0.6395(4)	-0.1602(5)	145(28)	274(31)	214(36)	-14(27)	-15(24)	-3(22)	220(14)
O12	0.111(1)	0.6278(5)	-0.3104(6)	265(35)	430(40)	254(46)	-1(33)	-24(30)	3(28)	330(17)
OW13	0.6736(9)	0.9851(4)	-0.1662(5)	220(31)	259(31)	273(40)	32(28)	-9(27)	-16(24)	261(15)
OW14	0.7168(9)	0.7657(4)	-0.1714(5)	195(29)	216(29)	255(39)	-24(27)	39(26)	8(22)	224(14)
OW15	0.338(1)	0.5153(4)	0.1656(6)	301(34)	221(30)	363(44)	54(29)	161(30)	40(24)	281(15)
OW16	0.3866(9)	0.7340(4)	0.1714(5)	246(32)	238(30)	241(39)	-4(27)	35(27)	-24(23)	245(14)
OW17	0.778(1)	0.5549(5)	0.4006(6)	246(35)	403(39)	451(52)	7(35)	35(32)	14(28)	374(18)
OW18	0.605(1)	0.7928(5)	0.4110(6)	414(42)	431(42)	399(52)	16(36)	158(36)	-32(32)	404(19)
OW19	0.412(1)	0.7126(5)	-0.4058(6)	387(42)	399(40)	404(51)	-22(36)	131(35)	-35(30)	390(18)
OW20	0.898(1)	0.8102(5)	-0.3901(6)	328(39)	412(40)	521(57)	59(38)	184(36)	14(30)	406(19)
OW21	0.238(1)	0.9481(5)	-0.3908(6)	288(37)	382(38)	498(54)	-15(36)	139(34)	-14(28)	382(18)
OW22	0.124(1)	0.6902(5)	0.3876(6)	310(38)	480(43)	436(53)	73(38)	113(34)	-14(31)	404(19)
OW23	0.704(1)	0.5437(5)	0.6008(6)	304(38)	437(42)	503(56)	1(38)	77(34)	-22(30)	418(19)
OW24	0.698(1)	0.0411(5)	-0.4079(6)	279(36)	449(41)	370(48)	13(35)	48(31)	-42(29)	371(18)

TABLE 5. ADAMSITE-(Y): SELECTED BOND LENGTHS(Å) AND ANGLES(°)

	Na polyhedra		
Na1-OW15	2.472(8)	Na2-OW13	2.452(7)
Na1-OW16	2.464(8)	Na2-OW14	2.459(8)
Na1-OW17	2.406(7)	Na2-OW19	2.536(8)
Na1-OW18	2.587(8)	Na2-OW20	2.383(8)
Na1-OW22	2.375(8)	Na2-OW21	2.446(7)
Na1-OW23	2.634(9)	Na2-OW24	2.594(8)
⟨Na1-OW⟩	⟨2.490⟩	⟨Na2-OW⟩	⟨2.478⟩
	Y polyhedra		
Y1-O1	2.383(6)	Y2-O1	2.538(6)
Y1-O7	2.396(6)	Y2-O2	2.419(6)
Y1-O7a	2.407(5)	Y2-O2a	2.387(5)
Y1-O8	2.525(7)	Y2-O3	2.237(6)
Y1-O9	2.241(6)	Y2-O4	2.385(6)
Y1-O10	2.438(7)	Y2-O5	2.446(7)
Y1-O11	2.377(7)	Y2-O8	2.381(6)
Y1-OW15	2.517(7)	Y2-OW13	2.521(6)
Y1-OW16	2.492(6)	Y2-OW14	2.489(6)
⟨Y1-ϕ⟩	⟨2.420⟩	⟨Y2-ϕ⟩	⟨2.423⟩
	Carbonate polyhedra		
C1-O1	1.28(1)	O1-C1-O2	115.7(7)
C1-O2	1.28(1)	O1-C1-O3	123.2(7)
C1-O3	1.27(1)	O2-C1-O3	121.1(7)
⟨C1-O⟩	⟨1.28⟩	⟨O-C1-O⟩	⟨120.0⟩
C2-O4	1.31(1)	O4-C2-O5	116.6(9)
C2-O5	1.29(1)	O4-C2-O6	121.3(8)
C2-O6	1.27(1)	O5-C2-O6	122.1(8)
⟨C2-O⟩	⟨1.29⟩	⟨O-C2-O⟩	⟨120.0⟩
C3-O7	1.30(1)	O7-C3-O8	114.2(7)
C3-O8	1.28(1)	O7-C3-O9	121.4(7)
C3-O9	1.26(1)	O8-C3-O9	124.3(8)
⟨C3-O⟩	⟨1.28⟩	⟨O-C3-O⟩	⟨120.0⟩
C4-O10	1.32(1)	O10-C4-O11	114.4(9)
C4-O11	1.31(1)	O10-C4-O12	123.1(8)
C4-O12	1.27(1)	O11-C3-O12	122.6(9)
⟨C4-O⟩	⟨1.30⟩	⟨O-C4-O⟩	⟨120.0⟩
	H-bonded O's		
O6-OW18	2.79(1)	O12-OW17	2.81(1)
O6-OW21	2.83(1)	O12-OW19	2.74(1)
O6-OW22	2.83(1)	O12-OW20	2.84(1)
O6-OW24	2.74(1)	O12-OW23	2.76(1)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of adamsite-(Y) has four large-cation sites with two distinct polyhedra. The two *Na* sites, each with six-fold coordination, occupy [Na(H_2O)$_6$] polyhedra that may be described as a bifurcated tetragonal pyramid with the Na atom slightly above the square base. This base consists of four H_2O groups, whereas the bifurcated apex has two additional H_2O groups. The nine-fold coordination (seven O atoms and two H_2O groups) around each *Y* site may be described as a monocapped square antiprism. All (CO_3) polyhedra share edges with this (Yϕ_9) polyhedron (ϕ is an unspecified ligand).

The crystal structure of adamsite-(Y) is layered on (001) (Fig. 4). The layering of *REE*-bearing carbonates is described in detail by Grice *et al.* (1994). In adamsite-(Y), there are thick slabs (Fig. 4) composed of a unit of Y atoms and parallel "flat-lying" (CO_3) polyhedra sandwiched between layers of Na(H_2O)$_6$ polyhedra and perpendicular "standing-on-end" (CO_3) polyhedra (Grice *et al.* 1994). These [NaY(CO_3)] slabs are H-bonded together, and it is these H-bonds that give rise to the perfect {001} cleavage and the relatively unstable nature of adamsite-(Y).

Adamsite-(Y), $NaY(CO_3)_2•6H_2O$, and thomasclarkite-(Y), $NaY(HCO_3)(OH)_3•4H_2O$ (Grice & Gault 1998), are found intimately associated with one another at Mont Saint-Hilaire. These two minerals share similarities in chemical composition and crystal structure. In both minerals, there is a distinctive fundamental unit that consists of a stacked, edge-sharing unit of three polyhedra centered by a C, a Y and a Na atom (Fig. 5). Although the two sets of polyhedra differ in coordination number (Y polyhedron) and ligands (OH groups *versus* H_2O groups in both the Na and Y polyhedron), the fundamental building block is essentially the same. In adamsite-(Y), the Na–Y–C tri-polyhedra form planes and have a strong cross-linkage in the (001) plane with the (YO_9) polyhedra, sharing corners and edges and being further reinforced by the "flat-lying" carbonate groups (Fig. 5a). In thomasclarkite-(Y), the Na–Y–C tri-polyhedra share edges, forming single chains parallel to [001] (Fig. 5b).

Genesis of adamsite-(Y)

Adamsite-(Y) occurs as a very late-stage, low temperature, hydrothermal phase within cavities in an alkaline pegmatite dike in the nepheline syenite intrusion. In these cavities, adamsite-(Y) appears to crystallize after rhodochrosite and petersenite-(Ce), is contemporaneous with horváthite-(Y) and donnayite-(Y), and precedes thomasclarkite-(Y), which has been observed as an epitactic growth on adamsite-(Y) (pers. commun., L. Horváth). This sequence of crystallization is indicative of lowering carbonate activity and Lewis basicity. Comparing the formulae of the minerals involved shows a decrease in the ratio of carbonate groups relative to the number of cations plus the other chemical species involved [(H_2O), (OH), F]. The lowering of Lewis basicity is effected by the distribution of the H atoms. As H bonds to O, the basicity decreases; for example, typical Lewis base strengths (valence units) (O'Keeffe & Navrotsky 1981) are: $(CO_3)^{2-}$ 0.22, $(HCO_3)^{-}$ 0.17, O^{2-} 0.50, $(OH)^{-}$ 0.40, (H_2O) 0.20. Thus in the transition from adamsite-(Y) to thomasclarkite-(Y), there is a shift from a carbonate to a bicarbonate. Grice & Gault (1998) and Grice (1991) discussed the typical formation of bicarbonate minerals at low-temperature, slightly acidic conditions. Similarly, in this transition, more of the O atoms become protonated, thus lowering the Lewis base strength of thomasclarkite-(Y) relative to adamsite-(Y).

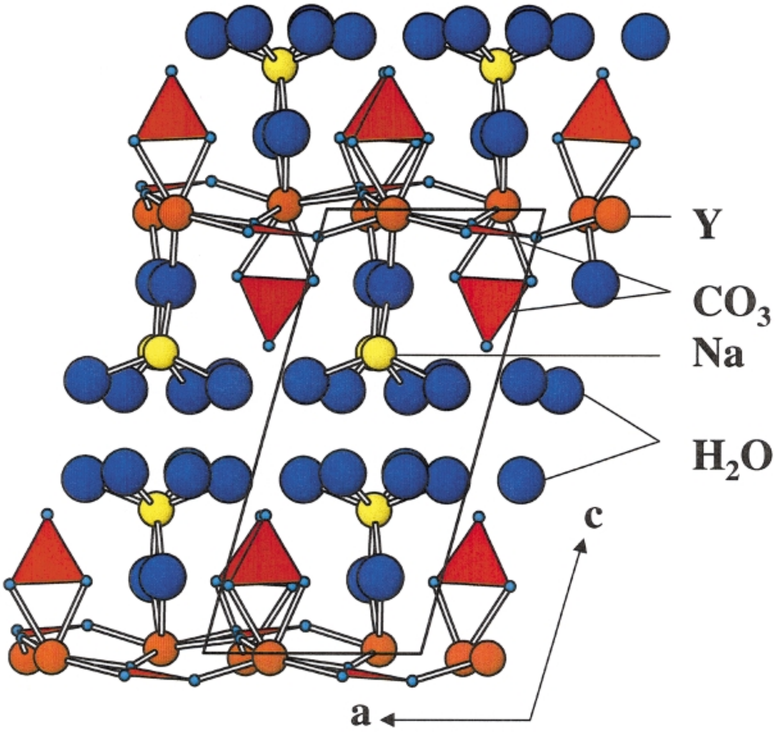

FIG. 4. The adamsite-(Y) structure projected along [010]. Red triangles represent (CO_3) polyhedra, the Na atoms are yellow, the Y atoms are orange, and the (H_2O) groups are blue. The unit cell is outlined.

ACKNOWLEDGEMENTS

The authors thank Gregory Young and Elizabeth Moffatt, Canadian Conservation Institute, Ottawa, for the thermogravimetric and infrared-absorption analyses, respectively, and Dr. F.C. Hawthorne, University of Manitoba, for use of the fully automated CCD-equipped four-circle diffractometer. Dr. Peter Tarassoff generously provided the specimens that were used in this study. We also thank László and Elsa Horváth for information regarding the occurrence and associated species of adamsite-(Y), Dr. Andrew McDonald, Laurentian University, for biographical information on F.D. Adams, and Dr. Terry Williams, The Natural History

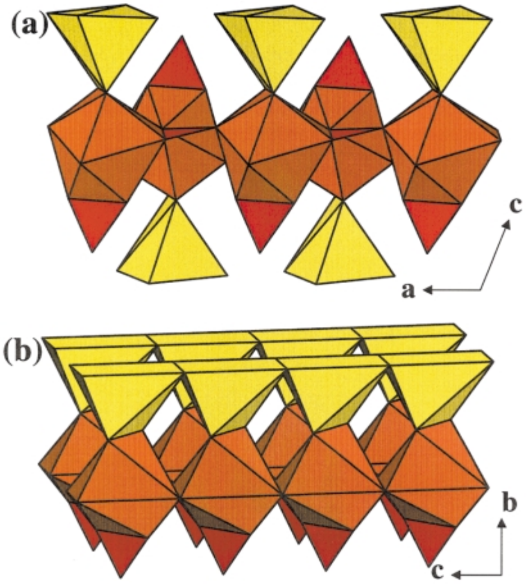

FIG. 5. a) The adamsite-(Y) structure projected along [010] with *c* vertical. Red triangles represent (CO_3) polyhedra, the Na polyhedra are yellow, and the Y polyhedra, orange. b) The thomasclarkite-(Y) structure projected on [100] with *b* vertical. Same color scheme as for adamsite-(Y).

Museum, London, for providing the photograph of adamsite-(Y) shown in Figure 1. The manuscript was improved by the comments and suggestions of two referees, Drs. Andrew McDonald and Carlo Gramaccioli and Editor Dr. Robert F. Martin. This research was made possible by the Canadian Museum of Nature.

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Received June 12, 2000, revised manuscript accepted September 30, 2000.