Crystal Structures and Phase Transition of Cementitious Bi-Anionic AFm-(Cl[−], CO₃^{2−}) Compounds

Adel Mesbah,^{‡,§} Jean-Philippe Rapin,^{¶,‡‡} Michel François,[¶] Céline Cau-dit-Coumes,[‡] Fabien Frizon,[‡] Fabrice Leroux,^{§,¶} and Guillaume Renaudin^{‡,§,‡‡}

[‡]Commissariat à l'Energie Atomique et aux Energies Alternatives, CEA DEN/DTCD/SPDE, 30207 Bagnols sur Cèze, France

[§]CNRS, UMR 6002, LMI, 63000 Aubière, France

[¶]Institut Jean Lamour – UMR 7198, Université Henri Poincaré, Nancy Université, 54500 Vandoeuvre les Nancy, France

[¶]Clermont Université, Université Blaise Pascal, Laboratoire des Matériaux Inorganiques, 63000 Clermont-Ferrand, France

^{‡‡}Clermont Université, ENSCCF, Laboratoire des Matériaux Inorganiques, 63000 Clermont-Ferrand, France

A single crystal X-ray diffraction study was performed on the compounds $[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [\text{Cl}_{1-x}(\text{CO}_3)_x] \cdot \sim 2.25\text{H}_2\text{O}$ belonging to the cementitious AFm family of general formulae $[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [X \cdot n\text{H}_2\text{O}]$, where X is a monovalent anion, or half a divalent anion. The so-called chloro-carboaluminate compound crystallizes in the rhombohedral $R\bar{3}c$ space group with: $a = 5.7400(4)$ Å, $c = 46.7402(4)$ Å, $V = 1333.7(2)$ Å³, $D_x = 2.054$ g/cm^{−3}, and $Z = 6$. Refinement of 283 independent reflections led to a residual R factor of 0.020. Chloride and carbonate anions are statistically distributed into the same crystallographic site (6a Wyckoff site). The structure of the chloro-carboaluminate compound corresponds to the high temperature phase of Friedel's salt, the equivalent chloride AFm compound with composition $[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [\text{Cl} \cdot 2\text{H}_2\text{O}]$. Three powdered samples of composition $[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [\text{Cl}_{1-x}(\text{CO}_3)_x] \cdot \sim 2.25\text{H}_2\text{O}$, with $x = 0.25$, 0.5, and 0.75, were synthesized and characterized in order to investigate the structure transition of Friedel's salt (from the rhombohedral HT-structure to the monoclinic LT-structure) versus the carbonate substitution level. Whereas a structure transition is observed around 35°C for the carbonate-free Friedel's salt, sample with $x = 0.25$ shows a similar structure transition around −15°C. The two other samples with $x = 0.5$ and 0.75, multiphase, exhibit a more complicated thermal behavior.

I. Introduction

THE AFm phases are hydrated tetracalcium aluminate compounds belonging to the lamellar double hydroxide (LDH) family. They occur during the hydration process of many kinds of cement. AFm phases are composed of positively charged main layer $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$ and negatively charged interlayer $[X \cdot n\text{H}_2\text{O}]^-$ where X is either one monovalent anion or half a divalent anion. The following general formulae $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaX}_2 \cdot n\text{H}_2\text{O}$ for monovalent anions or $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaX} \cdot n\text{H}_2\text{O}$ for divalent anions, are generally used in cement chemistry. AFm phases have been subject of numerous studies.^{1–3} However, only few complete structural characterizations have been reported in the literature. The first solved AFm structure

was the monosulfoaluminate $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ by Allmann.⁴ Next, the Friedel's salt $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ structure was investigated by Terzis *et al.*⁵ The crystallographic studies realized by François and colleagues have allowed to solve and refine several AFm structures during the last decade: structure solution of two modifications for the mono-carboaluminate $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$ phase^{6,7} revisiting of the Friedel's salt LT- and HT-structures (i.e., low-temperature and high-temperature structures) $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$,^{8,9} structure solution of the nitrated AFm phase (i.e., the binitroaluminate) $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$ ^{10,11} and the investigation of the Friedel's salt-related Cl[−]–Br[−]–I[−] halide series.^{12–14} All these structural characterizations have been mainly performed on single crystals from single-anionic AFm phases. To our knowledge, one crystallographic study on a bianionic AFm phase only is available in the literature: the Cl[−]–Br[−] mixed compounds.¹³ However, bianionic AFm phases have been extensively reported in the literature: the Kuzel's salt (chloride substitution for sulfate^{15,16}), the hemicarboaluminate (hydroxide substitution for carbonate¹⁷), and the natural hydrocalumite mineral (simultaneous presence of chloride and carbonate,¹⁸ a mineral related to the present study). The purpose of our study was to obtain a detailed crystallographic description of synthetic bianionic $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CaCl}_2 \cdot 1/2\text{CaCO}_3 \cdot \sim 10.5\text{H}_2\text{O}$ compound (named here the chloro-carboaluminate compound) that is supposed to appear in cement chemistry.

The chemical composition of the chloro-carboaluminate sample, described in the highly symmetrical $R\bar{3}c$ rhombohedral space group ($a = 5.7400(4)$ Å and $c = 46.7402(4)$ Å, $V = 1333.7(2)$ Å³, $Z = 6$), corresponds to the composition of the natural hydrocalumite mineral. Hydrocalumite has been described by Sacerdoti and Passaglia¹⁸ in the monoclinic $P2_1/c$ symmetry ($a = 10.020(1)$ Å, $b = 11.501(1)$ Å, $c = 16.286(3)$ Å, and $\beta = 104.22(1)^\circ$, $V = 1819.3$ (2) Å³, $Z = 8$ $[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [X \cdot n\text{H}_2\text{O}]$ motifs) with the following chemical composition $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CaCl}_2 \cdot 1/2\text{CaCO}_3 \cdot 10.8\text{H}_2\text{O}$. The authors indicate a true ordered description with chloride and carbonate anions located into independent, fully occupied, crystallographic sites. An average $C2/c$ description of the structure in a half unit cell (i.e., taking the half b monoclinic axis) is allowed by considering a statistical anionic disorder into the same crystallographic site. This average description is related to the monoclinic low temperature structure of Friedel's salt ($C2/c$ symmetry of Friedel's salt LT-structure below 35°C with $a = 9.960(4)$ Å, $b = 5.730(2)$ Å, $c = 16.268(7)$ Å, and $\beta = 104.471(2)^\circ$, $V = 898.97(1)$, $Z = 4$ ^{8,9}). Table I summarizes the crystallographic

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^{‡‡}Present address: University of Geneva, 24 quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland.

[†]Author to whom correspondence should be addressed. e-mail: guillaume.renaudin@ensccf.fr

Table I. Crystallographic Data of Selected AFm Phases Taken From the Literature

Compound name, Chemical composition, Symmetry, space group, Z (per $[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [X \cdot n\text{H}_2\text{O}]$ motifs)	Lattice parameters Unit cell volume	References
Monosulfoaluminate $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ Rhombohedral, $R\bar{3}$ 3	$a = 5.7586$ (3) Å $c = 26.745$ (1) Å $V = 769.50$ (2) Å ³	Allmann ⁴
Monocarboaluminate (ordered phase) $\text{O-}3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$ Triclinic, $P1$ 2	$a = 5.775$ (1) Å $b = 8.469$ (1) Å $c = 9.923$ (3) Å $\alpha = 64.77$ (2)° $\beta = 82.75$ (2)° $\gamma = 81.43$ (2)° $V = 433.0$ (2) Å ³	François <i>et al.</i> ⁶
Monocarboaluminate (disordered phase) $\text{D-}3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$ Triclinic, $P1$ 2	$a = 5.7422$ (4) Å $b = 5.7444$ (4) Å $c = 15.091$ (3) Å $\alpha = 92.29$ (1)° $\beta = 87.45$ (1)° $\gamma = 119.547$ (7)° $V = 432.5$ (1) Å ³	Renaudin <i>et al.</i> ⁷
Friedel's salt (low-temperature phase) $\text{LT-}3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ Monoclinic, $C2/c$ 4	$a = 9.960$ (4) Å $b = 5.730$ (2) Å $c = 16.268$ (7) Å $\beta = 104.471$ (2)° $V = 898.97$ (1) Å ³	Terzis and colleagues ^{5,8}
Friedel's salt (high temperature phase) $\text{HT-}3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ Rhombohedral, $R\bar{3}c$ 6	$a = 5.755$ (2) Å $c = 46.97$ (1) Å $V = 1324.8$ (7) Å ³	Rapin <i>et al.</i> ⁸ and Renaudin <i>et al.</i> ⁹
Hydrocalumite $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CaCl}_2 \cdot 1/2\text{CaCO}_3 \cdot 10.8\text{H}_2\text{O}$ Monoclinic, $P2_1/c$ 8	$a = 10.020$ (1) Å $b = 11.501$ (1) Å $c = 16.286$ (3) Å $\beta = 104.22$ (1)° $V = 1819.29$ (2) Å ³	Sacerdoti and Passaglia ¹⁸
Kuzel's salt $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CaCl}_2 \cdot 1/2\text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ Rhombohedral, $R\bar{3}c$ 12	$a = 5.74$ Å $c = 100.6$ Å $V = 2870.5$ Å ³	Kuzel ^{15,16}

Standard deviations for lattice parameters and unit cell volume are indicated in parentheses. Only lattice parameters are given.

data available in the literature for single- and bianionic AFm phases containing chloride, carbonate and sulfate anions.

The chloro-carboaluminate compound belongs to the AFm- $[\text{Cl}_{1-x} \cdot (\text{CO}_3^{2-})_{x/2}]$ series and is isotypic to the HT-structure of Friedel's salt. Friedel's salt presents a structure transition from the rhombohedral HT-structure to the monoclinic LT-structure at 35°C.^{5,8,9} The $[\text{Ca}_{1.96}\text{Al}_{1.04}(\text{OH})_6] \cdot [\text{Cl}_{0.76}(\text{CO}_3)_{0.14}] \cdot 2.10\text{H}_2\text{O}$ compound studied by Kirkpatrick *et al.*¹⁹, i.e. a carbonated Friedel's salt sample—has shown the same structure transition at 6°C only, indicating that the temperature of transition presumably varies with the amount of carbonate substitution. The rhombohedral symmetry observed for $\text{Ca}_2\text{Al}(\text{OH})_6 \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$ by Rousselot *et al.*²⁰ indicates a weak carbonation of the calcium aluminate sample (not only physisorbed- CO_2 , but presence of carbonate species in the AFm interlamellar space). The dependence of the temperature of transition upon the carbonate content has been investigated here, between -120° and 50°C , by considering the three AFm- $[\text{Cl}_{1-x} \cdot (\text{CO}_3^{2-})_{x/2}]$ samples with $x = 0.25, 0.5$, and 0.75 .

II. Experimental Section

(1) Synthesis

(A) *Single Crystals*: Single crystals of chloro-carboaluminate (nominal composition: $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CaCl}_2 \cdot 1/2\text{CaCO}_3 \cdot \sim 10.5\text{H}_2\text{O}$) were prepared by hydrothermal synthesis as previously described for the preparation of single-anionic AFm single crystals.^{6,7,9–11} The starting powders (homogeneous mixtures of $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, and CaCO_3 in molar ratio $3/2/0.5/0.5$) were introduced in a silver capsule and mixed with water (solid/water weight ratio = 0.5). The capsules were sealed under nitrogen atmosphere and placed at 120°C and 2 Kbar isotropic pressure for 2 months.

(B) *Powder Samples*: Three powder samples belonging to the $[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [\text{Cl}_{1-x} \cdot (\text{CO}_3)_{x/2} \cdot \sim 2.25\text{H}_2\text{O}]$, with $x = 0.25, 0.5$, and 0.75 , were synthesized in aqueous solution. A stoichiometric mixture of C_3A ($\text{Ca}_3\text{Al}_2\text{O}_6$), $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, and CaCO_3 was added in demineralized and decarbonated water to reach a water/solid ratio of 50. The suspensions

were stored at room temperature under nitrogen atmosphere and continuously stirred in closed polypropylene bottles for 4 weeks. They were then filtered and rinsed with isopropanol. The precipitates were subsequently dried in a dessiccator, under slight vacuum, over potassium acetate (23% RH), at room temperature. Samples were referred as AFm-[Cl_{1-x}·(CO₃²⁻)_{x/2}], with $x = 0.25, 0.5$, and 0.75 ; i.e., respectively, AFm-[Cl_{3/4}·(CO₃²⁻)_{1/8}], AFm-[Cl_{1/2}·(CO₃²⁻)_{1/4}], and AFm-[Cl_{1/4}·(CO₃²⁻)_{3/8}].

(2) Electron Microprobe Analyses

The chemical compositions of the chloro-carboaluminate single crystals from hydrothermal synthesis, as well as of the three AFm-[Cl_{1-x}·(CO₃²⁻)_{x/2}] powdered samples, were determined with a CAMECA SX50 electron microprobe (Gennevilliers, France). The determined chemical compositions were relatively close to the targeted nominal stoichiometries. The chemical compositions were obtained by averaging 10 analyses taken from five different crystals for each sample. The comparison of the 10 analyses showed the chemical homogeneity of each sample. The carbonate amount was calculated by assuming electroneutrality of the compounds.

(3) Thermogravimetric Analyses (TGA)

TGA of the chloro-carboaluminate samples were carried out in order to determine their interlayer water content. Measurement was performed on a TG/ATD 92-16.18 SETARAM instrument (Caluire, France) from room temperature up to 1000°C under dry nitrogen flux and using a heating rate of 1°C/min.

(4) Powder X-Ray Diffraction (PXRD)

PXRD patterns for the three AFm-[Cl_{1-x}·(CO₃²⁻)_{x/2}] powdered samples were recorded on a X'Pert Pro PANalytical (Almelo, the Netherlands) diffractometer, with θ - θ geometry (Bragg Brentano), equipped with the solid detector X'Celerator, a graphite back-end monochromator, and using CuK α radiation ($\lambda = 1.54184$ Å). PXRD patterns were recorded at room temperature in the interval $3^\circ < 2\theta < 120^\circ$, with a step size $\Delta 2\theta = 0.0167^\circ$ and a counting time of 30 s per step (about 3 h of total counting time).

Other spectra were recorded in temperature range between -120° and 50°C with interval of 20°C . Data were recorded in angular range between 3° and 120° (2θ) using a TTK 450 HT chamber (Anton Paar, Graz, Austria) under nitrogen atmosphere. Total time of counting was 1 h for each pattern.

(5) Single Crystal X-Ray Diffraction

(A) *Data Collection*: Transparent hexagonal single crystals of chloro-carboaluminate ([Ca₂Al(OH)₆]·[Cl_{0.45}·(CO₃)_{0.27}·0.27H₂O]) were chosen for diffraction measurements and mounted on a goniometer head for structural analysis. Full data sets were collected on a Nonius Kappa CCD diffractometer (Karlsruhe, Germany) at room temperature. Data collection and refinement parameters for the best single crystal are summarized in Table II (platy crystal with $0.150\text{ mm} \times 0.120\text{ mm} \times 0.030\text{ mm}$ size). The structure of the chloro-carboaluminate compound was refined in the rhombohedral $R\bar{3}c$ space group, with $a = 5.7400$ (4) Å and $c = 46.7402$ (4) Å. It corresponded to the rhombohedral symmetry of the Friedel's salt HT-structure (structure above 35°C), with a quite equivalent unit cell volume.^{8,9}

(B) *Structure Solution and Refinement Strategy*: The refinement of the chloro-carboaluminate structure was started using atomic coordinates from the rhombohedral description of the Friedel's salt HT-structure.⁹ The Wyckoff site $6a$ (fully occupied by Cl⁻ anions in HT-structure of Friedel's salt) was statistically occupied by C (central carbon atom from carbonate anion), Cl, and water molecule Ow2 according to the substitution law $2\text{Cl}^- = \text{CO}_3^{2-} + \text{H}_2\text{O}$. The site for the oxygen atoms from the carbonate anion, Oc, was located by difference Fourier maps. The structural model was refined by least square method

Table II. Crystal and Structure Refinement Data for Chloro-Carboaluminate

Name	Chloro-carboaluminate
Formula	[Ca ₂ Al(OH) ₆]·[Cl _{0.45} ·(CO ₃) _{0.27} ·0.27H ₂ O]
Formula weight (g/mol)	282.45
Temperature (K)	293 (2)
Wavelength (Å)	0.71073
Space group	$R\bar{3}c$
Lattice parameters	
a (Å)	5.7400 (4)
c (Å)	46.7402 (4)
Volume (Å ³)	1333.66 (2)
Z/density (g/cm ³)	6/2.11
Absorption coefficient (mm ⁻¹)	1.541
F000	849
Color	Colorless
Crystal size (mm)	$0.150 \times 0.120 \times 0.030$
Range for data collection (°)	$2.5 \leq \theta \leq 25.62$
Index ranges	$0 \leq h \leq 6; 0 \leq k \leq 6; 0 \leq l \leq 56$
Reflexion collected/unique	511/283
Refinement method	Least squares on F^2
Data/constraints/restraints/parameters	283/3/1/35
Goodness of fit	1.005
Final R indice [$I > 2\sigma(I)$]	$R1 = 0.0202$
R indices (all data)	$R1 = 0.0289$
	$wR2 = 0.0499$
Largest diffraction peak and hole (e/Å ³)	0.194 and -0.2550

using ShelX 97 program.²¹ The refinement of 35 parameters, with three constraints and one restraint, led to the final correlation factor of $R1 = 0.0202$ (from 283 independent reflections). The three constraints were: (1) the full occupancy of the anionic $6a$ site by considering the presence of water molecules with $X_{\text{Cl}} + X_{\text{C}} + X_{\text{Ow2}} = 1$ (X are occupancies), (2) $X_{\text{Cl}} + 2X_{\text{C}} = 1$ to respect the electroneutrality of the compound, and (3) $X_{\text{Oc}} = 3X_{\text{C}}$ to respect the carbonate anion geometry. One restraint was applied on the interatomic distance of the water molecule Ow1: $d_{\text{Ow1-Hw1}} = 0.90(5)$ Å. All non-H atoms were refined with anisotropic displacement parameters. Atomic coordinates and equivalent isotropic displacement parameters of the 10 independent atoms are given in Table III. The anisotropic displacements parameters of non-H atoms are reported in Table IV. For the H sites (Hh, respectively, Hw1), the individual isotropic displacement parameter was fixed at 120% of the equivalent isotropic displacement parameters of the connected oxygen site (Oh, respectively, Ow1). A unique set of anisotropic displacement parameters was considered for the three atoms statistically distributed on the same site $6a$ (chloride, carbon, and oxygen Ow2). Owing to statistical distribution of the carbonate group, chloride anion and water Ow2 molecule into the site $6a$, hydrogen atoms from water molecule Ow2 were not localized.

III. Results and Discussion

(1) Samples Characterization

(A) *Chemical Composition of the Sample Prepared by the Hydrothermal Method*: The chemical composition of the chloro-carboaluminate compound was determined by combining electron microprobe and TGA. The simultaneous presence of the two anions was evidenced with the following calculated anionic molar ratio: $\text{Cl}^-/\text{CO}_3^{2-} = 2.17$ with atomic ratios $\text{Ca}/\text{Al}/\text{Cl} = 2.00/1.01/0.52$ determined by electron microprobe analysis. According to the weight losses observed on the TGA curves (Fig. 1), the calculated chemical composition, including water

Table III. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Chloro-Carboaluminate

Atom	Wyckoff site	x	y	z	$U_{\text{eq}}^{\dagger} (\times 10^3)$	Occupancy
Al	6b	0	0	0	13.8 (3)	1
Ca	12c	0	0	0.6543 (1)	17.1 (2)	1
Oh	36f	0.3898 (3)	0.9732 (2)	0.6455 (1)	17.6 (4)	1
Hh	36f	0.453 (4)	0.998 (4)	0.6287 (3)	21 (—)	1
Ow1	12c	0	0	0.3984 (1)	57 (1)	1
Hw1	36f	-0.154 (5)	-0.092 (7)	0.4066 (7)	67 (—)	2/3 (—)
Cl	6a	0	0	1/4	27.7 (6)	0.45 (1)
C	6a	0	0	1/4	27.7 (6)	0.274 (6)
Oc	18e	0	0.218 (2)	1/4	44 (1)	0.274 (6)
Ow2	6a	0	0	1/4	27.7 (6)	0.274 (6)

[†] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

amount, corresponded to: $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0.52\text{CaCl}_2 \cdot 0.48\text{CaCO}_3 \cdot 10.65\text{H}_2\text{O}$; i.e. $[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [\text{Cl}_{0.52}(\text{CO}_3)_{0.24} \cdot 2.33\text{H}_2\text{O}]$. Observation of the TGA curve (Fig. 1) evidenced four distinct events. Three events were attributed to water releases: (1) broad weight loss between 100° and 350°C corresponding to dehydration (departure of the $2.25\text{H}_2\text{O}$ from interlayer region) and beginning of the dehydroxylation (departure of $1.5\text{H}_2\text{O}$ from the condensation of 3OH^- ; half of the dehydroxylation of main layer), (2) weight loss between 375° and 425°C corresponding to the departure of about $0.5\text{H}_2\text{O}$, and (3) weight loss between 600° and 700°C corresponding to the departure of about $1\text{H}_2\text{O}$. The two last events corresponded to the second half of the dehydroxylation process. The sharp event around 350°C was attributed to the decarbonation (as indicated by the sharp signal in the derivative DTGA curve), corresponding to the departure of about the expected 0.25CO_2 . Such a low temperature of decarbonation agrees with location of carbonate group at the center of the interlayer region of the structure; i.e. weakly (not directly) bonded to main layer.²²

(B) *Chemical Composition and PXRD Characterization of the Three Powdered Samples Belonging to the AFm- $[\text{Cl}_{1-x} \cdot (\text{CO}_3^{2-})_{x/2}]$ Series:* Electron microprobe analyses showed the homogeneous composition of each sample. Their average chemical composition was: $[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [\text{Cl}_{0.74}(\text{CO}_3)_{0.13} \cdot \sim 2\text{H}_2\text{O}]$ for the AFm- $[\text{Cl}_{3/4} \cdot (\text{CO}_3^{2-})_{1/8}]$ sample, $[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [\text{Cl}_{0.46}(\text{CO}_3)_{0.27} \cdot \sim 2\text{H}_2\text{O}]$ for the AFm- $[\text{Cl}_{1/2} \cdot (\text{CO}_3^{2-})_{1/4}]$ sample, and $[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [\text{Cl}_{0.24}(\text{CO}_3)_{0.38} \cdot \sim 2\text{H}_2\text{O}]$ for the AFm- $[\text{Cl}_{1/4} \cdot (\text{CO}_3^{2-})_{3/8}]$ sample. PXRD analyses indicated that AFm- $[\text{Cl}_{3/4} \cdot (\text{CO}_3^{2-})_{1/8}]$ sample was single phase, whereas AFm- $[\text{Cl}_{1/2} \cdot (\text{CO}_3^{2-})_{1/4}]$ and AFm- $[\text{Cl}_{1/4} \cdot (\text{CO}_3^{2-})_{3/8}]$ samples contained two phases (Fig. 2). The crystalline phase observed for AFm- $[\text{Cl}_{3/4} \cdot (\text{CO}_3^{2-})_{1/8}]$ powder was isotopic to the rhombohedral $R\bar{3}c$ HT-structure of Friedel's salt; i.e. isotopic to chloro-carboaluminate. The chemical microprobe analyses for AFm- $[\text{Cl}_{1/2} \cdot (\text{CO}_3^{2-})_{1/4}]$ and AFm- $[\text{Cl}_{1/4} \cdot (\text{CO}_3^{2-})_{3/8}]$ samples indicated that each powder was composed of two polymorphs having the same chemical composition. One polymorph was isotopic to the rhombohedral $R\bar{3}c$ HT-structure of Friedel's salt, and the other polymorph to the monoclinic $C2/c$ LT-structure of Friedel's salt (i.e., structure related to the natural hydrocalumite mineral); as recently observed in Balonis *et al.*³

Table IV. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) of Non-H Atoms for Chloro-Carboaluminate

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Al	9.0 (4)	9.0 (4)	23.5 (6)	4.5 (2)	0	0
Ca	11.2 (3)	11.2 (3)	28.8 (4)	5.6 (2)	0	0
O _H	13.5 (7)	12.6 (7)	24.8 (6)	5.1 (6)	-6 (6)	-15 (5)
Ow1	66 (2)	66 (2)	38 (2)	33.4 (8)	0	0
Cl, C	69 (2)	69 (2)	28 (1)	34 (1)	0	0
Ow2						
Oc	36 (6)	38 (5)	64 (5)	18 (3)	-7 (2)	-13 (4)

Rietveld refinements (without any exclusion of 2θ range), performed with the FullProf program,^{23,24} were performed to extract lattice parameters and quantitative phase analyses. Results are gathered in Table V. The weight ratio between the two polymorphs was quite similar (about 50 wt% for both polymorphs) for the two AFm- $[\text{Cl}_{1/2} \cdot (\text{CO}_3^{2-})_{1/4}]$ and AFm- $[\text{Cl}_{1/4} \cdot (\text{CO}_3^{2-})_{3/8}]$ samples. A detailed crystallographic study of the biphasic samples, as a function of $\text{Cl}^-/\text{CO}_3^{2-}$ ratio, will be published in a separate paper (A. Mesbah, C. Cau-dit-Coumes, F. Frizon, F. Leroux, J. Ravoux, and G. Renaudin unpublished data).

(2) Structure Description of the Chloro-Carboaluminate Compound of Composition

$[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [\text{Cl}_{0.52}(\text{CO}_3)_{0.24} \cdot 2.33\text{H}_2\text{O}]$

A general representation of the chloro-carboaluminate structure, refined from single crystal data, is reported in Fig. 3 (projection along $[110]$). The oxygen coordination of Al and Ca cations are six ($6 \times 1.90\text{\AA}$) and seven ($3 \times 2.36\text{\AA}$, $3 \times 2.45\text{\AA}$ and $1 \times 2.47\text{\AA}$), respectively, as usually encountered in AFm compounds. Chloro-carboaluminate has the layered structure characteristic of AFm phases.^{4,6-10,12,13} It can be described by the stacking of $[\text{Ca}_2\text{Al}(\text{OH})_6 \cdot 2\text{H}_2\text{O}]^+$ main layers and $[\text{Cl}_{0.45}(\text{CO}_3)_{0.27} \cdot 0.27\text{H}_2\text{O}]^-$ interlayers. Water molecules are included in the main layer chemical description. Actually, these water molecules belong to the sevenfold coordinated Ca polyhedra, $\text{Ca}(\text{OH})_6 \cdot \text{H}_2\text{O}$, from main layer. These water molecules (Ow1 site), bonded to Ca from main layer, insure the connection between main layers and interlayers. They participate to the hydrogen bonds network with anions and water molecules from interlayer (Ow2 site). The refined composition, $[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [\text{Cl}_{0.45(1)} \cdot (\text{CO}_3)_{0.27(1)} \cdot 2.27(1)\text{H}_2\text{O}]$, is close to the composition determined by TGA and chemical analyses $[\text{Ca}_2\text{Al}$

Fig. 1. Thermogravimetric analyses (TGA, solid line) and DTGA (dotted line) curves of chloro-carboaluminate sample $[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [\text{Cl}_{0.45} \cdot (\text{CO}_3)_{0.27} \cdot 0.27\text{H}_2\text{O}]$ prepared by hydrothermal synthesis.

Fig. 2. Powder X-ray diffraction (PXRD) patterns of the three powdered AFm-[Cl_{3/4}(CO₃²⁻)_{1/8}], AFm-[Cl_{1/2}(CO₃²⁻)_{1/4}], and AFm-[Cl_{1/4}(CO₃²⁻)_{3/8}] samples. Inset shows diffraction peaks (at low angles) relative to rhombohedral and monoclinic polymorphs.

(OH)₆]·[Cl_{0.52}·(CO₃)_{0.24}·2.33H₂O]. Both compositions are around the targeted AFm-[Cl_{1/2}·(CO₃²⁻)_{1/4}] stoichiometry for the hydrothermal synthesis. Selected interatomic distances, showing namely the structural role of Ow1, are reported in Table VI. Chloride and carbonate anions, as well as interlayer water molecule (Ow2) are statistically distributed into the same crystallographic site. Chloride anions and water molecules Ow2 share 10 hydrogen bonds with four bonded water molecules Ow1 and 6 hydroxyl anions. Oxygen atoms from carbonate groups also share hydrogen bonds with the same Ow1 water molecules and hydroxyl anions. The hydrogen bonds network is

Table V. Results from the Rietveld Analyses Performed on the Three Powdered Samples Synthesized in Aqueous Solution

Sample	Phase	Lattice parameters (Å) Unit cell volume (Å ³)	Weight amount (wt%)
AFm-[Cl _{3/4} ·(CO ₃ ²⁻) _{1/8}]	Rhombohedral $\bar{R}3c$	$a = 5.7465$ (1) $c = 47.041$ (1) $V = 1345.30$ (5)	100
AFm-[Cl _{1/2} ·(CO ₃ ²⁻) _{1/4}]	Rhombohedral $\bar{R}3c$	$a = 5.7557$ (1) $c = 46.947$ (1) $V = 1346.90$ (5)	53
	Monoclinic $C2/c$	$a = 10.0073$ (7) $b = 5.7580$ (3) $c = 16.232$ (1) $\beta = 103.68$ (1)° $V = 908.8$ (1)	47
AFm-[Cl _{1/4} ·(CO ₃ ²⁻) _{3/8}]	Rhombohedral $\bar{R}3c$	$a = 5.7630$ (3) $c = 46.783$ (1) $V = 1345.59$ (8)	49
	Monoclinic $C2/c$	$a = 9.9988$ (5) $b = 5.7593$ (2) $c = 16.349$ (1) $\beta = 102.72$ (1)° $V = 918.34$ (9)	51

represented in the detail of Fig. 3, and corresponding interatomic distances are available in Table VI.

The disordered chloro-carboaluminate structure is related to the hydrocalumite mineral which crystallizes in the monoclinic $P2_1/c$ space group with an ordering of the two anionic species into independent crystallographic sites. In the ordered hydrocalumite mineral, chloride, and carbonate anions (Cl⁻/CO₃²⁻ with a 2/1 ratio) occupy independent crystallographic sites.¹⁸ The rhombohedral structure of chloro-carboaluminate derives from the HT-structure of Friedel's salt. The two structures (respectively, chloro-carboaluminate and HT-structure of Friedel's salt) are isotypic: $R\bar{3}c$ symmetry with a quite equivalent unit cell volume (respectively, 1333.7 and 1324.8 Å³). The chloro-carboaluminate structure is obtained by the substitution of carbonate anion for chloride anion in the HT-structure of Friedel's salt. This latter would be the chloride end-member of an AFm-(Cl⁻,CO₃²⁻) solid solution. One carbonate anion and one water molecule should substitute for two chloride anions to insure charge balance in the AFm-[Cl_{1-x}·(CO₃²⁻)_{x/2}] series. The single-anionic AFm-CO₃²⁻ compound (i.e., monocarboaluminate) should not be considered as the other end-member of the solid solution due to its triclinic symmetry ($P\bar{1}$ for D-3CaO·Al₂O₃·CaCO₃·11H₂O or $P1$ for O-3CaO·Al₂O₃·CaCO₃·11H₂O,^{6,7} and due to the position of the carbonate group which is directly bonded to main layer via Ca²⁺ cations (and not inserted at the center of the interlayer as observed here). Raman spectroscopic data (which were already efficiently used to characterize sulfated cement hydrates^{25,26} and C-S-H samples^{27,28}) are consistent with the different bonding of carbonate groups in monocarboaluminate and in AFm-[Cl_{1-x}·(CO₃²⁻)_{x/2}] series (Raman results will be published in a separate paper (A. Mesbah, C. Cau-dit-Coumes, F. Frizon, F. Leroux, J. Ravoux, and G. Renaudin unpublished data)).

(3) Study of the Friedel's Salt Structure Transition in the AFm-[Cl_{1-x}·(CO₃²⁻)_{x/2}] Series

Chloro-carboaluminate belongs to the AFm-[Cl_{1-x}·(CO₃²⁻)_{x/2}] solid solution, isotypic to HT-structure of Friedel's salt. Friedel salt presents a structure transition from the rhombohedral HT-

Fig. 3. Projection along [110] of the chloro-carboaluminate structure: general view (left) and detail showing the hydrogen bond network within the interlayer region (right). Green and blue polyhedra are, respectively, sixfold Al polyhedra and sevenfold Ca polyhedra. White, grey, red, green, blue, yellow, and black spheres represent, respectively, hydroxyl anions, water molecules, carbonate groups, Al, Ca, Cl, and H atoms. To clarify the representation, statistical occupancies of chloride, carbonate and water Ow2 have been ordered.

Table VI. Selected Interatomic Distances (Å) in Rhombohedral Chloro-Carboaluminate Structure		
Chloro-carboaluminate		
Al	6 × Oh	1.902 (1)
Ca	3 × Oh	2.354 (1)
	3 × Oh	2.450 (1)
	1 × Ow1	2.462 (3)
Oh	Hh	0.93 (1)
Ow1	2 × Hw1	0.86 (1)
C	3 × Oc	1.247 (7)
Cl, Ow2	4 × Hw1	2.52 (1)
	6 × Hh	2.64 (1)
Oc	1.33 × Ow1	1.65 (1)
	2 × Oh	2.17 (1)

structure to the monoclinic LT-structure at $T_s \approx 35^\circ\text{C}$.^{5,8,9} The $[\text{Ca}_{1.96}\text{Al}_{1.04}(\text{OH})_6] \cdot [\text{Cl}_{0.76}(\text{CO}_3)_{0.14}] \cdot 2.10\text{H}_2\text{O}$ compound studied by Kirkpatrick *et al.*¹⁹ has shown the same structure transition at $T_s \approx 6^\circ\text{C}$ only, indicating that the temperature of transition presumably varies with the amount of carbonate

substitution. The structure behavior of the three powdered AFm- $[\text{Cl}_{1-x} \cdot (\text{CO}_3^{2-})_{x/2}]$ samples ($x = 0.25, 0.5$ and 0.75) was thus investigated between -120° and 50°C .

(A) *Structure of AFm- $[\text{Cl}_{3/4} \cdot (\text{CO}_3^{2-})_{1/8}]$ Sample Versus Temperature:* By comparison with the thermal behavior of Friedel's salt^{8,9} and with the carbonated Friedel's salt compound studied by Kirkpatrick *et al.*,¹⁹ a structure transition from the rhombohedral HT-structure to the monoclinic LT-structure is expected below 6°C for the AFm- $[\text{Cl}_{3/4} \cdot (\text{CO}_3^{2-})_{1/8}]$ due to its composition $[\text{Ca}_2\text{Al}(\text{OH})_6] \cdot [\text{Cl}_{0.74}(\text{CO}_3)_{0.13}] \cdot \sim 2\text{H}_2\text{O}$. Low-temperature PXRD measurements showed that the structure transition actually occurred from the monoclinic LT-structure to the rhombohedral HT-structure at $T_s \approx -15^\circ\text{C}$ when increasing the temperature from -115° to 45°C (Fig. 4). Both polymorphs are observed in the X-ray powder pattern recorded at -15°C . The temperature dependence of lattice parameters and unit cell volume clearly illustrates the structure transition around T_s (Fig. 5 illustrates the presence of the two polymorphs at -15°C). As already observed for Friedel's salt,⁸ the a , c , and β lattice parameters decreased, whereas the b lattice parameter increased during the transition from the monoclinic to the rhombohedral (transposed into the monoclinic lattice) structure. Similarly to Friedel's salt, the structure transition of the AFm-

Fig. 4. Powder X-ray diffraction (PXRD) temperature dependence for AFm- $[\text{Cl}_{3/4}(\text{CO}_3^{2-})_{1/8}]$ powdered sample between -115° and 45°C .

Fig. 5. Lattice parameters and unit cell volume of $\text{AFm}[\text{Cl}_{3/4} \cdot (\text{CO}_3^{2-})_{1/8}]$ as a function of temperature. Above the phase transition temperature, the hexagonal lattice is described with the monoclinic sublattice according to the relationships $\bar{a}_m = -2\bar{a}_h - \bar{b}_h$, $\bar{b}_m = -\bar{b}_h$, and $\bar{c}_m = \frac{2}{3}\bar{a}_h + \frac{1}{3}\bar{c}_h$.

$[\text{Cl}_{3/4} \cdot (\text{CO}_3^{2-})_{1/8}]$ phase was reversible. A nonlinear variation and a strong decrease of T_s versus the carbonate substitution level (Ca/Cl ratio) were observed (see Fig. 6).

Fig. 6. Transition temperature, T_s , in $\text{AFm}(\text{Cl}^-, \text{CO}_3^{2-})$ versus the Ca/Cl ratio.

(B) *Structure of $\text{AFm}[\text{Cl}_{1/2} \cdot (\text{CO}_3^{2-})_{1/4}]$ and $\text{AFm}[\text{Cl}_{1/4} \cdot (\text{CO}_3^{2-})_{3/8}]$ Versus Temperature:* Extrapolation of the curve in Fig. 6 indicates that, for samples $\text{AFm}[\text{Cl}_{1/2} \cdot (\text{CO}_3^{2-})_{1/4}]$ and $\text{AFm}[\text{Cl}_{1/4} \cdot (\text{CO}_3^{2-})_{3/8}]$ (Ca/Cl = 4.35 and 8.33, respectively), T_s should be largely negative. When increasing the carbonate substitution level, the powdered samples were composed of two polymorphs (one rhombohedral and one monoclinic) without observed chemical composition heterogeneity. The rhombohedral polymorph, observed at room temperature, agrees with the temperature-dependent structure transition of carbonated Friedel's salt (the HT-structure should be observed when T_s is below room temperature). Decreasing the temperature down to -120°C did not allow to observe the transformation of the rhombohedral polymorph into the monoclinic polymorph. If this structure transition actually persists for the rhombohedral carbonated polymorph in $\text{AFm}[\text{Cl}_{1/2} \cdot (\text{CO}_3^{2-})_{1/4}]$ and $\text{AFm}[\text{Cl}_{1/4} \cdot (\text{CO}_3^{2-})_{3/8}]$ samples, this means that it occurs at a temperature lower than -120°C . Supplementary experiments at much lower temperature should be necessary to evidence this transition. The monoclinic polymorph observed in samples $\text{AFm}[\text{Cl}_{1/2} \cdot (\text{CO}_3^{2-})_{1/4}]$ and $\text{AFm}[\text{Cl}_{1/4} \cdot (\text{CO}_3^{2-})_{3/8}]$ at room temperature should be metastable (as it is also probably the case for the natural hydrocalumite mineral with the monoclinic symmetry at room temperature). The metastability feature of the monoclinic polymorph was checked by heating these two samples up to 50°C , and then cooling at

room temperature, with *in situ* X-ray measurements. The monoclinic polymorph transformed into the rhombohedral polymorph around 45°C when heating for the two samples. Surprisingly, and inconsistently with the supposed metastability feature of the monoclinic polymorph, this transition was reversible when cooling from 50°C to room temperature (a detailed study on the coexistence of the two polymorphs will be published in a separate paper (A. Mesbah, C. Cau-dit-Coumes, F. Frizon, F. Leroux, J. Ravoux, and G. Renaudin unpublished data)).

IV. Conclusion

The crystal structure of the bianionic AFm-[Cl⁻, CO₃²⁻] compound, named chloro-carboaluminate, has been solved and fully described by single crystal X-ray diffraction. Single crystals of composition [Ca₂Al(OH)₆]·[Cl_{0.52}(CO₃)_{0.24}·2.33H₂O] have been synthesized by the hydrothermal method. Chloro-carboaluminate has a layered structure built with the sequence of main layer and interlayer usually encountered in cementitious AFm phases. Characteristic main layer is composed of six- and sevenfold coordinated aluminum and calcium cations. The interlayer region presents a statistical disorder. Chloride and carbonate anions, as well as water molecules, are located in the same crystallographic site. Carbonate anions substitute chloride anions from the Friedel's salt HT-structure; two chlorides are substituted by one carbonate anion and one water molecule to insure charge balance. The existence of an AFm-[Cl_{1-x}·(CO₃²⁻)_{x/2}] solid solution has been observed, as well as the existence of a (apparently) metastable monoclinic polymorph, related to the natural hydrocalumite mineral, when increasing the carbonate substitution level. Studying the temperature dependence of the Friedel's salt structure transition versus the carbonate amount has shown that AFm-[Cl_{1-x}·(CO₃²⁻)_{x/2}] solid solution corresponds to carbonation of Friedel's salt compound. The temperature of transition ($T_s \approx 35^\circ\text{C}$ for noncarbonated Friedel's salt) strongly decreases when chloride anions are substituted by carbonate anions into the Friedel's salt structure. The carbonate anions are located at the center of the interlayer region of the structure. For this reason, monocarboaluminate (in which carbonate anions are directly bonded to main layer of the structure) cannot belong to this AFm-[Cl_{1-x}·(CO₃²⁻)_{x/2}] solid solution.

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