

FORMICAITE

β -formicaite & α -Ca-formiate
 $\text{Ca}(\text{HCO}_2)_2$

MINERAL OR NO ?

Roger Warin

INTRODUCTION

Participation in a large mineralogy forum often provides interesting information that is not highlighted in our other readings. This is particularly the case when browsing Jordi Fabre's FMF forum. As in the Forum of Rome more than 2000 years ago, one "listens" to various gossip which often arouses interest. We also discover excellent photos of various amateurs from around the world showing off the pearls from their collections or other very naive questions from people who discover our hobby by chance, often with a magnet that is too powerful. Subjects far from our habits can hatch. This can concern the localities of deposits which are then admirably described, but also general subjects of Mineralogy.



*Fig. 1 - α -Ca-formate – Alkali Lake, Oregon. © Cesar Menor Salvan.
The hair (an animal hair) in the crydstals were trapped during crystallization.*

This is how Cesar Menor Salvan recently recalled (2021) that he had published the complete description of a new mineral found in the sediments of Alkali Lake (Oregon Lake, USA). This author thus defined calcium alpha-formate. As I knew neither this lake nor the mineral, my attention was drawn to a discussion which to aroused during the days which followed. Immediately, it was said that this mineral had a biogenic origin and inevitably the discussions turned to its status: was it a real mineral ?



Fig. 2 - α -Ca-formiate – Alkali Lake, Valley Falls – Oregon. Coll. & © R. Warin.



Fig. 3 - α -Ca-formiate – Alkali Lake, Valley Falls – Oregon. Coll. & © R. Warin.

Thinking this way is old fashioned, and it have already been raised about the weddellite $\text{Ca}(\text{C}_2\text{O}_2) \cdot (2.5-x)\text{H}_2\text{O}$, whose crystallization circumstances are similar on limestone lake bottom sediments (The Weddell Sea, Antarctica).

As to ask questions, gypsum also comes from an evaporate of the Mediterranean Sea, forming huge deposits in its center around Sicily. The enormous deposits of salt (halite) in Poland also result from the drying up of the seas. By their importance, being otherwise ores, they undoubtedly acquired the status of minerals, despite their solubility.

POLYMORPHISM

Four different structures characterize synthetic minerals whose molecular composition is $\text{Ca}(\text{HCO}_2)_2$, of which the only mineral accepted by the IMA is formicaite, the polymorph β (known since 1998). As for him, Cesar Menor established the structure of a new species of the same composition, not yet accepted by the IMA. His name remains to be determined. It is tentatively designated by the chemical name α -Ca-formate.

If the β -formicaite from Russia does not seem to produce beautiful crystals, those from Oregon are remarkable. They appear in places where the summers are arid. Indeed, the solubility of calcium formate is much greater than that of calcium carbonate for example, respectively 162 g/l for Ca formate, while for calcite it is $6.17 \cdot 10^{-4}$ g/100 ml and $7.75 \cdot 10^{-4}$ g/100 ml for aragonite.

β -FORMICAITE

β -Formicaite is a relatively recently discovered mineral. Its status was approved by the IMA only in 1998. However, its chemical formula is of rare simplicity: $\text{Ca}(\text{HCOO})_2$ (Fig.4). It is the β polymorph of calcium formate. The name recalls the chemical composition, formic acid and calcium). This salt thus derives from the action of formic acid on Ca^{2+} ions. Because of this, it is formally considered an organic salt, since formic acid is the simplest of the carboxylic acids, the next term being acetic acid (vinegar) with the formula $\text{CH}_3\text{-COOH}$.

Type locality : "The Solondo borno deposit", Buryatia and the Novofrolovskoye copper deposit, Urals, Russia.

Other deposit : Alkali Lake, Lake Co., Oregon, USA.

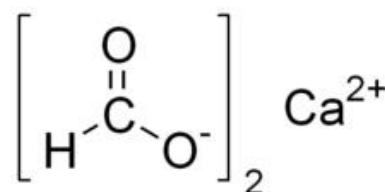


Fig. 4 - β -formicaite.



*Fig. 4 – Formicaite – Alkali Lake, Oregon. Taille : 1,3 x 1 x 0,3 cm.
Credit : New Brand Minerals.*



α -Ca-formate, Alkali Lake, Oregon
© Cesar Menor S.

Fig. 5 - α -Ca-formate – Alkali Lake, Oregon. © Cesar Menor Salvan.

PROPERTIES

β -formicaite belongs to the tetragonal System, trapezohedral class.

Symbol H-M (422). Space group $P 4_12_12$

Unit cell: $a = 6.77 \text{ \AA}$, $c = 9.463 \text{ \AA}$ $Z = 4$.

Perfect cleavage according to $\{001\}$. Density: 1.9 g/cm^3 (1.99 g/cm^3 cal.).

Hardness: 1 (that of talc). Solubility: 162 g/l.

The white crystals, slightly tinged with blue, often form compact aggregates.



Fig. 6 - α -Ca-formiate – Alkali Lake, Oregon. Vue supérieure Fig.5 © Cesar Menor Salvan.

α - $\text{Ca}(\text{HCO}_2)_2$ ¹

Formicaite is obviously known in organic chemistry as anhydrous calcium formate $\text{Ca}(\text{HCO}_2)_2$. In the crystalline state (synthetic crystals), four polymorphic structures do exist and they are denoted α , β , γ and δ .

¹ Biogenic Orthorhombic α -Calcium Formate from Sediments of Alkali Lake, Oregon, USA - Nikita V. Chukanov 1,2, Cesar Menor-Salvan & al. – Minerals 2021, 11, x.

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The α phase is new mineral, not named yet.

If the γ and δ structures are high temperature phases (150°-300°C), the α , β phases persist at ordinary temperatures. The β phase can however evolve into γ and δ by heating. The α phase does not transform into another polymorph. α -formicaite seems the most stable if we consider the sequence $\alpha \rightarrow \delta$.

Cesar Menor S. carried out a detailed comparative study. The reader can find the author's discussion in the referenced article. In particular, he shows that a Ca atom is differentiated by a Ca atom of α -Ca(HCOO)₂ coordinated by seven O atoms of two unique formate groups.

CRYSTALLOGRAPHY

α -Ca-formate is orthorhombic.

Space group: *Pbca*.

Unit : a (Å) 10.22943 b (Å) 6.25587 c (Å) 13.24297

V (Å³) 847.47 Z = 8 D(calc) = 2.040

The Ca atoms are distributed in dioctahedral layers.

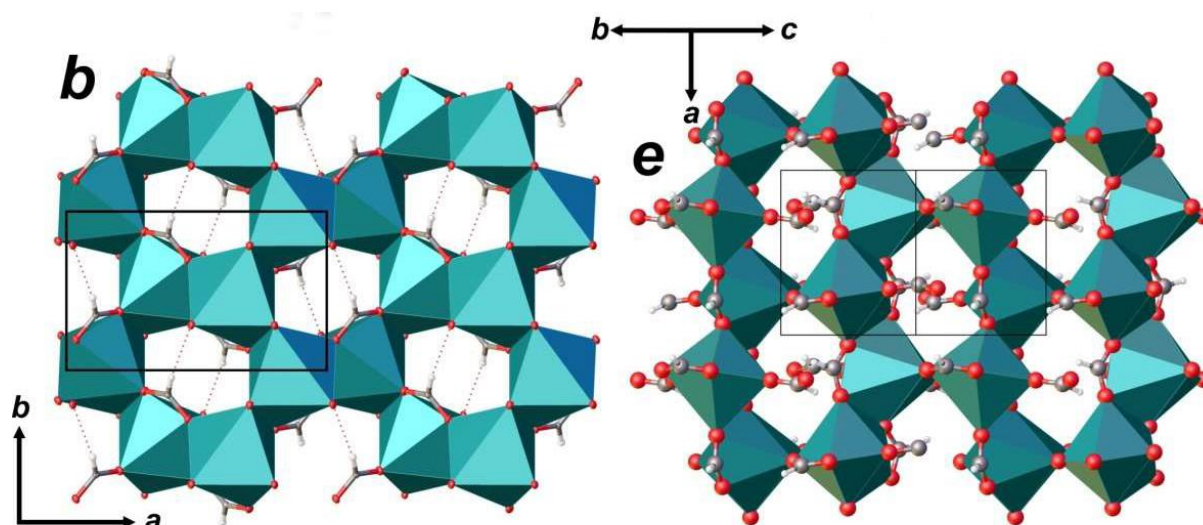


Fig. 7 – The two stable polymorphic phases of calcium formate.
 (b) α -Ca-formate - (e) Formicaite: Partial figure of article Ref. 3.
 Courtesy credit of Cesar Menor Salvan (2021).

WEDDELLITE $\text{Ca}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$

Given the organic origin of β -formicaite $\text{Ca}(\text{HCOO})_2$, many authors have denied it the status of mineral. However, its origin does not seem to us to be of an anthropogenic nature but rather biotic, since a similar molecule, weddellite, was discovered in Antarctica. It takes its name from the Weddell Sea. It is also

present in Oregon (USA). Formic acid (CH_2O_2 or HCOOH) is frequently found in nature. It is present in ants, in the stings of bees or in the stinging leaves of nettles. It intervenes in a preponderant way in the living as an elementary molecular brick. Its origin does not appear detrital. Its formula is $\text{Ca}(\text{C}_2\text{O}_4) \bullet 2\text{H}_2\text{O}$. Present in the Fleischer Glossary, it crystallizes in the tetragonal System.



Fig. 8 - Weddellite – Biggs, Sherman Co. Oregon, USA. © Saul Krotki 2009.

Weddellite, insoluble in water, is in fact the calcium oxalate of organic chemists. It has, however, been recognized as a mineral, since it was discovered in Nature, in Antarctica itself. It was defined under this name by the IMA in 1942. Moreover, it often (unfortunately) has an unexpected anthropogenic origin since it is one of the main components of kidney stones.

MINERAL OR NO ?

α -Ca-formiate - PROPRIETES²

Following his analysis of this polymorph of calcium formate $\alpha\text{-Ca}(\text{HCO}_2)_2$, Cesar Menor Salvan recently (May 1, 2021) introduced his discussion of its origin with these words :

² Biogenic Orthorhombic α -Calcium Formate from Sediments of Alkali Lake, Oregon, USA - Nikita V. Chukanov 1,2, Cesar Menor-Salvan & al. – Minerals 2021, 11, x. Formicaite_minerals-1190999(1).pdf.

"The extraordinary crystals of what in a first view were identified as formicaite (beta-calcium formate) turned out to be the orthorhombic polymorph, alpha-calcium formate.

To me, this is a very interesting finding not only because it is a previously undescribed mineral, but because it is a very remarkable example of a biomineral formed in very peculiar conditions.

The accumulation of formate to the point of precipitation and crystallization of centimetre-size crystals implies that the biological consortium are not metabolizing formate, accumulated by the anaerobic fermentation of organic matter. We hypothesized that this situation could be explained by the unique ecology of the Alkali lake (extremophilic, highly saline and high pH) and/or by a dramatic chemical contamination episode that suffered the lake decades ago, when tons of organochlorine compounds derived from the industrial synthesis of "orange agent" polluted the Alkali lake system. In any case, it is extraordinary the size and quality of the specimens. We performed a simulation of the conditions of the lake, and to form those crystals in that size it is necessary a high local formate concentration. Whether completely anthropogenic or not, the specimens are remarkable and, if you have one in your collection, you have a piece of a unique biochemical process and a piece to think about the long term effects of our interaction with environment."

Cesar Menor Salvan posed the problem this way :

Is this new mineral of anthropogenic origin? It is very likely because "agent orange" (used in Vietnam as a defoliant) is a cocktail of a dioxin and derivative products.

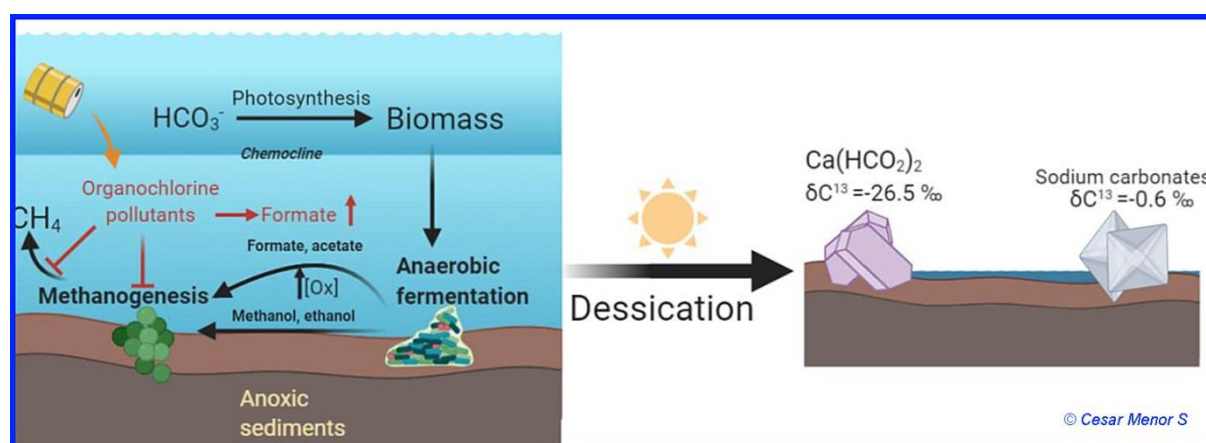


Fig. 9 – Origin of α - and β -Formicaites. © Cesar Menor Salvan.

However, apart from being the result of serious industrial pollution, one could wonder what other origin of a biotic nature (other than a polluting source)

could have given this new organic mineral such as, for example, what is the origin Antarctic weddellite, the source of which was certainly not anthropogenic. One might think that these organic radicals, whose structure is very simple, are likely to form under the conditions of a fetid (anaerobic) fermentation of plant debris.

However, it seems to us that formic acid has such a primary composition that it can be considered as one of the elementary bricks of Life, even before the intervention of amino acids, already much more elaborate molecules in which nitrogen takes part. We never talk about it, but formic acid is found in the development of DNA.

In fact the anthropic action was limited, by an unscrupulous coincidence, to "harden the environment" of the lake by pollution, to the point of eliminating the possibility of existence of some bacteria which usually destroy any source of formic acid. Consequently, formicaite (polymorph- β) was able to develop "naturally" in this specific environment, thanks to pollution but without its intervention in the constitution of the mineral. The attribution of mineral status is therefore justified. Although made up of an organic radical, and therefore not inorganic, it belongs to the Mineral Kingdom, which brings together the natural minerals of our planet.

This extension of the mineral world to organic minerals is not new, although there are only a few examples. This fact is supported by the case of urea recognized as a mineral since 1974 (The American Mineralogist 59, 874).

Urea formula: $\text{CO}(\text{NH}_2)_2$. Tetragonal System.

Yet urea is the very type of molecule of biological origin. Its role is very important because it participates in the degradation of nitrogen molecules in the body.

Wöhler made the first artificial synthesis of it, which caused a revolution at the time. He had synthesized an organic compound outside of a living organism.

DISCUSSION

Nature is adorably complex. Man therefore had to divide Science into various chapters. We find this dichotomy even in hospitals. The most important break differentiates Chemistry from Physics. It is obvious that sometimes there is no well-defined boundary between these disciplines. The same is true for inorganic chemistry and organic chemistry. The first is a more inorganic, the second more correlated to the world of carbon, in permanent expansion for

inert materials (plastics, drugs, etc.) and living (biochemistry). The IMA (International Mineralogical Association) recognized 5,780 official mineral species, in January 2022.

Among the 92 stable chemical elements, there is a very large exception, **carbon**. Physicochemists easily explain its properties. Carbon can unite with all the other elements of the Earth, and above all with itself, in moderately particular conditions. The bonds of organic compounds can be very stable or, on the contrary, have an extreme and subtle lability. The usual partners are found in the chemistry of Life, oxygen, sulphur, nitrogen, phosphorus, etc. (biochemistry) but carbon also combines with metals (organometallic chemistry putting so-called transition metals in unprecedented electronic (valence) situations, sometimes very unstable, thus allowing various catalytic reactions).

Fictionists (they are not "dangerous" but they could induce "fake news") have imagined that Life on other planets would be based on the chemistry of silicon, the closest chemical counterpart of carbon (homologous electron configuration). It is a total impossibility, silicon not possessing the flexibility of reactivity possessed by carbon. Generally speaking, silicon can almost only give very stable Si-O bonds (Si-Si bonds are exceptional), far too strong to initiate any Life whatsoever. The concepts of hybridizations of orbitals are unknown to it whereas they take part in the explanation of the performances of carbon (steric variability of chemical bonds).

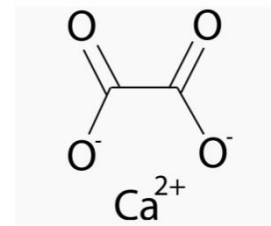
Since carbonic acid is also an organic compound that forms the limestone CaCO_3 , one could say that its carbonated salts (the limestone rock CaCO_3), should not be part of the minerals either, which in itself would be an absurd conclusion.

Indeed, we can consider that formicaite is written on a new palimpsest : biochemistry was erased there.

Isn't this return to the basics of organic chemistry, to the building blocks, a return to the mineral world? In which case the two polymorphs of formicaite would therefore be mineral species, in the proper sense of the term. It would be the same, although their constitution is more imposing, for other species such as whewellite, urea, thymine and others. There is also a common denominator to these molecules, they are all soluble in water. Water, as a solvent, is the source (the medium) in which Life can hatch.

The α -formicaite crystal is orthorhombic, but its structure is not yet published in the AMS reference tables.

For their part, supporters of the exclusive mineral world admit whewellite as a mineral because it is deposited in veins of hydrothermal origin. However, given the very tiny solubility of calcium oxalate CaC_2O_4 (0.0006 g/100 g (water, 18°C), it must be the result of a chemical decomposition reaction and not the result of hot solubilization of pre-existing CaC_2O_4 , in which there would be an original similarity with the crystallization of formicaite polymorphs.



Calcium oxalate.

In these particular crystallizations of oxalates and formates, these organic minerals are formed either because these molecules formed are very insoluble, or because the polluted environment has suppressed the bacteria that destroy the organic anion, whereas the corresponding salt is relatively soluble in water.

In addition, many other oxalates exist in which only the nature of the cation changes:

Weddellite	$\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	Tetragonal	4/m
Mellite	$\text{Al}_2\text{C}_6(\text{COO})_6 \cdot 16\text{H}_2\text{O}$	Tetragonal	4/m 2/m 2/m
Humboldtine	$\text{Fe}^{2+}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$	monoclinic	2/m
Glushinskite	$\text{Mg}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$	monoclinic	2/m
Katsarosite	$\text{Zn}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$	monoclinic	2/m
Lindbergite	$\text{Mn}^{2+}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$	monoclinic	2/m

And other cations like Ni^{2+} , Co^{2+} , etc.

Thus, oxalate anions from organic systems precipitated all these cations forming these rare, highly insoluble mineral species.

And formates anions form crystals by the drying out of the system in a very exceptional arid environment (Alkaly Lake, Oregon, for example).

Consequently, if we consider one of them as a mineral salt, all should be.