



## Study and analysis of the properties of organic and hydrocarbon aromatic metals

Hayfaa A. Mubarak <sup>1\*</sup>, Hussein Abdulkadhim Al-khafaji <sup>1</sup>, Wisam Abdul Jaleel Jawad <sup>1</sup>

<sup>1</sup> Babylon University, IRAQ

\*Corresponding author: [Haa82016@gmail.com](mailto:Haa82016@gmail.com)

### Abstract

Organic minerals are naturally occurring organic compounds with both a defined chemical composition & crystallographic properties. Their presence reflects the high concentration of certain organic compounds in natural environments. Therefore, the origin & the processes of formation of organic minerals will allow us to understand & the fate & behavior of organic molecules in the lithosphere. In order to contribute to the development of new developments in mineralogy, we divide organic minerals into two groups: (1) ionic organic minerals, in which organic anions & various cations are linked by ionic bonds, & (2) molecular organic minerals, in which organic electron molecules are linked to each other by weak intermolecular interactions. This overview includes four main themes. The first section deals with the general definition of organic minerals & the two groups named above. The second deals with the crystallochemistry & geochemistry of oxalates, the most typical ionic organic minerals. We first discuss the role of (H<sub>2</sub>O) <sub>0</sub>, because most minerals in this group incorporate (H<sub>2</sub>O) <sub>0</sub> in their crystal structures. Then, we describe the phase relationships among oxalated calcium minerals, hydrated & anhydrous, & in particular their structural hierarchy, these compounds being the most abundant organic ionic minerals. In addition, we describe by way of example the weak effect of Jahn-Teller caused by the Fe<sup>2+</sup> ion in humboldtin, [Fe<sup>2+</sup> (C<sub>2</sub>O<sub>4</sub>) • 2H<sub>2</sub>O]. The Fe<sup>2+</sup> ion causes a distortion of the octahedra of this organic mineral, although the effect is barely detected in inorganic minerals. The third theme deals with crystallochemistry & the formation process of aromatic polycyclic hydrocarbon (PAH) minerals, which are the most typical of the class of molecular organic minerals. In particular, we examine the case of karpatite (C<sub>24</sub>H<sub>12</sub>) & idrialite (C<sub>22</sub>H<sub>14</sub>). We conclude with a summary of the characteristics of organic minerals & a discussion of their contribution to the earth sciences & planets.

**Keywords:** Organic minerals, hydrocarbon, ionic, molecular

Mubarak HA, Al-khafaji HA, Jaleel Jawad WA (2020) Study and analysis of the properties of organic and hydrocarbon aromatic metals. Eurasia J Biosci 14: 651-657.

© 2020 Mubarak et al.

This is an open-access article distributed under the terms of the Creative Commons Attribution License.

### INTRODUCTION

All the organic mineral describe in a *Systems of Mineralogy*, are classified as *salts of organic acids*; however, molecular organic crystals like that karpatite (coron, C<sub>24</sub>H<sub>12</sub>) should be grouped separately, as salt are compound produce by the neutral reactions of acid & base. In additions, minerals species are traditional classified on the basic of the main, e.g., O<sup>2-</sup>, S<sup>2-</sup>, & Cl<sup>-</sup>, anionic complex, e.g., OH<sup>-</sup>, SO<sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> & Si<sub>x</sub>O<sub>y</sub><sup>z-</sup>, or lack of an anion, e.g., graphite native gold, & diamon (Mills et al. 2009). According to this traditional classification, organic minerals are to dived in this review into 2 groups:

(1) ionic organic mineral, in which organic anion & various cation is main held together by ionic bond, & (2) molecular organic minerals, in which electro- neutral organic molecules are bonded by weak intermolecular interactions. In other words, these two types of organic minerals can be distinguished by whether their structural unit is electrically charged (ionic organic mineral) or

neutral (molecular organic mineral). The former group contains 27 species of organic minerals, & the latter comprises 18 species; all 45 species of organic minerals in the current list of the Commission on New Minerals, Nomenclature & Classification of International Mineralogical Association (IMA/CNMNC list of mineral names: Nickel and Nichols 2008) & the newly reported ammine mineral, ammineite (Bojar et al. 2010) are classified into either of the two groups. Note the anionic parts of all ionic organic minerals contain relatively weak polar bonds, e.g., C-C, C-H, C-N, & N-H bonds, whereas electroneutral molecules in molecular organic minerals consist mainly of these bonds, being the most distinguishing characteristics of organic minerals.

In this review, we describe the crystal chemistry & geochemistry of oxalate & polycyclic aromatic

Received: August 2019

Accepted: November 2019

Printed: March 2020

hydrocarbon (PAH) minerals in detail to illustrate a new model of mineral formation, since they are the most common minerals in ionic & molecular organic minerals, respectively.

### DESCRIBE OF THE ORGANIC IN THE REVIEW

Some textbook in the geosciences define mineral as crystal line inorganic material that occur in natural environment (Kolay 2007). However, mineral are not limit to inorganic substance. The CNMNC IMA define mineral as follow *the mineral substance is a natural occurring solid that have been forme by using geological processes, either on Earth or in extrater- restrial bodie*. It have been known since the mid18th century that some organic compound, like hydrocarbon substance & organic salt, crystallize in natural environment (Brooke & Miller 1852). Mason & Berry (1968) mentioned oxalate & hydrocarbon mineral occurring in peat & coal, which demonstrate that organic mineral has been recognize since the early stage of modern mineral science.

### THE TRADITIONAL DEFINITION EXPLAIN THAT MINERAL IS

Formed by inorganic processes, but it is increase recognize that mineral may also be produce organically, e.g., calcium carbonate of mollusk shell (Klein and Dutrow 2008). Crystal of calcium oxalate, one of the most common organic mineral, they are also producing in the urinary systems in the humans body (Wesson and Ward 2007). Recognition of these materials have spawne a littele area of research, biomineralization, which is the study of the processes by which organism produce mineral (Weiner and Dove 2003). In addition, the definition of a mineral require both well-defined chemical composition & highly ordered atomic arrangement, criteria that exclude amber, the best known organic solid substance in the lithosphere, from the minerals catalogue.

In this review, graphite is excluded from the list of organic minerals. Polymorphs of carbon, e.g., diamond & fullerenes, should be included in a list of organic minerals if graphite is recognized as an organic mineral. The authors of the reviews & textbooks on organic geochemistry do discuss the occurrences & isotopic geochemistry of disordered graphite & carbonaceous substances. In addition, silicate minerals with organic ions, tsaregorodtsevite  $[N(CH_3)_4[Si_2(Si_{0.5}Al_{0.5})O_6]_2]$  (Pautov et al. 1993), kyan- oxalite  $[(Na,Ca,K)_8Al_6Si_6O_{24}(C_2O_4)_2]$  (Chukanov et al. 2009), & melanophlogite  $(Si_{46}O_{92} \cdot C_{2.2}H_{17.3}O_{5.4}S_{0.1})$  (Žák 1972) hosting organic molecules are not consid- ered as organic minerals in this review. This is because they are framework (alumino)silicate minerals similar to zeolite, & their basic crystal structure consist of  $SiO_4$  &  $AlO_4$  tetra hedra. A organic ions & mole- cules hoste by use them don't subs tan contribute to builds their framework

structures. On the other h&s, oxalate anion in sulfateoxalate mineral, coskrenite-(Ce)  $[(Ce,Nd,La)_2(SO_4)_2(C_2O_4) \cdot 8(H_2O)]$ , are electrostatic link to cations polyhedra, being the one of building block in the structures.

### BACKGROUND INFO

A lithosphere holds over 98.99% of a carbon on the Earth (Kempe 1979). Inorganic carbon, like in carbonate mineral, accounts for the 75%, & organic carbon, such as kerogen, makes up the rest. Sedimentary rock is the larg reposit of organic carbon, & account for over 40,000 time as that of living matters at the Earth surface. This high abundance shows that organic carbon in the lithosphere are important for a carbon cycle of the Earth. The approve mineral catalogue of the CNMN of lists only 45 specie of organic mineral, compare to over 4300 species of inorganic mineral. In the past, over 210 names of organic mineral existed; most of them were rejected as independent minerals species in later investigation). In *The System of Mineralogy*, 6<sup>th</sup> edition, Dana (1892) listed 75 minerals name for natural organic compound; however. The main reason for rejection is the problem of determining chemicals composition. Karpatite, the molecular crystal of coro- nene  $(C_{24}H_{12}, XII)$ , were first described as the  $C_{33}H_{17}O$  substance investigate by Piotrovskii (1955). However, Frank-Kamenetskii et al. 1967) revealed that karpatite from Trans-Carpathia & "pendletonite" from San Benito are the same species, as determined by an X-ray crystallographic study. Hence, the later name "pendletonite" was discredited (Nickel and Nichols 2008).

The possible reason for the confusion over chemical composition is follows: (1) several gram of mineral specimen was requiring for the chemical analysis in 1960s (Geissman et al. 1967), & (2) amorphous organic matters coexist with karpatite from Trans-Carpathia .). Hence it were assume that specimens of Piotrovskii (1955) is contaminated.

The few review & textbook regarding the occur- rences, chemistry, & crystal structures of organic minerals have been published so far (Dondi and Puggioli 1990, 1991, Gaines et al. 1997). Some textbook on organic geochemistry has chapter describe organic mineral. In this review, recent advanced in crystal chemistry & isotope geochemistry of organic mineral since the publication of these reference will be mention. In particular, oxalate & polycyclic aromatic hydrocarbon (PAH) mineral is the focus here; we discussed their contribution to new development in the mineral science.

### OXALATE MINERAL

Carboxylate mineral, e.g., oxalate (App.XIV), formate (App. XV), & acetate (App. XVI) mineral, constitute the largest family of organic minerals (24 species, **Table 1**).

**Table 1.** List of ionic organic minerals

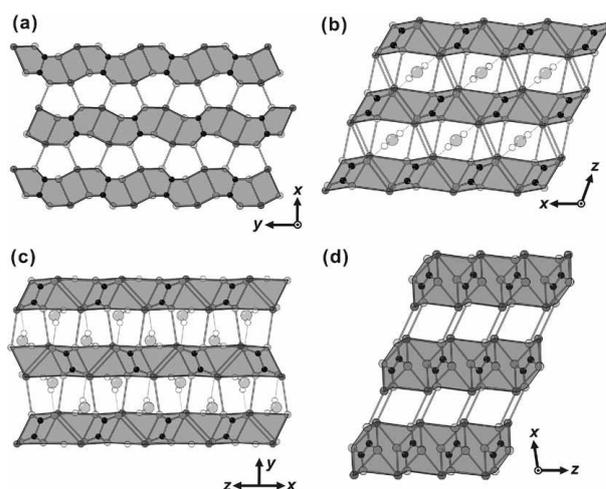
Classification	Mineral names	Chemical formula	References
Formate minerals	Formicite	Ca(HCOO) <sub>2</sub>	Chukanov <i>et al.</i> (1999)
	Dashkovaite	Mg(HCOO) <sub>2</sub> ·2H <sub>2</sub> O	Chukanov <i>et al.</i> (2000)
Acetate minerals	Hoganite	Cu <sup>2+</sup> (CH <sub>3</sub> COO) <sub>2</sub> ·H <sub>2</sub> O	Hibbs <i>et al.</i> (2002)
	Pacelite	CaCu(CH <sub>3</sub> COO) <sub>4</sub> ·6H <sub>2</sub> O	Hibbs <i>et al.</i> (2002)
	Calcicite	Ca <sub>2</sub> Cl(CH <sub>3</sub> COO) <sub>4</sub> ·10H <sub>2</sub> O	Van Tassel (1945)
Oxalate minerals	Natroxalate	Na <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> )	Khomyakov <i>et al.</i> (1996)
	Oxanmite	(NH <sub>4</sub> ) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> )·H <sub>2</sub> O	Winchell & Benoit (1951)
	Glushinskite	Mg(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	Wilson <i>et al.</i> (1980)
	Whewellite	Ca(C <sub>2</sub> O <sub>4</sub> )·H <sub>2</sub> O	Hofmann & Bemasoni (1998)
	Weddellite	Ca(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	Bannister & Hey (1936)
	Caoxite	Ca(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	Basso <i>et al.</i> (1997)
	Novgorodovite	Ca <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> )Cl <sub>2</sub> ·2H <sub>2</sub> O	Chukanov <i>et al.</i> (2001)
	Lindbergtite	Mn <sup>2+</sup> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	Atencio <i>et al.</i> (2004)
	Humboldtine	Fe <sup>2+</sup> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	Manasse <i>et al.</i> (1911)
	Moolooite	Cu <sup>2+</sup> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·nH <sub>2</sub> O	Clarke & Williams (1986)
	Stepanovite	NaMgFe <sup>3+</sup> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·8-9H <sub>2</sub> O	Knipovich <i>et al.</i> (1963)
	Zhemchuzhnikovite	NaMg(Al,Fe <sup>3+</sup> )(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	Knipovich <i>et al.</i> (1963)
	Wheatleyite	Na <sub>2</sub> Cu(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	Rouse <i>et al.</i> (1986)
	Minguzsite	K <sub>2</sub> Fe <sup>2+</sup> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	Garavelli (1955)
	Zugshunite-(Ce)	(Ce,Nd,La)Al(SO <sub>4</sub> ) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> )·8H <sub>2</sub> O	Rouse <i>et al.</i> (2001)
	Levinsonite-(Y)	(Y,Nd,La)Al(SO <sub>4</sub> ) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> )·12H <sub>2</sub> O	Rouse <i>et al.</i> (2001)
	Coskrenite-(Ce)	(Ce,Nd,La) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> )·8H <sub>2</sub> O	Peacor <i>et al.</i> (1999)
Mellitate mineral	Mellite	Al <sub>2</sub> (C <sub>6</sub> (COO) <sub>4</sub> ) <sub>2</sub> ·16H <sub>2</sub> O	Barth & Ksanda (1933)
Citrate mineral	Earlandite	Ca <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	Bannister & Hey (1936)
Cyanide mineral	Kafeyhydrocyanite	K <sub>2</sub> Fe <sup>2+</sup> (CN) <sub>2</sub> ·3H <sub>2</sub> O	Povarennykh & Rusakova (1973)
Thiocyanate mineral	Julienite	Na <sub>3</sub> Co <sup>2+</sup> (SCN) <sub>4</sub> ·8H <sub>2</sub> O	Schoep (1928)
Ammine mineral	Ammineite	Cu <sup>2+</sup> Cl <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub>	Bojar <i>et al.</i> (2010)

Their crystal structure consist of both carboxylatebearing anion & various cation. Most of them incorporate electro statically neutral water molecule, (H<sub>2</sub>O)<sup>0</sup>, into their crystal structure.

Oxalate mineral is the large group of organic mineral; 18 specie are reporte so far (**Table 1**). Organic compound has 2 carboxylic groups in each molecule is called dicarboxylic acids (Vollhardt and Schore 2002). Oxalic acid is the smalle & simple compound in dicarboxylic acids & is ubiquitou in natural environment, e.g., soil natural water (Klarup 1997), & aerosol (Kawamura and Kaplan 1987, Yu et al. 2005). Oxalate mineral contain various cation like alkalis, alkaline earth, transition metal, & rare earth element. The crystal chemistry of the simple system, oxalate compound containing monovalent cation, will be describe in the following section, & the role of the H<sub>2</sub>O molecule in their crystal structure will be discuses.

### The Role of Water Molecule in the Crystal Structure of Oxalate Salt

The general formula of monovalent oxalate salt can be expresse as:  $M_2(C_2O_4) \cdot nH_2O$  ( $M = Ag, Li, Na, K, Rb, Cs, NH, Tl; n = 0, 1, 2$ : Note that in this review, we are concerne only with stable compound at room temperatures & pressure, since their stable regime depend on the hydration numbers (Dinnebier et al. 2003, Weller et al. 2007). Their crystal structure is commonly layer, & consist of a monovalent cation & an oxalate anion (**Fig. 1**), & H<sub>2</sub>O molecules is occluded between interlayer spaces ( $M = NH, K, Rb, Cs$ ). It is notable that both anhydrous  $Rb_2(C_2O_4)$  &  $Cs_2(C_2O_4)$  are unstable in air & immediately hydrate to  $Rb_2(C_2O_4) \cdot H_2O$  &  $Cs_2(C_2O_4) \cdot 2H_2O$ , respective (Dinnebier et al. 2003). This instability suggest that interlayer H<sub>2</sub>O molecule stabilize



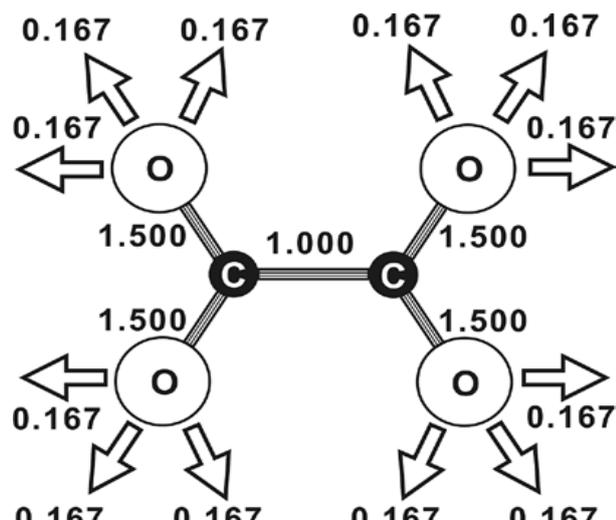
**Fig. 1.** Crystal structure of (a) natroxalate, Na<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>) (Jeffrey and Parry 1954), (b) Rb<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)·H<sub>2</sub>O (Echigo and Kimata 2006)

their crystal structure in air. This role of the H<sub>2</sub>O molecule were explained quantitative by Echigo & Kimata (2006) in term of bond valence theory

(Brown 1981, 2002, 2009), which is based on the Lewis acid–base concept (Lewis 1923, 1966).

From any ionic crystals, the empty valence shell of action interact with the filled valence shell of an anion: the former act as an electron donor, & the latter as an electron acceptor (West 1988). Their behavior toward a bonding electron pair corresponded to Lewis acid & base, respective, & thus we can defined the Lewis acid strength of the cation & the Lewis base strength of the anion by Brown definition (1981, 2002, 2009): the Lewis acid or base strength of the cation or anion are equal to characteristic valence = atomic (formal) valence divid by the mean coordination number. This definition of Lewis acid & base strengths lead to a specific criterion for chemical bonding, *the valence-match principle* (Brown 1981, 2002, 2009): the most stable structure will form if the Lewis acid strength of the cation close matche the Lewis base strength of the anion. Developing this concept, a *binary representation of crystal structure* were proposed (Hawthorne 1985, 1992a). Only one describe both the interaction between the Lewis acid parts & Lewis base parts of crystal structure & their relationship with stabil. These concept is general use to validate the chemical composition & crystal structures of mineral. The roles of H<sub>2</sub>O molecule in hydrous mineral are also examine in light of these concept (Hawthorne 1992b, 1994, 1997, Schindler & Hawthorne 2001a, 2004).

In oxalate salt, the oxalate anions are the Lewis base, & the cations are the Lewis acid component in term of the abovementioned concept. The Lewis acidity of various cation, which are deduce from the statistical analysis of the inorganic crystalstructure database (ICSD, Allen 2002), can be taken from the tables of Brown (1988, 2002). On the other h&, the Lewis basic of

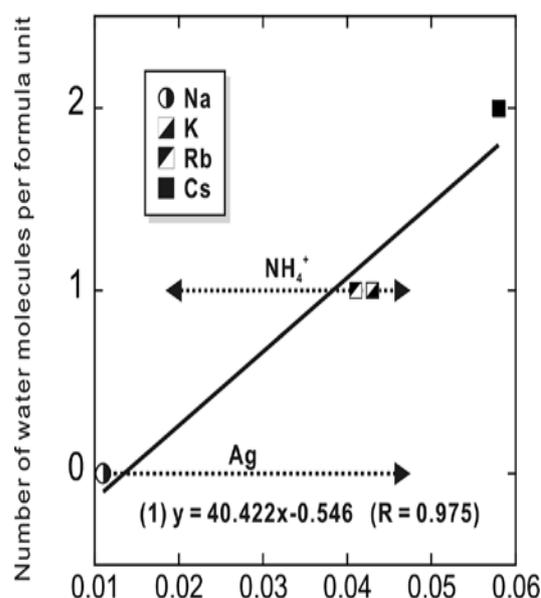


**Fig. 2.** Computing of Lewis basic ( $\nu u$ ) for oxalate anions  $[(C_2O_4)^{2-}]$  depends on the assumptions that each constituents atom of O2 is 4-coordinat

organic anion include the oxalate anion is not listed in these tables. Hence we have to calculate the Lewis base strength of the oxalate anion to examine an interaction of Lewis acid & base in oxalate salt.

This calculation is successfully constrained by the general observation (Hawthorne 1992b) that normal, it is adequate for one to use the coordination numbers of [4] for O2. On the basis of the connective that assumes a coordination number of [4] for O2, then the oxalate anion needs 12 additional bonds from the bonding cation (**Fig. 2**). These 12 bonds must satisfy the requirement from  $(C_2O_4)^{2-}$ , & thus the average bond valence required by the anion is  $2/12 \approx 0.168 \nu u$  (valence units); this is the Lewis basicity of the oxalate anion (Echigo and Kimata 2006). This bond valence value ( $0.167 \nu u$ ) is an ideal value for the oxalate anion, which matches up with the Lewis acidity of  $0.157 \nu u$  for Na (Brown 1988). The  $Na^+-(C_2O_4)^{2-}$  bond certainly fits the valence matching principle, & therefore sodium oxalate is the stable mineral. It occurs in the hydrothermally altered pegmatite (Khomyakov 1996). Echigo & Kimata (2006) first demonstrated that the Lewis basicity of the organic anion can be deduced.

(c)  $Cs_2(C_2O_4) \cdot 2H_2O$  (Kholodkovskaya et al. 1990) & (d)  $Tl_2(C_2O_4)$  (Nagy et al. 2005). All the oxalate complexes have a layer structure. S, rubidium, cesium, & thallium atoms are shown in dark gray, O2 in pale gray, C in black, & H in white. In the same way as for inorganic O, & both the *valence-matching principle* & the *binary presentations of a crystal structure* are applicable to organic minerals. Our work suggests that the Lewis basicity of other organic anions, format (App&acetate App. XVI) anion, can be deduced in the same way, & that the organizations of organic minerals into the structural hierarchy are indispensable to minerals. These organizations should provide a significant aid in determining unknown structures & will be provided considerable



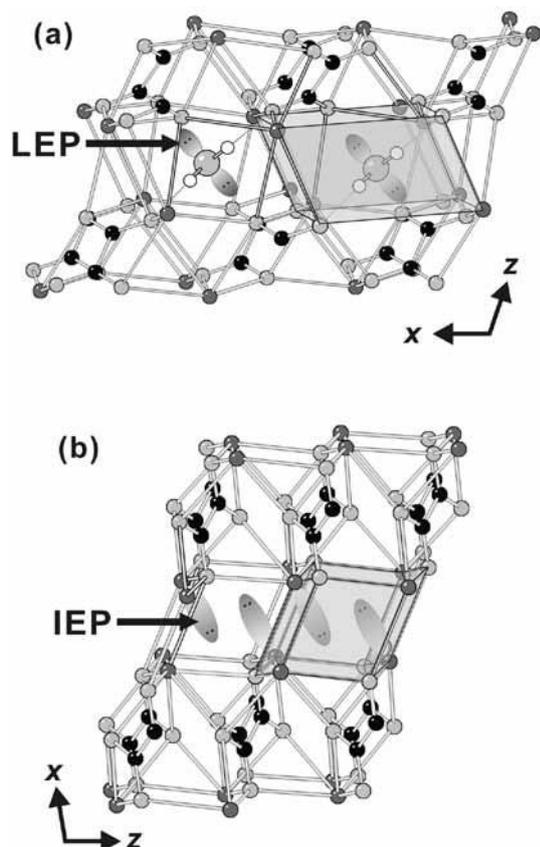
Difference between the Lewis acidity of cations and the Lewis basicity of anions ( $\nu u$ )

**Fig. 3.** Difference between the Lewis acidity of cations and the Lewis basicity of anions ( $\nu u$ )

insight into an underlying control on the topology of chemical bonds & mineral paragon. These types of application, which succeed in phosphate.

Most actions don't match up with the Lewis basicity of the oxalic anions,  $0.1670 \nu u$ , &  $H_2O$  molecules commonly must incorporate into the structures of an oxalate salt. Consider the solvent-free alkali oxalates, the Lewis basicity of K, Rb, & Cs is  $0.1260$ ,  $0.1240$ , &  $0.1090 \nu u$ , respectively. In terms of the valence matching principles, the supposed anhydrous alkali oxalate is not a stable compound because they have a significant difference in Lewis basicity or acidity strengths between these alkali cations & oxalic anions. An anhydrous oxalate hydrate readily in the presence of  $H_2O$  to produce hydrous oxalates, as expected (Dinnebier et al. 2003); this instability is explained by the violation of the valence matching principles. Thus, the incorporation of  $H_2O$  molecules into the structures leads to compensation for the differences between the Lewis acidity of a cation & the Lewis.

Oxalate anions, which show that the  $H_2O$  molecule in the hydrous oxalate salt plays a crucial role as a bond valence mediator. **Fig. 3** shows the positive correlations between the difference in Lewis acidity or basicity & the numbers of  $H_2O$  molecules per formula unit. These correlations can be simply approximated by the equations shown in **Fig. 3**, although Ag &  $NH_4^+$  are omitted from the calculation because they exhibit wide ranges of Lewis acidity.



**Fig. 4.** Crystal structures of (a)  $\text{Rb}_2(\text{C}_2\text{O}_4)\cdot$ . These 2 complex has a layer structures, where inter layer occupant are  $\text{H}_2\text{O}$  molecule & LEPs in the former, & the only IEPs in the latter. IEPs is nearly parallel to each other in the similar structure. Rubidium & thallium atom is show in dark gray, O2 in pale gray, C in black, & H in white. LEP: lone electronS pair, IEP: inert electron S pair.

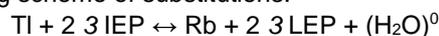
### Ti Electron as a Proxy for the H<sub>2</sub>O in Oxalate Complex

The  $\text{H}_2\text{O}$  molecules have a pair of lone electron, so the TI actions have a pair of nonbonding electron call “insert electrons pair (IEP).” Thus the coordination’s environments of TI are distort (Downs 1993). The anhydrous thallium oxalate (Fig. 1d) have a layer structures, a same as other monova oxalates complex, & the IEPs of TI cation is position between the interlay space (Fig. 4b). The crystal structures of rubidium oxalate monohydrates (Fig.1b) are close simi to that of anhydrous thallium oxalates, though the former have  $\text{H}_2\text{O}$  molecule in the interlayer space (Fig. 4a). This structur similar can ascrib to their ionic radii, 1.590 Å for TI& 1.610 Å for Rb (Shannon 1976); however, the lack of  $\text{H}_2\text{O}$  molecule in thallium oxalate cannot account for only by a ionic radii.

**Fig. 3.** Hydration numbers in oxalate complex *versus* the differences between Lewis acidity of their cation & Lewis basic of their anions. The regressions line, which are direct correlat to K,NA,Cs & Rb oxalate, are giv by equations (1). The dott arrow represent the range of their

difference for NH & Ag oxalate; they offer the wide ranges of Lewis acidity (Brown 2002).

Either IEPs or  $\text{H}_2\text{O}$  molecule in these 2 structures reveal that both the position & direction of IEPs in TI cation is close similar to those of lone electrons pairs (LEPs) in  $\text{H}_2\text{O}$  molecule (Fig. 4), which lead to the following scheme of substitutions:



where represent vacant interlayer site. This equations suggest that inter layer non bonding electron pair, both IEP & LEP contribute to the stabilization of crystal structures’ of the like topology.

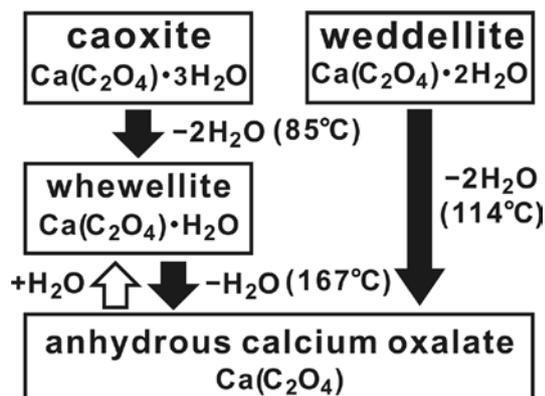
Substitution including nonbonding electron pair & the role of  $\text{H}_2\text{O}$  molecule in oxalate complex is revealed by examining monovalent oxalate complexes in terms of elemental chemical-bonding theory. We have no other examples corresponding to this series. Hydrated crystals of isotypic structures containing *p*-block elements, e.g.,  $\text{Pb}^{2+}$  &  $\text{Sn}^{2+}$ , might have the same mechanism of substitution.

### Crystal Chemistry & Geochemistry of Calcium Oxalate Minerals

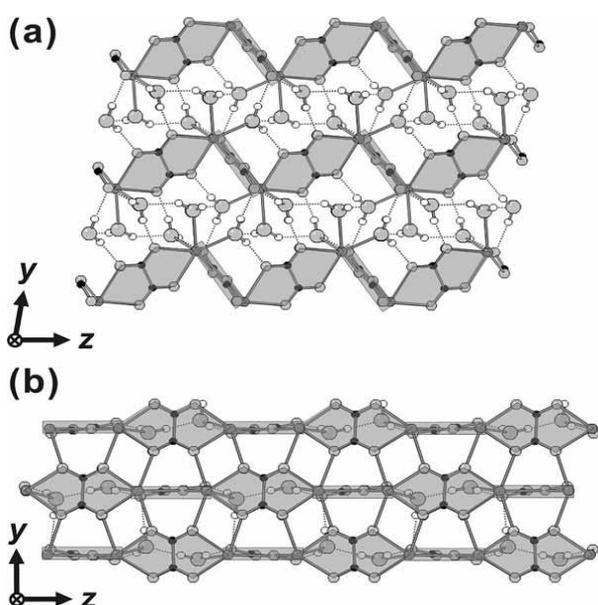
Calcium oxalate minerals (COMs) are the most common family of organic minerals in natural environments (Gaines et al. 1997). This group consists of whewellite [ $\text{Ca}(\text{C}_2\text{O}_4)\cdot\text{H}_2\text{O}$ ], weddellite [ $\text{Ca}(\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$ ], & caoxite [ $\text{Ca}(\text{C}_2\text{O}_4)\cdot 3\text{H}_2\text{O}$ ] (Basso et al. 1997). These minerals commonly occur in carbonate concre- tions, marine & lake sediments, hydrothermal veins, & lignite (Gude et al. 1960, Hyde and L&y 1966, Matsubara and Ichikura 1975, Žák and Skála 1993, Kouk- ouzas et al. 2010). Whewellite is the only COM that occurs in meteorites (Fuchs et al. 1973), formed by hydrothermal alteration of the parent body (Brearley and Jones 1999, Tyra et al. 2007). Note that COMs are the most common biominerals in plants (Franceschi and Horner 1980, Franceschi and Nakata 2005), & they also are widely recognized in the life sciences because of their common association with kidney stone disease (Lowenstam and Weiner 1989, Wesson and Ward 2007).

### Hydration–Dehydration Mechanisms in COMs

Whewellite, the monohydrate COM, is the most common & stable mineral among the three COMs (Gaines et al. 1997). Fig. 5 shows the dehydration temperature of those COMs; that of whewellite is the highest (whewellite: 167°C, weddellite: 114°C, caoxite: 85°C). The physical properties of COMs vary depending on the hydration states (Basso et al. 1997), which suggests that  $\text{H}_2\text{O}$  molecules in their crystal structures play a significant role. The hydration–dehy- dration processes of COMs have been extensively studied by many investigators (Frost and Weier 2003, 2004, Klopogge et al. 2004, Wiedemann and Bayer 1988), & COMs are even used as st&ard samples for calibration of thermal analysis instruments (Sepe 1997, Wunderlich 2005). In this review, the hydration– dehydration



**Fig. 5.** Scheme of the phase transitions in the calcium oxalate minerals. Black & white arrows show the dehydration & hydration reactions, respectively



**Fig. 6.** Crystal structures of (a) caoxite,  $\text{Ca}(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$  (Basso et al. 1997) & (b) whewellite,  $\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$  (Echigo et al. 2005). Both of the structures consist of shaded sheet structures

mechanisms of COMs will be described in light of the topology of chemical bonds in their crystal structures (Clausen 2018, Ogamba et al. 2017).

**Fig. 5** is a summary of hydration–dehydration paths compiled from various sources in the literature (Echigo et al. 2005, Frost and Weier 2003, Wiedemann and Bayer 1988). As shown in **Fig. 5**, caoxite, the trihydrate COM, dehydrates & transforms into whewellite directly, not through the dihydrate COM, weddellite. Whewellite dehydrates & transforms into anhydrous COM, which hydrates on cooling & returns to whewellite. However, whewellite does not hydrate into caoxite. Echigo et al. (2005) examined the network of hydrogen bonds in whewellite & revealed the dehydration mechanism of caoxite from its bonding topology. **Fig. 6** shows the crystal structures of caoxite (Deganello et al. 1981) & whewellite (Echigo et al. 2005); both of them have

similar layer structures. Both layer structures consist of  $\text{Ca}^{2+}$  & the oxalate anion, though those of caoxite are corrugated (**Fig. 6a**) & those of whewellite are flat (**Fig. 6b**). The corrugated layer structure of caoxite is attributed to the interlayer  $\text{H}_2\text{O}$  molecules that link the layers *via* the hydrogen bonds (**Fig. 6a**). On the other h&, whewellite does not have interlayer  $\text{H}_2\text{O}$  molecules & the Ca–oxalate bonds link the layers directly (**Fig. 6b**). Echigo et al. (2005) pointed out that the corrugated layers in caoxite get flattened & bonded directly upon dehydration.

## CONCLUSION

The remarkable characteristics of organic minerals are summarized as follows:

(1) Organic minerals are divided into ionic organic minerals and molecular organic minerals.

(2) Pairs of non-bonding electrons play a significant role in the crystal structures of ionic organic minerals, which accounts for the roles of  $\text{H}_2\text{O}$  molecules, inert lone pairs, and the Jahn–Teller effect in those structures.

(3) Molecular mixing occurs in molecular organic minerals and leads to molecular solid-solutions.

(4) In the process of formation of organic minerals, the formation of structural units, such as organic acid anion and PAH molecules, precedes their migration and concentration. The first stage includes the formation or cleavage of C–C bonds, but the latter stage does not. Minerals are the basic materials of the Earth, and virtually everything one does in the Earth Sciences involves minerals in one way or another (Hawthorne 1993). Although we have used the strict and traditional definition of a mineral in this review, it is not necessary to limit subjects in mineralogy to that definition, since they range widely from biominerals to non-crystalline materials, and from a living body to an extraterrestrial body. In natural environments, the distinction between inorganic and organic materials is obscure, and thus the interactions between inorganic and organic materials are ubiquitous. Lichens and fungi living on mineral surfaces produce organic acids and facilitate the dissolution of heavy metals such as Cd, Pb, and Zn (Fomina et al. 2005). Many oxalate minerals, such as moolooite  $[\text{Cu}_2+(\text{C}_2\text{O}_4) \cdot n\text{H}_2\text{O}]$  and glushinskite  $[\text{Mg}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}]$ , are products of the interaction (Wilson et al. 1980, Clarke and Williams 1986). Organic minerals are expected to be promising biomarkers in the detection of life and in the recognition of biological activity in the geological records of extraterrestrial material, such as Mars (Frost et al. 2003, Jehlička and Edwards 2008, Jehlička et al. 2009). If we consider such products of organic–inorganic interactions and living organisms as members of the mineral kingdom, we could make unlimited contributions to many branches of Earth and planetary sciences.

## REFERENCES

- Allen F (2002) The Cambridge structural database: a quarter of a million crystal structures and rising. *Acta Crystallogr B* 58: 380-388.
- Anderson KB, Crelling JC. (1995) *Amber, Resinite, and Fossil Resins*. American Chemical Society (ACS Symp. Ser. 617), Washington, D.C.
- Atencio D, Coutinho JMV, Graeser S, Matioli PA, Menezes Filho LAD (2004) Lindbergite, a new Mn oxalate dihydrate from Boca Rica mine, Galileia, Minas Gerais, Brazil, and other occurrences. *Am. Mineral* 89: 1087-1091.
- Bailey EH (1962) Mercury in the United States. *U.S. Geol. Surv., Mineral Resources Map* 30.
- Bannister RFA, Hey MH (1936) Report on some crystalline components of the Weddell Sea deposits. *Disc. Rep* 13: 60-69.
- Barth TFW, Ksanda CJ (1933) Crystallographic data on mellite. *Am. Mineral* 18: 8-13.
- Basso R, Lucchetti G, Zefiro L, Palenzona A (1997) Ca oxite,  $\text{Ca}(\text{H}_2\text{O})_3(\text{C}_2\text{O}_4)$ , a new mineral from the Cerchiara mine, northern Apennines, Italy. *Neues Jahrb. Mineral., Monatsh.* 84-96.
- Becker U, Prieto M (2006) Solid solutions: from theory to experiment. *Chem. Geol* 225: 173-175.
- Blair NE, Carter Jr. WD (1992) The carbon isotope biogeochemistry of acetate from a methanogenic marine sediment. *Geochim. Cosmochim Acta* 56: 1247-1258.
- Blumer M (1975) Curtisite, idrialite and pendletonite, polycyclic aromatic hydrocarbon minerals: their composition and origin. *Chem. Geol* 16: 245-256.
- Bojar H-P, Walte RF, Baumgartner J, Färber G (2010) Ammineite,  $\text{CuCl}_2(\text{NH}_3)_2$ , a new mineral species with an ammine complex: mineral data and crystal structure. *Can. Mineral* 48: 1359-1371.
- Bouška V, Císařová I, Skála R, Dvořák Z, Zelinka J, Žák K (1998) Hartite from Bílina. *Am. Mineral* 83: 1340-1346.
- Bowen NL (1928) *The Evolution of The Igneous Rocks*. Princeton University Press, Princeton, New Jersey.
- Brearley AJ, Jones RH (1999) Chondritic meteorites. In *Planetary Materials* (J. J. Papike, ed.). *Rev. Mineral* 36: 3-1 – 3-398.
- Bridge PJ (1973) Urea, a new mineral, and neotype phosphamite from Western Australia. *Mineral. Mag* 39: 346-348.
- Clausen E (2018) Probable deep erosion by continental ice sheet melt water floods: Chalk Buttes area of Carter County, Montana, USA. *International Journal of Geography and Geology*, 7(1): 14-26.
- Ogamba EN, Ebere N, Ekuere MC (2017) Assessment of Physico-Chemical and Zooplankton Assemblages in Some Ponds within Wilberforce Island, Nigeria. *J. Environ. Treat. Techniq*, 5(1): 38-50.