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CRYSTAL CHEMISTRY AND GENESIS OF ORGANIC MINERALS: A REVIEW OF OXALATE AND POLYCYCLIC AROMATIC HYDROCARBON MINERALS

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ABSTRACT

Organic minerals are natural organic compounds with both a well-defined chemical composition and crystallographic properties; their occurrences reveal traces of the high concentration of certain organic compounds in natural environments. Thus the origin and process of formation of organic minerals will lead us to understand the fate and behavior of the organic molecules in the lithosphere. With the aim of their contribution to new developments in mineralogy, we subdivide organic minerals into two groups: (1) ionic organic minerals, in which organic anions and various cations are held together by ionic bonds, and (2) molecular organic minerals, in which electroneutral organic molecules are bonded by weak intermolecular interactions. This review is composed of four sections. The first section is concerned with the definition of both organic minerals and the above two groups. The second deals with crystal chemistry and geochemistry of oxalate minerals, which are the most typical ionic organic minerals. In this section, the role of (H₂O)⁰ is first discussed, as most oxalate minerals incorporate (H₂O)⁰ into their crystal structures. Then the phase relationships among hydrous and anhydrous calcium oxalate minerals, namely their structural hierarchy, are described, owing to the fact that they are the most abundant ionic organic minerals. In addition, the weak Jahn–Teller effect of the Fe²⁺ ion is exemplified in humboldtine [Fe²⁺(C₂O₄)•2H₂O]. The Fe²⁺ ion causes distortions of octahedra in this organic mineral, though the effect has hardly been observed in inorganic minerals. In the third section, we describe the crystal chemistry and process of formation of polycyclic aromatic hydrocarbon (PAH) minerals, which are the most typical molecular organic minerals. Those of karpatite (C₂₄H₁₂) and idrialite (C₂₂H₁₄) are particularly considered in detail. In the fourth section, we summarize the characteristics of organic minerals and discuss their contribution to Earth and planetary sciences.

Keywords: organic minerals, oxalate, polycyclic aromatic hydrocarbons, whewellite, karpatite, ionic crystals, molecular crystals, structural units, structural hierarchy, carbon isotopic composition.

SOMMAIRE

Les minéraux organiques sont des composés organiques naturels ayant à la fois une composition chimique et des propriétés cristallographiques bien définies. Leur présence témoigne de la concentration élevée de certains composés organiques dans les milieux naturels. Donc, l'origine et les processus de formation des minéraux organiques nous permettront de comprendre le sort et le comportement de molécules organiques dans la lithosphère. Dans le but de contribuer à l'essor de nouveaux développements en minéralogie, nous divisons les minéraux organiques en deux groupes: (1) minéraux organiques ioniques, dans lesquels les anions organiques et divers cations sont liés par des liaisons ioniques, et (2) minéraux organiques moléculaires, dans lesquels

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les molécules organiques électroneutres sont liées les unes aux autres par de faibles interactions intermoléculaires. Cette vue d'ensemble comprend quatre thèmes principaux. La première section porte sur la définition générale des minéraux organiques et des deux groupes nommés ci-haut. La deuxième porte sur la cristallographie et la géochimie des oxalates, les minéraux organiques ioniques les plus typiques. Nous discutons d'abord du rôle de $(\text{H}_2\text{O})^0$, parce que la plupart des minéraux de ce groupe incorporent $(\text{H}_2\text{O})^0$ dans leurs structures cristallines. Ensuite, nous décrivons les relations de phases parmi les minéraux oxalatés de calcium, hydratés et anhydres, et en particulier leur hiérarchie structurale, ces composés étant les minéraux organiques ioniques les plus abondants. De plus, nous décrivons à titre d'exemple le faible effet de Jahn–Teller causé par l'ion Fe^{2+} dans la humboldtine, $[\text{Fe}^{2+}(\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}]$. L'ion Fe^{2+} cause une distorsion des octaèdres de ce minéral organique, quoique l'effet est à peine décelé dans les minéraux inorganiques. Le troisième thème traite de la cristallographie et du processus de formation de minéraux hydrocarbonés polycycliques aromatiques (PAH), qui sont les plus typiques de la classe de minéraux organiques moléculaires. En particulier, nous examinons le cas de la karpatite ($\text{C}_{24}\text{H}_{12}$) et de l'idrialite ($\text{C}_{22}\text{H}_{14}$). Nous terminons avec un résumé des caractéristiques des minéraux organiques et une discussion de leur contribution aux sciences de la Terre et des planètes.

(Traduit par la Rédaction)

Mots-clés: minéraux organiques, oxalate, hydrocarbures polycycliques aromatiques, whewellite, karpatite, cristaux ioniques, cristaux moléculaires, unités structurales, hiérarchie structurale, composition isotopique du carbone.

INTRODUCTION

All organic minerals described in *The System of Mineralogy*, 8th edition (Gaines *et al.* 1997), are classified as *salts of organic acids*; however, molecular organic crystals such as karpatite (coronene, $\text{C}_{24}\text{H}_{12}$) should be grouped separately, as salts are compounds produced by the neutralization reaction of acid and base (Myers 2003). In addition, mineral species are traditionally classified on the basis of the main anion, *e.g.*, O^{2-} , S^{2-} , and Cl^- , anionic complex, *e.g.*, OH^- , SO_4^{2-} , CO_3^{2-} , PO_4^{3-} and $\text{Si}_x\text{O}_y\text{Z}^{z-}$, or lack of an anion, *e.g.*, native gold, graphite, and diamond (Mills *et al.* 2009). According to this traditional classification, organic minerals are divided in this review into two groups: (1) ionic organic minerals, in which organic anions and various cations are mainly held together by ionic bonds, and (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, and the latter comprises 18 species; all 45 species of organic minerals in the current list of the Commission on New Minerals, Nomenclature and Classification of International Mineralogical Association (IMA/CNMNC list of mineral names: Nickel & Nichols 2008) and 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, and N–H bonds, whereas electro-neutral 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 and geochemistry of oxalate and polycyclic aromatic hydrocarbon (PAH) minerals in detail to illustrate a

new model of mineral formation, since they are the most common minerals in ionic and molecular organic minerals, respectively.

DEFINITION OF ORGANIC MINERALS IN THIS REVIEW

Some textbooks in the geosciences define minerals as crystalline inorganic materials that occur in natural environments (*e.g.*, Wills & Napier-Munn 2006, Koly 2007). However, minerals are not limited to inorganic substances. The CNMNC of IMA defines minerals as follows (Nickel & Grice 1998): *a mineral substance is a naturally occurring solid that has been formed by geological processes, either on Earth or in extraterrestrial bodies*. It has been known since the mid-18th century that some organic compounds, such as hydrocarbon substances and organic salts, crystallize in natural environments (Brooke & Miller 1852). Mason & Berry (1968) mentioned oxalate and hydrocarbon minerals occurring in peat and coal, which demonstrates that organic minerals have been recognized since the early stages of modern mineral science.

The traditional definition explains that minerals are formed by inorganic processes, but it is increasingly recognized that minerals may also be produced organically, *e.g.*, calcium carbonate of mollusk shells (Klein & Dutrow 2008). Crystals of calcium oxalate, one of the most common organic minerals, are also produced in the urinary system in the human body (Wesson & Ward 2007). Recognition of these materials has spawned a new area of research, biomineralization, which is the study of the processes by which organisms produce minerals (Weiner & Dove 2003). In addition, the definition of a mineral requires both well-defined chemical composition and highly ordered atomic arrangement, criteria that exclude amber, the best known organic solid substance in the lithosphere, from the mineral catalogue. For the purpose of this review, the traditional and restrictive distinction of mineral is used, as many comprehensive reviews and textbooks concerning

amorphous organic matter and biominerals have been published (Lowenstam & Weiner 1989, Anderson & Crelling 1995, Franceschi & Nakata 2005).

In this review, graphite is excluded from the list of organic minerals. Polymorphs of carbon, *e.g.*, diamond and fullerenes, should be included in a list of organic minerals if graphite is recognized as an organic mineral. The authors of the reviews and textbooks on organic geochemistry do discuss the occurrences and isotopic geochemistry of disordered graphite and carbonaceous substances. In addition, silicate minerals with organic ions, tsaregorodtsevite $[\text{N}(\text{CH}_3)_4[\text{Si}_2(\text{Si}_{0.5}\text{Al}_{0.5})\text{O}_6]_2]$ (Pautov *et al.* 1993), kyanoxalite $[(\text{Na},\text{Ca},\text{K})_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{C}_2\text{O}_4)_2]$ (Chukanov *et al.* 2009), and melanophlogite $(\text{Si}_{46}\text{O}_{92}\cdot\text{C}_{2.2}\text{H}_{17.3}\text{O}_{5.4}\text{S}_{0.1})$ (Žák 1972) hosting organic molecules are not considered as organic minerals in this review. This is because they are framework (alumino)silicate minerals similar to zeolite, and their basic crystal structures consist of SiO_4 and AlO_4 tetrahedra. The organic ions or molecules hosted by them do not substantially contribute to building their framework structure. On the other hand, oxalate anions in sulfate–oxalate minerals, *e.g.*, coskrenite-(Ce) $[(\text{Ce},\text{Nd},\text{La})_2(\text{SO}_4)_2(\text{C}_2\text{O}_4)\cdot 8(\text{H}_2\text{O})]$, are electrostatically linked to cation polyhedra, being one of building blocks in the structure (Peacor *et al.* 1999).

BACKGROUND INFORMATION

The lithosphere holds over 99.99% of the carbon on Earth (Kempe 1979). Inorganic carbon, such as in carbonate minerals, accounts for the 75%, and organic carbon, such as kerogen, makes up the rest (Hunt 1995). Sedimentary rocks are the largest repository of organic carbon, and account for over 30,000 times as much as that of living matter at the Earth's surface (Ishiwatari 2004). This high abundance shows that organic carbon in the lithosphere is important for the carbon cycle of the Earth.

The approved mineral catalogue of the CNMNC of IMA (Nickel & Nichols 2008) lists only 44 species of organic minerals, compared to over 4200 species of inorganic minerals. In the past, over 200 names of organic minerals existed; most of them, however, were rejected as independent mineral species in later investigations (Dondi & Puggioli 1990, 1991). In *The System of Mineralogy*, 6th edition, Dana (1892) listed 74 mineral names for natural organic compounds; however, the 8th edition (Gaines *et al.* 1997) contains descriptions of only nine species among them. The main reason for rejection is the problem of determining chemical composition. Karpatite, a molecular crystal of coronene ($\text{C}_{24}\text{H}_{12}$, App. XII), was firstly described as the $\text{C}_{33}\text{H}_{17}\text{O}$ substance investigated by Piotrovskii (1955). Afterward, Murdoch & Geissman (1967) discovered the same mineral from San Benito, California, determined the chemical composition as $\text{C}_{24}\text{H}_{12}$, and named it “pendletonite”. However, Frank-Kamenetskii *et al.*

(1967) revealed that karpatite from Trans-Carpathia and “pendletonite” from San Benito are the same species, as determined by an X-ray crystallographic study. Hence, the later name “pendletonite” was discredited (Nickel & Nichols 2008). The possible reasons for the confusion over chemical compositions are as follows: (1) several grams of mineral specimen were required for a chemical analysis in 1960s (Geissman *et al.* 1967), and (2) amorphous organic matter coexists with karpatite from Trans-Carpathia (Piotrovskii 1955). Hence it was assumed that specimens of Piotrovskii (1955) are contaminated.

A few reviews and textbooks regarding the occurrences, chemistry, and crystal structures of organic minerals have been published so far (Dondi & Puggioli 1990, 1991, Gaines *et al.* 1997). Some textbooks on organic geochemistry have chapters describing organic minerals (Simoneit 1993, Sherlock 2000, Hofmann 2004). In this review, recent advances in crystal chemistry and isotope geochemistry of organic minerals since the publication of those references will be mentioned. In particular, oxalate and polycyclic aromatic hydrocarbon (PAH) minerals are the focus here; we discuss their contribution to new developments in the mineral sciences. The authors of this review recently published an article on similar subject in the *Japanese Magazine of Mineralogical and Petrological Sciences* (Echigo & Kimata 2009); however, to be of benefit to mineralogists all over the world, it is now published in English in *The Canadian Mineralogist*.

OXALATE MINERALS: THE MOST COMMON IONIC ORGANIC MINERALS

Carboxylate minerals, *e.g.*, oxalate (App. XIV), formate (App. XV), and acetate (App. XVI) minerals, constitute the largest family of organic minerals (24 species, Table 1). Their crystal structures consist of both carboxylate-bearing anions and various cations. Most of them incorporate electrostatically neutral water molecules, $(\text{H}_2\text{O})^0$, into their crystal structures (Krishnamurty & Harris 1961).

Oxalate minerals are the largest group of organic minerals; 17 species are reported so far (Table 1). Organic compounds having two carboxylic groups in each molecule are called dicarboxylic acids (Vollhardt & Schore 2002). Oxalic acid is the smallest and simplest compound in dicarboxylic acids and is ubiquitous in natural environments, *e.g.*, soil (Krzyzowska *et al.* 1996), natural water (Klarup 1997), and aerosol (Kawamura & Kaplan 1987, Yu *et al.* 2005). Oxalate minerals contain various cations such as alkalis, alkaline earths, transition metals, and rare-earth elements. The crystal chemistry of the simplest system, oxalate compounds containing monovalent cations, will be described in the following section, and the role of the H_2O molecule in their crystal structures will be discussed.

TABLE 1. LIST OF IONIC ORGANIC MINERALS

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

The role of water molecules in the crystal structures of oxalate salts

The general formula of monovalent oxalate salts can be expressed as: $M_2(C_2O_4) \cdot nH_2O$ ($M = Ag^+, Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Tl^+$; $n = 0, 1, 2$; Echigo & Kimata 2006). Note that in this review, we are concerned only with stable compounds at room temperature and pressure, since their stable regime depends on the hydration number (Dinnebier *et al.* 2003, Weller *et al.* 2007). Their crystal structures are commonly layered, and consist of a monovalent cation and an oxalate anion (Fig. 1), and H₂O molecules are occluded between interlayer spaces ($M = NH_4^+, K^+, Rb^+, Cs^+$). It is notable that both anhydrous Rb₂(C₂O₄) and Cs₂(C₂O₄) are unstable in air and immediately hydrate to Rb₂(C₂O₄)•H₂O and Cs₂(C₂O₄)•2H₂O, respectively (Dinnebier *et al.* 2003). This instability suggests that interlayer H₂O molecules stabilize their crystal structures in air. This role of the H₂O molecule was explained quantitatively by Echigo & Kimata (2006) in terms of bond-valence theory

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

In any ionic crystal, the empty valence-shell of a cation interacts with the filled valence-shell of an anion: the former acts as an electron donor, and the latter as an electron acceptor (West 1988). Their behaviors toward a bonding electron pair correspond to Lewis acid and base, respectively, and thus we can define the Lewis acid strength of the cation and the Lewis base strength of the anion by Brown's definition (1981, 2002, 2009): the Lewis acid or base strength of the cation or anion is equal to characteristic (bond-) valence = atomic (formal) valence divided by the mean coordination-number. These definitions of Lewis acid and base strengths lead to a specific criterion for chemical bonding, the *valence-matching principle* (Brown 1981, 2002, 2009): the most stable structures will form if the Lewis acid strength of the cation closely matches the Lewis base strength of the anion. Developing this concept, a *binary representation of crystal structures* was proposed (Hawthorne 1985, 1992a). With this

concept, one describes both the interaction between the Lewis acid part and Lewis base part of crystal structures and their relationship with stability. These concepts are generally used to validate the chemical composition and crystal structure of minerals. The roles of H_2O molecules in hydrous minerals are also examined in light of these concepts (Hawthorne 1992b, 1994, 1997, Schindler & Hawthorne 2001a, 2004).

In oxalate salts, the oxalate anion is the Lewis base, and the cation is the Lewis acid component in terms of the above-mentioned concepts. The Lewis acidity of various cations, which is deduced from the statistical analysis of the inorganic crystal-structure database (ICSD, Allen 2002), can be taken from the tables of Brown (1988, 2002). On the other hand, the Lewis basicity of organic anions including the oxalate anion is not listed in these tables. Hence we have to calculate the Lewis base strength of the oxalate anion to examine the interaction of Lewis acid and base in oxalate salts.

This calculation is successfully constrained by the general observation (Hawthorne 1992b) that normally, it is adequate for one to use the coordination number of [4] for oxygen. On the basis of the connectivity that assumes a coordination number of [4] for oxygen, then oxalate anion needs 12 additional bonds from the bonding cations (Fig. 2). These 12 bonds must satisfy the requirement from $(\text{C}_2\text{O}_4)^{2-}$, and thus the average bond-valence required by the anion is $2/12 \approx 0.167 \text{ vu}$ (valence units); this is the Lewis basicity of oxalate anion (Echigo & Kimata 2006). This bond-valence value (0.167 vu) is an ideal value for oxalate anion, which matches up with the Lewis acidity of 0.156 vu for Na^+ (Brown 1988). The $\text{Na}^+-(\text{C}_2\text{O}_4)^{2-}$ bond certainly fits the valence-matching principle, and therefore natroxalate is a stable mineral. It occurs in a hydrothermally altered pegmatite (Khomyakov 1996).

Echigo & Kimata (2006) first demonstrated that the Lewis basicity of an organic anion can be deduced

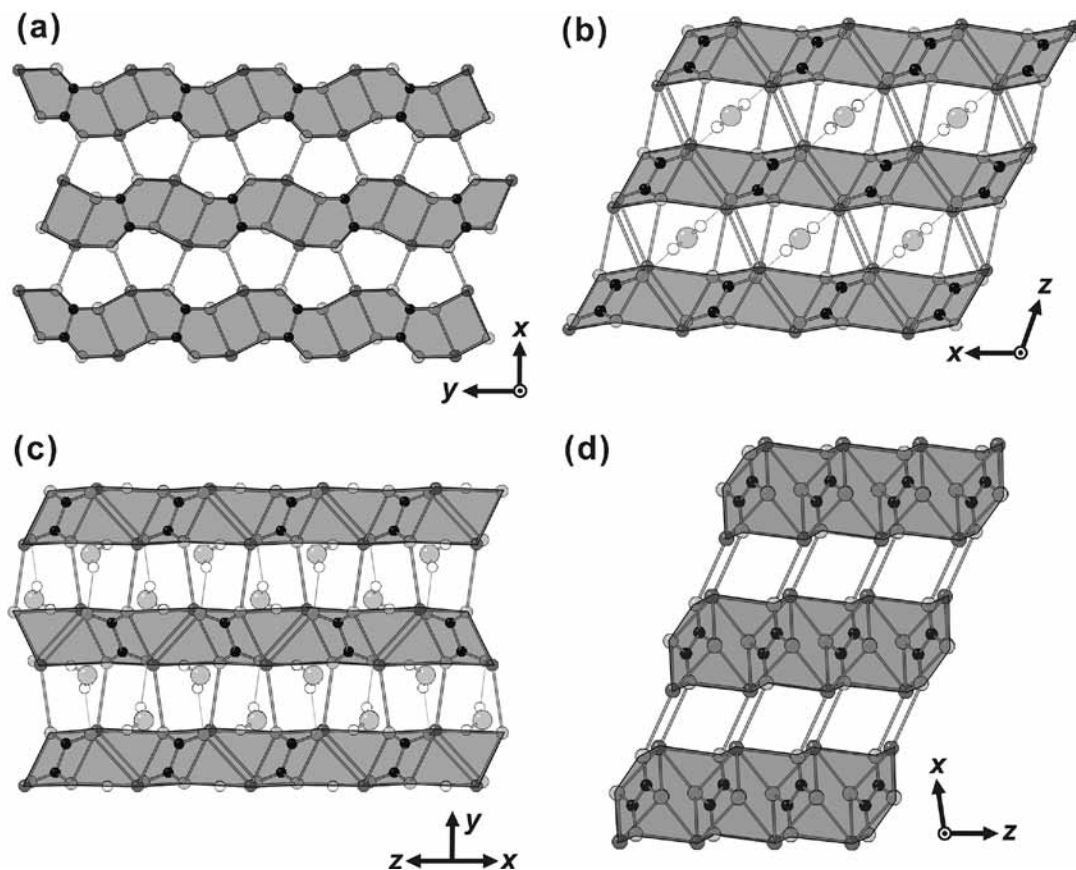


FIG. 1. Crystal structures of (a) natroxalate, $\text{Na}_2(\text{C}_2\text{O}_4)$ (Jeffrey & Parry 1954), (b) $\text{Rb}_2(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ (Echigo & Kimata 2006), (c) $\text{Cs}_2(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ (Kholodkovskaya *et al.* 1990) and (d) $\text{Tl}_2(\text{C}_2\text{O}_4)$ (Nagy *et al.* 2005). All the oxalate complexes have a layer structure. Sodium, rubidium, cesium, and thallium atoms are shown in dark gray, oxygen in pale gray, carbon in black, and hydrogen in white.

in the same way as for inorganic oxyanions, and both the *valence-matching principle* and the *binary presentation of a crystal structure* are applicable to organic minerals. Our work suggests that the Lewis basicity of other organic anions, *e.g.*, formate (App. XV) and acetate (App. XVI) anions, can be deduced in the same way, and that the organization of organic minerals into a structural hierarchy is indispensable to mineralogy. This organization should be a significant aid in determining unknown structures and will provide considerable insight into the underlying controls on the topology of chemical bonds and mineral paragenesis. This type of application, which succeeded in phosphate (Moore 1973, Hawthorne 1998), borate (Schindler & Hawthorne 2001a, b), and uranyl minerals (Schindler & Hawthorne 2004), will be of geological interest in future.

Most cations do not match up with the Lewis basicity of the oxalic anion, 0.167 *vu*, and H₂O molecules commonly must be incorporated into the structure of an oxalate salt. Considering the solvent-free alkali oxalate, the Lewis basicity of K⁺, Rb⁺, and Cs⁺ are 0.126, 0.124, and 0.109 *vu*, respectively. In terms of the valence-matching principle, the supposed anhydrous alkali oxalates are not stable compounds because they have significant differences in Lewis basicity or acidity strength between these alkali cations and oxalic anion. The anhydrous oxalates hydrate readily in the presence of H₂O to produce hydrous oxalate, as expected (Dinnebier *et al.* 2003); this instability is explained by the violation of the valence-matching principle. Thus incorporation of H₂O molecules in the structure leads to compensation for the difference between the Lewis acidity of a cation and the Lewis basicity of the

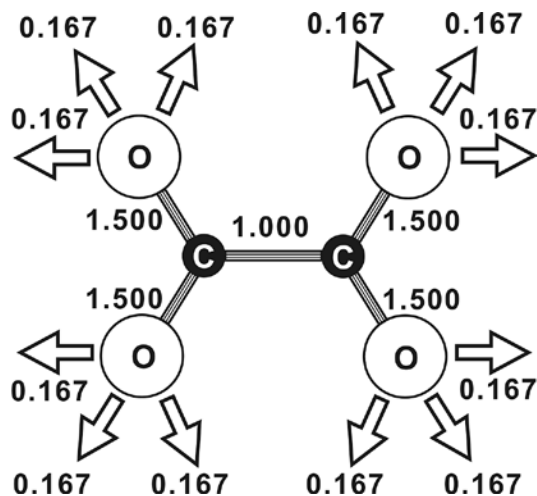


FIG. 2. Calculation of Lewis basicity (*vu*) for oxalate anion [(C₂O₄)²⁻] based on the assumption that each constituent atom of oxygen is four-coordinated.

oxalate anion, which shows that the H₂O molecules in the hydrous oxalate salts play a crucial role as a bond-valence mediator. Figure 3 shows a positive correlation between the differences in Lewis acidity or basicity and the number of H₂O molecules per formula unit. This correlation can be simply approximated by the equation shown in Figure 3, although Ag⁺ and NH₄⁺ are omitted from the calculation because they exhibit a wide range of Lewis acidity.

INERT ELECTRON PAIR OF Tl⁺ AS PROXY FOR H₂O MOLECULES IN OXALATE COMPLEXES

As the H₂O molecule has a pair of lone electrons, so the Tl⁺ cation has a pair of non-bonding electrons called “inert electron pair (IEP)”. Thus the coordination environment of Tl⁺ is distorted (Downs 1993). The anhydrous thallium oxalate (Fig. 1d) has a layered structure, the same as other monovalent oxalate complexes, and the IEPs of Tl⁺ cations are positioned between the interlayer spaces (Fig. 4b). The crystal structure of rubidium oxalate monohydrate (Fig. 1b) is closely similar to that of anhydrous thallium oxalate, though the former has H₂O molecules in the interlayer spaces (Fig. 4a). This structural similarity can be ascribed to their ionic radii, 1.59 Å for Tl⁺ and 1.61 Å for Rb⁺ (Shannon 1976); however, the lack of H₂O molecules in thallium oxalate cannot be accounted for only by the ionic radii. Comparison between interlayer spaces occupied by

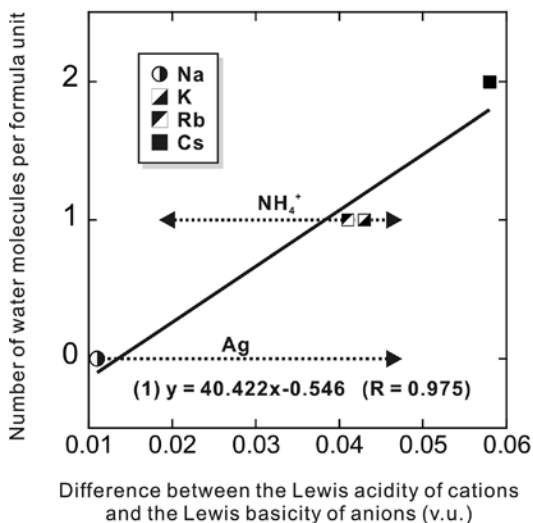


FIG. 3. Hydration number in oxalate complexes *versus* the difference between Lewis acidity of their cations and Lewis basicity of their anions. The regression line, which is directly correlated to Na, K, Rb and Cs oxalate, is given by equation (1). The dotted arrows represent the ranges of their differences for NH₄⁺ and Ag oxalate; they offer the wide range of Lewis acidity (Brown 2002).

either IEPs or H₂O molecules in these two structures reveals that both the positions and directions of IEPs in Tl⁺ cations are closely similar to those of lone electron pairs (LEPs) in H₂O molecules (Fig. 4), which leads to the following scheme of substitution:



where \square represents vacant interlayer sites. This equation suggests that interlayer non-bonding electron pairs, both IEP and LEP, contribute to the stabilization of crystal structures of the same topology.

Substitution including non-bonding electron pairs and the role of H₂O molecules in oxalate complexes are

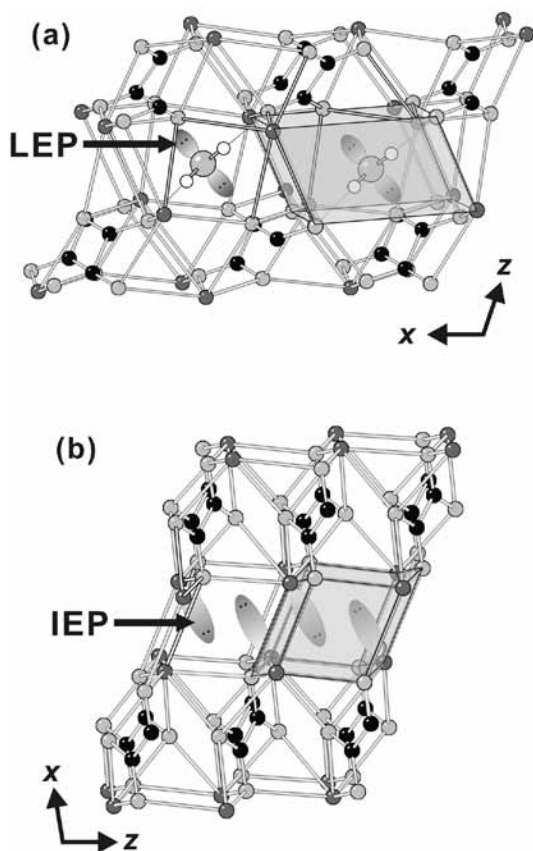


FIG. 4. Crystal structures of (a) Rb₂(C₂O₄)·H₂O (Echigo & Kimata 2006) and (b) Tl₂(C₂O₄) (Nagy *et al.* 2005). These two complexes have a layer structure, where interlayer occupants are H₂O molecules and LEPs in the former, and the only IEPs in the latter. LEPs and IEPs are nearly parallel to each other in a similar structure. Rubidium and thallium atoms are shown in dark gray, oxygen in pale gray, carbon in black, and hydrogen in white. LEP: lone electron pair, IEP: inert electron pair.

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 isotopic structures containing *p*-block elements, *e.g.*, Pb²⁺ and Sn²⁺, might have the same mechanism of substitution.

Crystal chemistry and 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 [Ca(C₂O₄)·H₂O], weddellite [Ca(C₂O₄)·2H₂O], and caoxite [Ca(C₂O₄)·3H₂O] (Basso *et al.* 1997). These minerals commonly occur in carbonate concretions, marine and lake sediments, hydrothermal veins, and lignite (Gude *et al.* 1960, Hyde & Landy 1966, Matsubara & Ichikura 1975, Žák & Skála 1993, Koukouzas *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 & Jones 1999, Tyra *et al.* 2007). Note that COMs are the most common biominerals in plants (Franceschi & Horner 1980, Franceschi & Nakata 2005), and they also are widely recognized in the life sciences because of their common association with kidney stone disease (Lowenstam & Weiner 1989, Wesson & Ward 2007).

Hydration–dehydration mechanisms in COMs

Whewellite, the monohydrate COM, is the most common and stable mineral among the three COMs (Gaines *et al.* 1997). Figure 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

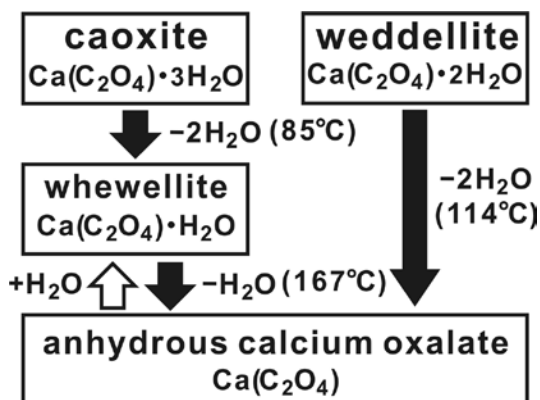


FIG. 5. Scheme of the phase transitions in the calcium oxalate minerals. Black and white arrows show the dehydration and hydration reactions, respectively.

depending on the hydration states (Basso *et al.* 1997), which suggests that H₂O molecules in their crystal structures play a significant role. The hydration–dehydration processes of COMs have been extensively studied by many investigators (Wiedemann & Bayer 1988, Frost & Weier 2003, 2004, Klopogge *et al.* 2004), and COMs are even used as standard samples for calibration of thermal analysis instruments (Sepe 1997, Wunderlich 2005). In this review, the hydration–dehydration mechanisms of COMs will be described in light of the topology of chemical bonds in their crystal structures.

Figure 5 is a summary of hydration–dehydration paths compiled from various sources in the literature (Wiedemann & Bayer 1988, Frost & Weier 2003, Echigo *et al.* 2005). As shown in Figure 5, caoxite, the trihydrate COM, dehydrates and transforms into whewellite directly, not through the dihydrate COM, weddellite. Whewellite dehydrates and transforms into anhydrous COM, which hydrates on cooling and

returns to whewellite. However, whewellite does not hydrate into caoxite. Echigo *et al.* (2005) examined the network of hydrogen bonds in whewellite and revealed the dehydration mechanism of caoxite from its bonding topology. Figure 6 shows the crystal structures of caoxite (Deganello *et al.* 1981) and whewellite (Echigo *et al.* 2005); both of them have similar layer structures. Both layer structures consist of Ca²⁺ and the oxalate anion, though those of caoxite are corrugated (Fig. 6a) and those of whewellite are flat (Fig. 6b). The corrugated layer structure of caoxite is attributed to the interlayer H₂O molecules that link the layers *via* the hydrogen bonds (Fig. 6a). On the other hand, whewellite does not have interlayer H₂O molecules and the Ca–oxalate bonds link the layers directly (Fig. 6b). Echigo *et al.* (2005) pointed out that the corrugated layers in caoxite get flattened and bonded directly upon dehydration.

Weddellite, the dihydrate COM, dehydrates into anhydrous COM directly, not through whewellite

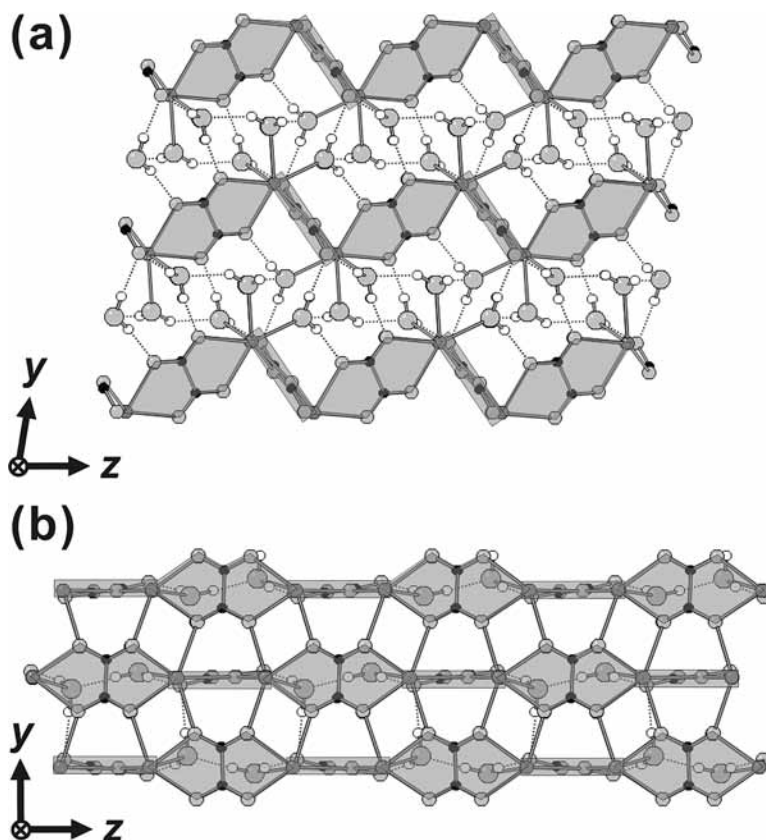


FIG. 6. Crystal structures of (a) caoxite, $\text{Ca}(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$ (Basso *et al.* 1997) and (b) whewellite, $\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ (Echigo *et al.* 2005). Both of the structures consist of shaded sheet structures. The former sheets are corrugated and linked by interlayer hydrogen-bonds.

(Frost & Weier 2003). However, the anhydrous COM hydrates and transforms into whewellite on cooling, which shows that the dehydration reaction of weddellite to anhydrous COM is irreversible (Fig. 5). Figure 7 shows the (010) section of weddellite; it consists of shaded zig-zag chains bonded by hydrogen bonds of H₂O molecules. The H₂O molecules linking the chains are removed on heating, and thus the crystal structure will be destabilized. After dehydration, the crystal structure of weddellite gets reconstructed so that the zig-zag chains link directly. The crystal structure of anhydrous COM formed by dehydration of weddellite is identical with that of the anhydrous COM formed by the dehydration of whewellite (Wiedemann & Bayer 1988). Hochrein *et al.* (2008) revealed that the structural framework of whewellite does not collapse upon dehydration, and the zig-zag chains of the same topology as those of weddellite are seen in the (100) section of both whewellite and the dehydrated phase (Figs. 7b, 7c). The direct linking of the zig-zag chains in weddellite on dehydration results in the formation of the anhydrous COM, of which the crystal structure is as shown in Figure 7c.

The hydration–dehydration relationship among COMs in Figure 5 is explained consistently on the basis of the connection of oxalate anion and the arrangement of H₂O molecules in their structures. Most inorganic minerals, including silicate, oxide, and sulfide minerals, vary their physicochemical properties according to the packing of anions, as do oxalate minerals. However, both planar geometry and the strong C–C bond, which are the most significant characteristics of the oxalate anion (App. XIV), emphasize the importance of the anion arrangement in the phase relationships of oxalate minerals.

The most stable COM in ambient temperature and pressure in air is whewellite, as the reaction of whewellite to anhydrous COM is reversible, whereas both the reactions of weddellite to anhydrous COM and of caoxite to whewellite are irreversible (Fig. 5). The structural relationship discussed above, therefore, accounts for the fact that whewellite is the most typical and common COM in natural environments.

Geochemistry of the calcium oxalate minerals (COMs)

The origin and formation of COMs are confirmed only for the occurrences associated with living

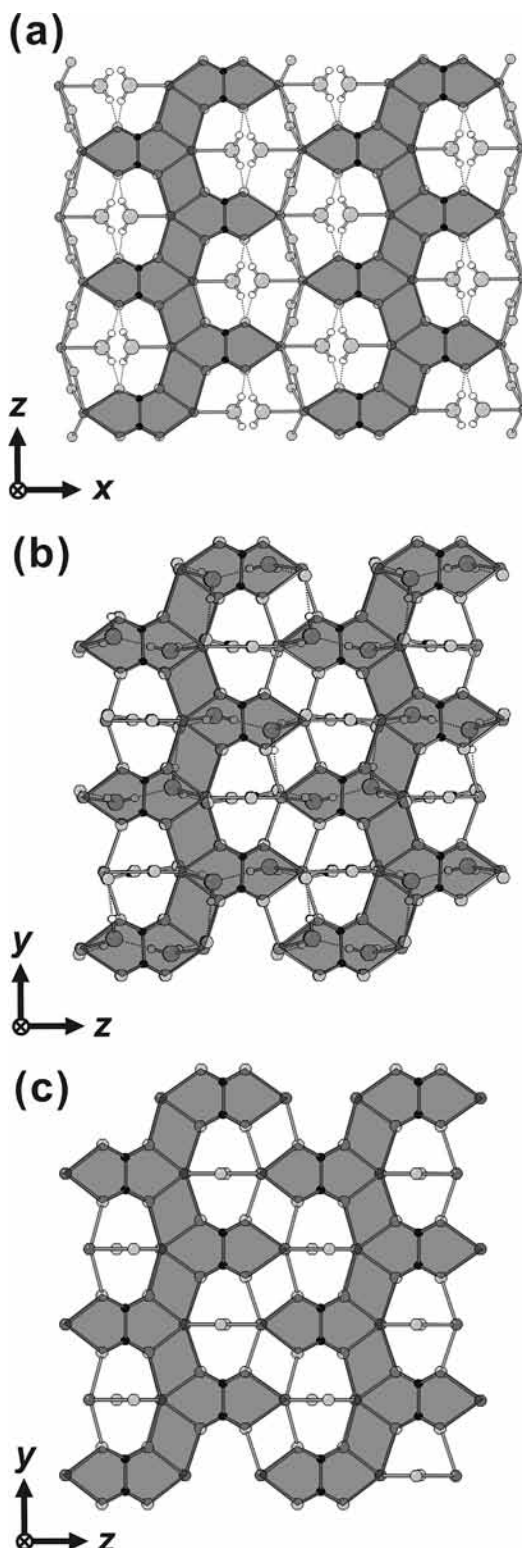


FIG. 7. Crystal structures of (a) weddellite, $\text{Ca}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ (Tazzoli & Domeneghetti 1980), (b) whewellite, $\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ (Echigo *et al.* 2005) and (c) anhydrous calcium oxalate, $\text{Ca}(\text{C}_2\text{O}_4)$ (Hochrein *et al.* 2008). These three structures consist essentially of shaded zig-zag chains. The chains in weddellite are linked by hydrogen-bonds.

organisms: on rock surfaces that interacted with lichen or microbes (Chen *et al.* 2000) and within angiosperms such as rhubarbs (Hoefs 1969), cactuses (Garvie 2003) and spinaches (Dohi *et al.* 2002). These COMs derive their origins from biogenic oxalic acid; hence these COMs are classified as biominerals by strict definition.

Hoefs (1969) first compared both carbon and oxygen isotopic compositions of whewellite from rhubarb and those from diagenetic septarian nodules from two localities (Hoheneggelsen, Germany and Huron River, Ohio) as follows: the $\delta^{13}\text{C}$ of whewellite from rhubarb is -29.3‰ , that from Germany is $+7.8$, and that from Ohio is $+0.6\text{‰}$. He mentioned that partial bacterial decomposition of the oxalate formed light volatile CO_2 , and the heavy residual oxalate precipitated as whewellite. Thereafter, some isotopic studies on COMs were published (Galimov *et al.* 1975, Žák & Skála 1993), and their occurrences and carbon isotope geochemistry were comprehensively reviewed by Hofmann & Bernasconi (1998). Discussing the very wide range of $\delta^{13}\text{C}$ values of COMs, from -31.7 to $+33.7\text{‰}$, Hofmann & Bernasconi (1998) ascribed the extremely variable composition to the fractionation by microbial agents or the thermal degradation of oxalate in the dissolved state prior to crystallization of the mineral. The organic matters in sedimentary materials from Cape Lookout, North Carolina, were examined, and the $\delta^{13}\text{C}$ of total organic carbon and acetic acid were -19.8 and -9.51‰ , respectively (Blair & Carter 1992). The results revealed that the $\delta^{13}\text{C}$ values of carboxylic acids are significantly heavier than that of total organic carbon. However, they concluded that the wide range of $\delta^{13}\text{C}$ of COMs is not explained only by the isotopic fractionation (Hofmann & Bernasconi 1998). The carbon isotopic fractionation on the thermal decomposition of whewellite was recently reported (Manning *et al.* 2008). However, detailed studies will be required to understand the carbon isotopic systematics of COMs, because isotopic fractionation of carbon depends highly on the reaction mechanism. In particular, this effect can be anomalously marked in the reactions involving free-radical pairs (Buchachenko 2001). Therefore, isotope analysis is of limited use in the determination of carbon origin in organic minerals whose mechanism of formation is not known in detail. The COMs contain calcium as a main component; thus they are suitable for strontium isotopic study to understand their origin and process of formation. In addition, COMs contain both oxygen and hydrogen, and hence isotopic studies should give some insight into paleoenvironments as well as origin and formation of COMs.

The detailed chemical composition of COMs, including trace elements, with information about COMs from various locations and occurrences, have not been reported so far. Although trace amounts of Si, Al, and Be were detected in COM from Ohio by semiquantitative spectrographic analysis (Leavens 1968), these might be due to small inclusions or surface contaminants. Both

major and trace elements of natural COMs should be examined using modern techniques of analysis, though their locations and the number of occurrences are few. The calcium oxalate minerals should yield significant insights into the fate and behavior of organic acids in surface environments of ancient Earth and thus be valuable subjects in organic geochemistry as well as in mineralogy, as remarked by Hofmann & Bernasconi (1998).

Oxalate minerals containing transition metals

Several oxalate minerals containing transition metals are known, *e.g.*, stepanovite [$\text{NaMgFe}^{3+}(\text{C}_2\text{O}_4)_3 \cdot 8\text{--}9\text{H}_2\text{O}$] from lignite (Knipovich *et al.* 1963) and moolooite [$\text{Cu}^{2+}(\text{C}_2\text{O}_4)_n \cdot n\text{H}_2\text{O}$] produced by the interaction between oxalic acids from guano and copper sulfide minerals (Clarke & Williams 1986). However, their chemical compositions, in particular, the number of H_2O molecules in the formula, are not established, and hence their crystal structures are not determined. In general, it is difficult to acquire the good-quality crystals of transition-metal-bearing oxalate complexes, even synthetic powder samples (Kitagawa *et al.* 1995). Recently, Echigo & Kimata (2008) succeeded in the synthesis of single crystals of humboldtine [$\text{Fe}^{2+}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$] and refined its crystal structure by single-crystal X-ray-diffraction. The crystal structure was not refined using powder neutron diffraction owing to the stacking faults that commonly occur in the crystal structure (Śledzińska *et al.* 1986, 1987). The great interest in this successful synthesis is that the Jahn–Teller effect of Fe^{2+} ion was observed in the structure of humboldtine, whereas the effect of the Fe^{2+} ion is barely observed in common inorganic minerals, since it is much weaker than that of Cu^{2+} or Mn^{3+} (Burns 1993).

Humboldtine [$\text{Fe}^{2+}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$] is a secondary mineral that occurs in lignite and granitic pegmatites, and its crystal structure is isotopic with that of lindbergite [$\text{Mn}^{2+}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$] (Garavelli 1955a, Atencio *et al.* 2004). Their crystal structures consist of chains in which oxalate anions link $M^{2+}\text{O}_6$ octahedra; the chains are bonded by hydrogen bonds (Fig. 8). Comparison between the geometrical parameters of octahedra in humboldtine and lindbergite shows that the former is horizontally elongate, and the latter is vertically elongate (Fig. 9). Bond-length distortions of $M^{2+}\text{O}_6$ octahedra, which is calculated from the following equation:

$$\frac{100}{n} \sum_{i=1}^n \left[\frac{\{(X-O)_i - \langle X-O \rangle\}}{\langle X-O \rangle} \right]$$

where n = number of bonds, $(X-O)_i$ = central cation – oxygen bond-length, and $\langle X-O \rangle$ = average bond-length (Renner & Lehmann, 1986), are 0.48% and 0.28% in humboldtine and lindbergite, respectively (Echigo & Kimata 2008). The slightly larger distortion of Fe^{2+}O_6

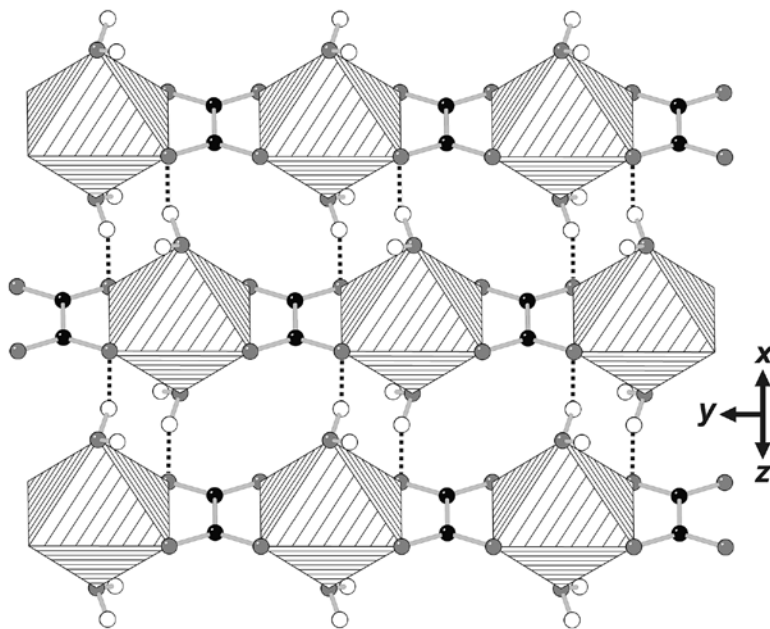


FIG. 8. Crystal structures of $M^{2+}(C_2O_4) \cdot 2H_2O$ (Echigo & Kimata 2008). Cation polyhedra are striped, carbon atoms are shown in black, oxygen in pale gray, and hydrogen atoms are white; dotted lines represent hydrogen bonds.

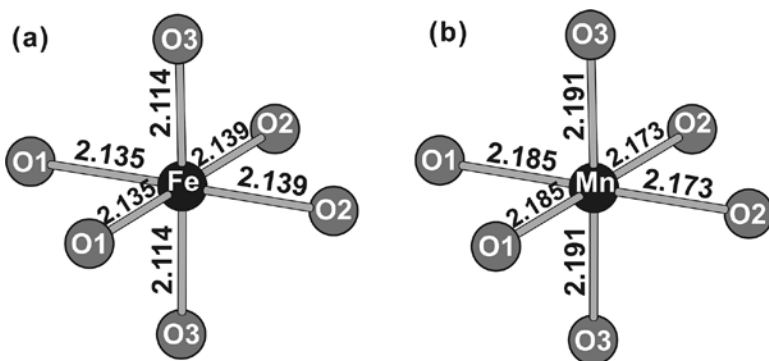


FIG. 9. Comparison between (a) the FeO_6 octahedron in humboldtine (Echigo & Kimata 2008) and (b) the MnO_6 octahedron in lindbergite (Soleimannejad *et al.* 2007). Observed bond-distances (Å) are given.

octahedra in humboldtine is attributed to the Jahn–Teller effect of the Fe^{2+} ion, enhanced by the oxalate ligands.

Figure 10 shows the geometries of the $M^{2+}O_6$ octahedra – oxalate chains in the two oxalate minerals. The geometry of the oxalate anion is almost identical in the two structures, whereas that of $M^{2+}O_6$ octahedra is significantly different. This relation indicates that oxalate anion is more rigid than the $M^{2+}O_6$ octahedra.

The rigidity of the oxalate anion gives rise to significantly narrow bond-angles, called “bite-angles”, defined as the angle $O-M-O$ where the oxygen atoms belong to the same oxalate anion (Stiefel & Brown 1972). The bite-angles that have values far from the ideal octahedral ones (90°) exert a crystal-chemical influence on the oxalate complexes containing transition metals (Calatayud *et al.* 2000, Castillo *et al.* 2001). Figure 10

shows the shape of d_{xy} orbitals that point to the regions where there is no ligand. However, a small repulsion due to the narrow bite-angles in humboldtine (77.83° and 78.12°) may occur between the orbitals and ligands. Thus the repulsion induced by the narrow bite-angles causes the Fe^{2+}O_6 octahedra to be horizontally elongate. The Mn^{2+}O_6 octahedra are less distorted than Fe^{2+}O_6 octahedra, whereas the bite-angles in lindbergite (76.61° and 76.67°) are narrower than those in humboldtine. Spectroscopic evidence, specifically the broadening and lowering the intensity of the $\text{Fe}^{2+}\text{-O}$ band in the Raman spectrum, are also shown in Echigo & Kimata (2008).

Humboldtine is a stable mineral that occurs even in granitic pegmatites (Matioli *et al.* 1997), although it involves a structural distortion caused by the Jahn–Teller effect due to the Fe^{2+} ion. This stability suggests that the structural distortion is compensated by the connectivity of the chemical bonds. The chains in both humboldtine and lindbergite are linked only by hydrogen bonds that have a wide range of lengths, from 2.4 to 3.5 Å (Nakamoto *et al.* 1955, Libowitzky 1999). The intrachain distortions are compensated by the interchain spaces, and thus humboldtine is a stable mineral.

The thermal decomposition of humboldtine and lindbergite, leading to the loss of the oxalate anion, occurs at

330°C and 322°C respectively (Macklen 1968), and that of moolooite [$\text{Cu}^{2+}(\text{C}_2\text{O}_4)\cdot n\text{H}_2\text{O}$] occurs at 240°C (Frost *et al.* 2004). The Jahn–Teller effect of the Cu^{2+} ion is much stronger than that of Fe^{2+} ion (Burns 1993). These thermal behaviors suggest that the Jahn–Teller effect of Fe^{2+} in humboldtine is compensated as mentioned above; on the other hand, that of Cu^{2+} in moolooite is not compensated, which decreases the stability of the structure. The structural refinement of moolooite has not been successfully completed owing to the difficulty in preparing the single crystal. Detailed crystal-chemical analyses of moolooite based on the single-crystal XRD data should provide structural insight into the stability of the oxalate minerals.

The molecules of H_2O in the interchain spaces are obliquely tied to the chains (Fig. 8). The electronic structure is schematically shown in Figure 11a, where both metal cation and oxalate anion constitute one-dimensional chains linked by ionic bonds ($-\text{M}^{2+} - \text{ox}^{2-} - \text{M}^{2+} - \text{ox}^{2-} - \text{M}^{2+} - : \text{M} = \text{Fe}$ or Mn , $\text{ox} = \text{oxalate}$). The H_2O molecule donates one of two LEPs to a metal cation to form a coordinate covalent bond (Fig. 11a). Thus, one of two LEPs of the H_2O molecule is shared with the corresponding cation and serves for chemical bonding, and the remaining LEP exists as one non-

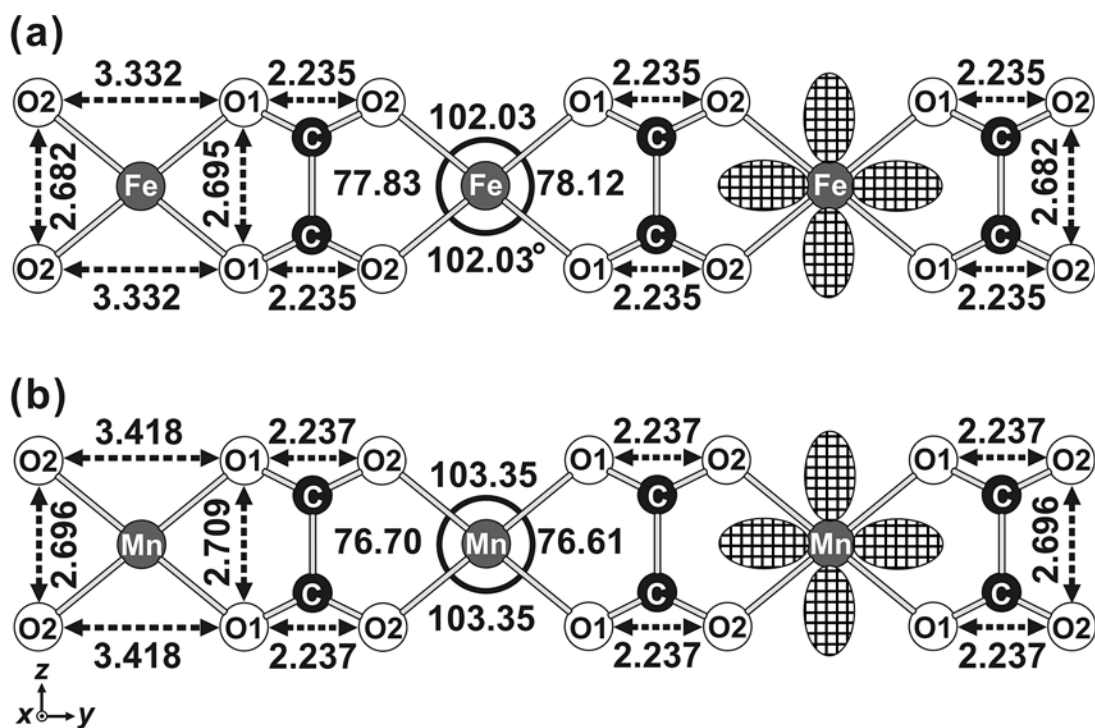


FIG. 10. Comparison between the geometries of the chain structures in (a) humboldtine (Echigo & Kimata 2008) and (b) lindbergite (Soleimannejad *et al.* 2007). Observed bond-distances (Å) and angles ($^\circ$) are given, respectively; the d_{xy} orbitals are cross-hatched.

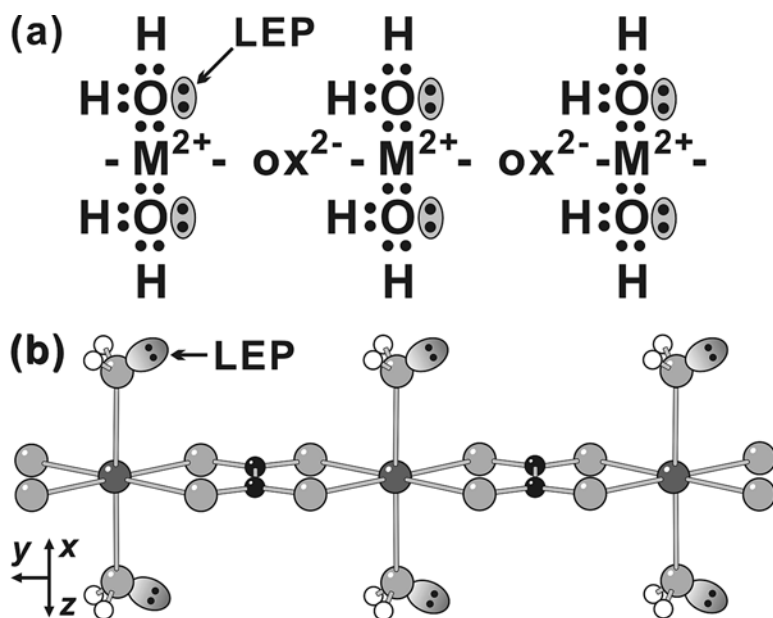


FIG. 11. (a) Schematic representation of electronic structure ($M = \text{Fe}$, humboldtine; Mn , lindbergite; ox , oxalate ion) of the chain structures in the oxalate minerals. (b) The three-dimensional structures of the chains. Metal ($\text{Fe}:\text{Mn}$) atoms are shown in dark gray, oxygen in pale gray, carbon in black, and hydrogen in white. The H_2O molecules tied to the chains tilt as a result of the spatial requirements for the lone electron pairs (LEPs).

bonding electron pair (Fig. 11a). The remaining LEP may impose a spatial requirement from the perspective of the valence-shell electron-pair repulsion (VSEPR) model (Gillespie 1972, Gillespie & Hargittai 1991); each pair of electrons in the valence shell is localized in a way that minimizes the repulsion between them (Fig. 11b). The interchain hydrogen bonds accept the spatial requirement of the LEPs, which shows the high tolerance of hydrogen bonds. Oxalate minerals have both strong C–C covalent bonds and weak hydrogen bonds in their crystal structures. This style of chemical bonding is the reason why the Jahn–Teller effect of the Fe^{2+} ion is observable in oxalate minerals, whereas it is barely observed in most inorganic minerals.

POLYCYCLIC AROMATIC HYDROCARBON (PAH) MINERALS: THE MOST COMMON MOLECULAR ORGANIC MINERALS

The characteristics of molecular crystals are briefly summarized as follows (Wright 1995): molecular crystals differ from other classes of solids in being made up of discrete molecules. Although intramolecular forces are strong, intermolecular forces are generally weaker and short-range in their effect. This mixture of strong and weak forces is in marked contrast to the dominance

of strong long-range coulombic forces in simple ionic crystals such as sodium chloride, and it introduces diversity to the properties of molecular crystals.

The crystal chemistry and mechanism of formation of molecular organic minerals (Table 2) are also different from those of inorganic minerals because of the above intrinsic characteristics. In this review, the most typical molecular organic minerals, karpatite ($\text{C}_{24}\text{H}_{12}$) and idrialite ($\text{C}_{22}\text{H}_{14}$), will be described in detail. Both minerals occur together with hydrothermal mercury minerals such as cinnabar (hexagonal HgS), metacinnabar (cubic HgS), and native mercury (Hg^0) in subduction-zone environments, and their geochemical relationship also will be mentioned.

Crystal structures of PAH minerals: solid solution in molecular crystals

Karpatite is reported from Trans-Carpathia, Ukraine (Piotrovskii 1955), Picacho Peak area, San Benito, California (Fig. 12, Murdoch & Geissman 1967), and Tamvatnei, Kamchatka Peninsula (Gorchakov *et al.* 1981). Idrialite is reported from the Idrija mercury deposit in Slovenia (Dumas 1832) and Skaggs Springs, California (Fig. 12, Wright & Allen 1930). It is notable that all the occurrences are associated with hydrothermal

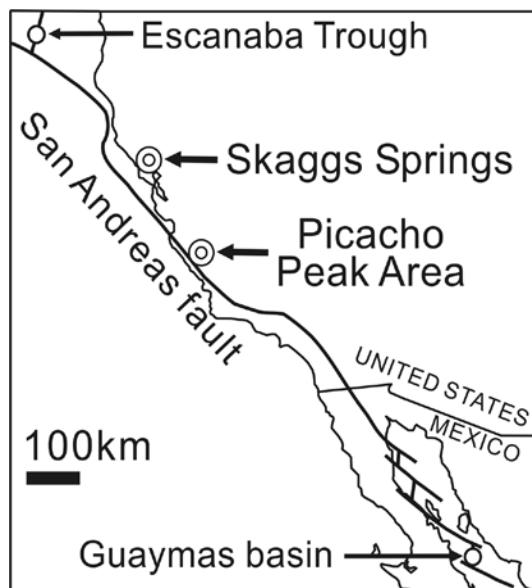


FIG. 12. Locations of the Picacho Peak area and Skaggs Springs, California in the West Coast. The location of Escanaba Trough and Guaymas Basin also are shown.

mercury deposits, and thus both organic minerals crystallized from hydrothermal fluids. The crystal-chemical characteristics and mechanism of formation of both minerals are revealed by crystal structural and carbon isotopic studies (Echigo *et al.* 2007a, 2009).

Karpatite is a molecular crystal of coronene ($C_{24}H_{12}$, App. XII) in which seven benzene rings (App. I) are circularly bonded, and the coronene molecules are linked by van der Waals bonds. The herringbone arrangement of coronene molecules can be viewed from the [001] direction (Fig. 13). This arrangement results from the following two intermolecular interactions (Echigo *et al.* 2007a): the face-to-face interaction ($\pi-\pi$ stacking interaction) between parallel molecules, and the edge-to-face interaction ($CH-\pi$ interaction) between perpendicular molecules. The edge-to-face arrangement is the most stable one, in which two independent molecules of benzene are close to each other (Muehldorf *et al.* 1988, Kim *et al.* 1998). The coronene molecule is a two-dimensionally extended molecule, and thus the contribution of face-to-face interaction increases to hold the molecules in the crystal structure (Jorgensen & Severance 1990). In addition to these attractive intermolecular interactions, hydrogen atom and π -electron repel each other; therefore, the relative positions of coronene molecules slightly shift in their

TABLE 2. LIST OF MOLECULAR ORGANIC MINERALS

Classification	Mineral names	Chemical formula	Chemical nomenclature	References
Amide minerals	Urea	$CO(NH_2)_2$	Urea	Bridge (1973)
	Acetamide	CH_3CONH_2	Acetamide	Srebrodol'skii (1975)
	Kladnoite	$C_6H_4(CO)_2NH$	Phthalimide	Rost (1942)
Purine minerals	Uricite	$C_5H_4N_4O_3$	Uric acid	Bridge (1974)
	Guanine	$C_5H_5N_5O$	Guanine	Bridge (1974)
Quinone mineral	Hoelite	$(C_6H_4)_2(CO)_2$	Anthraquinone	Oftedal (1922)
Alcohol mineral	Flagstaffite	$C_{10}H_{18}(OH)_2 \cdot H_2O$	cis-Terpin	Guild (1920, 1921)
Pimaric acid mineral	Refikite	$C_{19}H_{31}COOH$	13-dihydro-d-pimaric acid	Strunz & Contag (1965)
Polycyclic aromatic hydrocarbon minerals	Kratochvilitite	$(C_6H_4)CH_2(C_6H_4)$	Fluorene	Rost (1937)
	Ravatite	$C_{14}H_{10}$	Phenanthrene	Nasdala & Pekov (1993)
	Simonellitite	$C_{19}H_{24}$	1,1-dimethyl-7-isopropyl-1,2,3,4-tetrahydro-phenanthrene	Foresti & Riva di Sanseverino (1969)
	Fichtelitte	$C_{19}H_{34}$	1-a-dimethyl-7-isopropyl-perhydro-phenanthrene	Strunz (1962), Mace & Peterson (1995)
	Dinite	$C_{20}H_{36}$	1-ethyl-1,5,5',13-tetramethyl-perhydro-phenanthrene	Franzini <i>et al.</i> (1991)
	Hartite	$C_{20}H_{34}$	(+)-Phyllocladane	Bouška <i>et al.</i> (1998)
	Idrialite	$C_{22}H_{14}$	Picene	Strunz & Contag (1965)
Karpatite	$C_{24}H_{12}$	Coronene	Piotrovskii (1955)	
Alkane mineral	Evenkite	$(CH_3)(CH_2)_{22}(CH_3)$	n-Tetracosane	Skropyshev (1953)
Porphyrim complex mineral	Abelsonite	$Ni^{2+}C_{31}H_{32}N_4$	Nickel porphyrin	Milton <i>et al.</i> (1978)

stacking (Fig. 13). Graphite, which is extremely two-dimensionally polymerized benzene, has only face-to-face interaction in its crystal structure. Hence graphite can occlude atoms or molecules in the interlayer space, which results in the formation of graphite intercalation compounds (GICs: Dresselhaus & Dresselhaus 2002). Natural GICs having ammonia molecules are reported from graphite schist from the Sanbagawa metamorphic belt, Japan (Echigo *et al.* 2004).

Although karpatite is a highly pure crystal of coronene, idrialite is a mixed crystal; in other words, it is a molecular solid-solution. The ideal chemical formula of idrialite, $C_{22}H_{14}$, corresponds to the one of the PAHs, picene (App. V). However, all chemical analyses of idrialite (Geissman *et al.* 1967, Blumer 1975, Wise *et al.* 1986) and the spectroscopic analyses (Jehlička *et al.* 2006, Frank *et al.* 2007) show that it contains other molecules than picene, such as chrysene ($C_{18}H_{12}$, App. III), sulfur-bearing PAHs (SPAHS, App. VI), and nitrogen-bearing PAHs (NPAHS, App. VIII). As mentioned in the introduction, there is possibility of contamination by coexisting organic matter in the chemical analysis of organic minerals. Echigo *et al.* (2009) examined the single crystal of idrialite from Skaggs Springs, California (Fig. 12) using microbeam techniques, *i.e.*, micro X-ray diffraction, electron microprobe, and micro-infrared spectroscopy, and confirmed that both SPAHS and NPAHS are incorporated into the crystal structure of idrialite. The idrialite from Skaggs Springs contains 10% of benzo-phenanthro-thiophene (App. VI) in the crystal structure (Wise *et al.* 1986). The arrangement of those molecules in the crystal structure

is schematically represented in Figure 14. The crystal system of idrialite is orthorhombic owing to the other molecules, whereas that of a pure crystal of picene is monoclinic (De *et al.* 1985).

Mixing of other molecules in a crystal structure is reported from some molecular organic minerals. In particular, molecular solid-solution in evenkite has been studied in detail (Kotel'nikova *et al.* 2004, 2007). These authors revealed, from chromatographic data, that evenkite is a ten-component mixture of *n*-paraffins ($19 < n < 28$, App. XXII), and the distribution of homologues by number of carbon atoms in a molecule (number *n*) is almost symmetrical. The schematic interpretation of the molecular packing within the crystal structure of evenkite, which is called a "two-layered orthorhombic unit-cell" (Fig. 15), is well reproduced by a synthetic sample of a paraffin crystal following the chemical composition of a natural specimen (Platonova & Kotel'nikova 2006).

Hartite from Bilina is a high-purity crystal of phyllocladane ($C_{20}H_{34}$, App. VII); however, it contains two types of compounds (Bouška *et al.* 1998): 95.69% of (+)-phyllocladane is the dominant constituent, and 4.31% of (–)-phyllocladane, which is the stereoisomer of (+)-phyllocladane. Hoelite and flagstaffite were first described by Oftedal (1922) and Guild (1920, 1921), respectively. The authors reported that those natural crystals show a darker color than a pure crystal of the corresponding compounds (hoelite: anthraquinone, App. XI; flagstaffite: *cis*-terpin, App. XVIII), and concluded that some impurities in the crystal structures influence the color. It is not surprising that natural organic minerals are identified as mixed crystals, as mineralo-

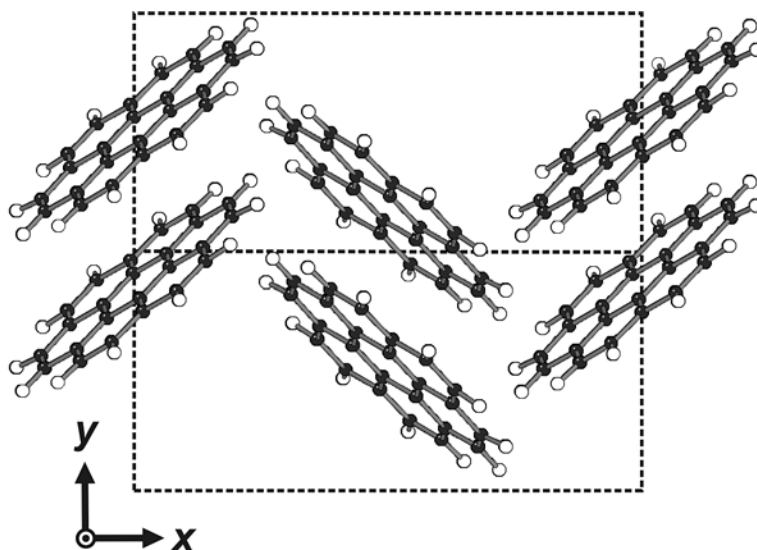


FIG. 13. Molecular packing in the crystal structure of karpatite (Echigo *et al.* 2007a). Each molecule of coronene is shown.

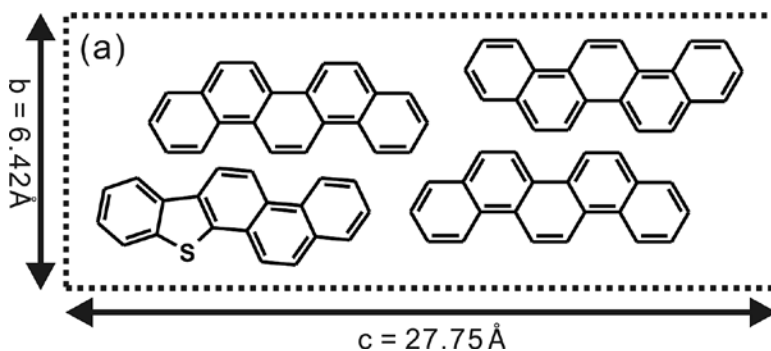


FIG. 14. Molecular packing in the idrialite (Echigo *et al.* 2009) schematically shown as a mixed crystal of picene ($C_{22}H_{14}$) and benzo-phenanthro-thiophene ($C_{20}H_{12}S$); the former is polycyclic aromatic hydrocarbon (PAH), and the latter is sulfur-bearing PAH (SPA).

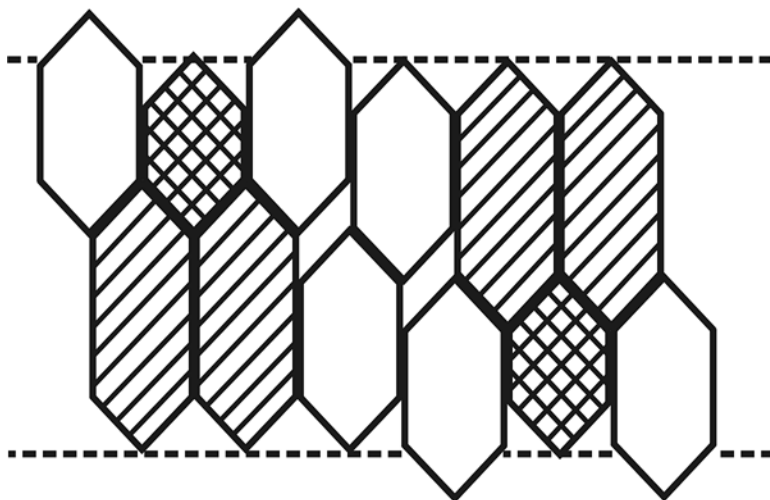


FIG. 15. Schematic image of molecular packing in evenkite with a two-layered orthorhombic unit-cell (Kotel'nikova *et al.* 2007). Evenkite is a molecular crystal of paraffin hydrocarbon (C_nH_{2n+2}), and the proportion of short- ($n = 19-22$, cross-hatching), medium- ($n = 23-24$, white), and long- ($n = 25-28$, hatching) chains is 1:3:2.

gists are quite familiar with solid solution of minerals (Geiger 2001, Becker & Prieto 2006). Careful crystal-chemical investigation will be effective to elucidate whether or not certain molecules are incorporated into the crystal structure and provide insight into their condition of formation.

PROCESS OF FORMATION OF MOLECULAR ORGANIC MINERALS

As mentioned above, karpatite at San Benito, California occurs within quartz veins intruding magnesite-quartz breccias, and thus apparently formed by hydrothermal activity (Murdoch & Geissman 1967). The PAHs are highly stable organic compounds in general (Stein 1978), and coronene is the most stable compound among the PAHs that have similar molecular

weights and size (Stein & Fahr 1985). Hence the coronene molecules could have migrated, without thermal degradation, by transport in hydrothermal fluids.

The carbon isotopic composition of karpatite at San Benito, $\delta^{13}\text{C}$, is $-22.39 \pm 0.18\%$ (Echigo *et al.* 2007a), which suggests that the coronene molecules of karpatite are derived from organic matter in oceanic sediments (Hoefs 2004). Note that PAH molecules such as coronene (App. XII) and phenanthrene (App. II) are detected from hydrothermally altered organic matter called "hydrothermal petroleum" (Simoneit & Lonsdale 1982) from the Escanaba Trough (Simoneit *et al.* 1997) and Guaymas Basin (Simoneit & Schoell 1995), located along the San Andreas Fault (Fig. 12). Organic compounds in such hydrothermal petroleum were decomposed or evaporated by successive hydrothermal activity. However, coronene molecules remain in the hydrothermal fluids owing to their stability, thus their concentration in hydrothermal fluids increased, and these molecules crystallized at the end of hydrothermal activity.

Some aspects of the above-mentioned process remain unstudied. The hydrothermal petroleum on the seafloor contains less than 100 ppm of coronene molecules (Simoneit & Fetzner 1996, Simoneit *et al.* 1997). Karpatite is a high-purity crystal of coronene; thus the concentration of coronene molecules in the hydrothermal fluids must be much higher than that in hydrothermal petroleum. The process of concentration, its mechanism, and the kinetics of coalescence of coronene molecules in the hydrothermal system are still unknown. In addition, the mechanism of formation of coronene molecules directly from sedimentary organic matter also is unknown. The hydrothermal migration process of PAHs in the lithosphere is related to the behavior of heavy metal elements as described in a later section, and will be interesting from the perspective of economic geology (Peabody & Einaudi 1992, Sherlock 2000).

Idrialite has a more straightforward process of formation than karparite (Echigo *et al.* 2009). Its primary constituent molecule is picene, the molecular skeleton of which is the same as higher-plant terpenoids such as β -amyryn (App. IX) and taraxerol (App. X). It is well known that these hydrocarbons undergo aromatization (reduction of H:C ratio) during diagenesis and convert to picene (Simoneit 1986, Hayatsu *et al.* 1987). In addition, the carbon isotopic composition of idrialite is $-24.429 \pm 0.090\%$ (Echigo *et al.* 2009), consistent with that of the organic matter derived from higher plants (Deines 1980, Galimov 1995). Picene and picene-like molecules were both extracted from sedimentary rocks and migrated *via* hydrothermal fluids; afterward, they became saturated in the fluids and crystallized as a mixed crystal, idrialite (Echigo *et al.* 2009).

It is noteworthy that the formation of coronene and picene molecules occurs at a distinctly different

stage than the crystallization of karpatite and idrialite, respectively. The formation of molecular species is a static process in which organic matter in sediments changes its structure into a stable one, and migrates in a dynamic process *via* hydrothermal fluids. Some of the other molecular organic minerals similarly have two discrete stages in their formation.

Abelsonite, a molecular crystal of Ni-porphyrin complex (App. XIX), was reported from the Green River Formation in Utah (Milton *et al.* 1978). Mason *et al.* (1989) reviewed the distribution and occurrences of abelsonite and concluded that it occurs only in the cavities in Parachute Creek Member, which is close to porous volcanic rocks. Hydrothermal fluids extracted porphyrin molecules from the surrounding sediments and passed through the porous rocks that behaved as a filter or chromatographic column. The Ni-porphyrins in the hydrothermal fluids became concentrated in this way. Hartite, a molecular crystal of phyllocradene (App. VII), is reported from a siderite nodule in lignite (Bouška *et al.* 1998). This mineral also crystallized after the concentration of phyllocradene molecules by hydrothermal activity, because this mineral occurs as a product of distillation in a water-bearing fracture (Bouška *et al.* 1998).

We examine the models for the mechanism of formation of molecular organic minerals as follows:

(1) Direct bonding model: unbonded carbon and hydrogen atoms aggregate and form a regular ordered structure, for example, halite (NaCl) crystallizes from solution through this type of chemical process.

(2) Polymerization of structural unit model: smaller molecules than the constituent molecules, *e.g.*, the benzene ring as a structural unit for PAHs, aggregate and polymerize in hydrothermal fluids. Afterward, their crystal structure can be formed by stacking of the polymerized molecules. It is well known that many silicate minerals crystallized through this process, *e.g.*, by polymerization of SiO_4 tetrahedra.

(3) Model for both static formation of molecules and dynamic migration: this model consists of two discrete stages. In the first stage, constituent molecules, *e.g.*, coronene molecules in the case of the karpatite crystal, are formed from sedimentary organic matter. Thereafter, highly stabilized molecules migrate in a fluid phase, and less stable molecules are decomposed or removed from the fluids. Concentration of molecules in mobile fluids increases by the latter process, and a molecular crystal is precipitated from the fluids on cooling.

Molecular organic minerals are formed by process (3), not by (1) or (2). Examination of the above-mentioned examples shows that the mechanism of their formation is different from that of common inorganic minerals such as halides and silicates. Organic minerals are rare mineral species because of the strict requirements: the discrete static and dynamic stages in this model. The restrictions suggest, in turn, that organic

minerals favor unusual geological conditions where certain organic compounds achieved a high concentration in natural environments.

PAH MINERALS IN MERCURY MINES IN A SUBDUCTION-ZONE SETTING

From 1850 to 1980, California mines were the source of 3 million flasks (\square 103 million kg) of mercury, about 88 percent of the mercury production in the United States (Pemberton 1983). All the PAH minerals occurring in California were discovered in the hydrothermal mercury mine (Echigo *et al.* 2007a, 2009). Not only organic minerals, but also bitumen, thick tars, and low-viscosity oils occur together with cinnabar and metacinnabar in some mercury mines in California (Sherlock 2000), *e.g.*, the Geysers geothermal system and Sulfur Creek District. Peabody & Einaudi (1992) studied the PAH-enriched kerogen from the Culver-Baer mine in the Geysers geothermal system, revealed that its carbon isotopic composition $\delta^{13}\text{C}$ is -27.22% , and concluded it was derived from the surrounding sedimentary rocks.

Miedaner *et al.* (2005) examined the solubilities of native mercury in organic solvents, toluene ($\text{C}_6\text{H}_5\text{CH}_3$, App. IV), octane (C_8H_{18} , App. XX), and dodecane ($\text{C}_{12}\text{H}_{26}$, App. XXI), and estimated the solubility of mercury in 200°C petroleum at 1,190 ppm. Their laboratory experiments suggest that the organic matter was entrained in the hydrothermal system and played a role in concentrating mercury. Note that PAHs are also reported from other types of heavy-metal deposits, such as Zn–Pb–Ba deposits in McArthur River, Australia (Chen *et al.* 2003) and Pb–Zn–Ag deposits in Trèves and Les Malines, France (Disnar 1996). Many investigators inferred that the association of organic matter with concentrations of heavy metals is due to both common source and the selective transport in the hydrothermal fluids rather than due to a direct chemical link, *e.g.*, formation of organometallic compounds in hydrothermal system (Wilhelm & Bloom 2000).

The Japanese island arc, which faces California on the other side of the Pacific Ocean, hosts many mercury deposits (Sasaki & Ishihara 1979). Mercury deposits in Japan occur along the Median Tectonic Line and volcanic front (Imai *et al.* 2006), which is similar in that mercury deposits in California are along the San Andreas Fault. Many mercury deposits in both Japan and California are epithermal deposits and associated with a subduction-zone setting, which implies the potential occurrences of PAH minerals in mercury deposits in Japan. Recently, kerogen-like solidified organic matter was reported from the mercury ore at the Itomuka mine, Hokkaido, Japan (Echigo *et al.* 2007b). The Itomuka mine is an epithermal mercury deposit formed during the Miocene–Pliocene (Imai *et al.* 2006). Most mercury deposits in California were formed in the Pliocene

(Bailey 1962). It seems that PAH minerals might be discovered in mercury deposits in Japan more recent than the Itomuka mine.

RELATIONSHIP BETWEEN CRYSTAL-STRUCTURE UNITS AND MECHANISMS OF FORMATION OF ORGANIC MINERALS

The oxalate anion $[(\text{C}_2\text{O}_4)^{2-}]$, App. XIV], fundamental structural unit of oxalate minerals, is one of the chain carboxylic anions, and the number of carbon atoms is two. The smallest structural unit of ionic organic minerals is the formate anion $[(\text{HCOO})^-]$, App. XV], and the largest one is the citrate anion, $[(\text{C}_3\text{H}_5\text{O}(\text{COO})_3)^{3-}]$, App. XVII]. Palmitic acid ($\text{C}_{15}\text{H}_{31}\text{COOH}$, App. XXIII) is the most common chain carboxylic acid, also called saturated fatty acid (Bruce 2001). In PAH minerals, phenanthrene ($\text{C}_{14}\text{H}_{10}$, App. II) is the smallest structural unit, and coronene ($\text{C}_{24}\text{H}_{12}$, App. XII) is the largest one. The PAH molecules occurring in natural environments offer a broad variety, from benzene (C_6H_6 , App. I) to ovalene ($\text{C}_{32}\text{H}_{14}$, App. XIII), as observed by Simoneit & Fetzner (1996). Hence we suggest that structural units of organic minerals are smaller than common organic molecules in natural environments. The organic compounds that have a large number of carbon atoms, such as palmitic acid and ovalene, do not occur as crystalline materials, although they are highly stable compounds and exist in natural environments. In contrast, silicate minerals, the most typical inorganic minerals, can have highly polymerized structural units. The structural units of silicate minerals range from an isolated SiO_4 tetrahedron (orthosilicate) to a three-dimensionally polymerized SiO_4 framework (tectosilicate) successively; the degree of tetrahedron condensation corresponds to the order of precipitation from silicate melt (Bowen's discontinuous reaction series: Bowen 1928).

The most distinguishing characteristic in the process of formation of organic minerals is the relationship between their structural units and a mechanism of formation. The formation of the structural units, highly stable organic ion or molecules, should be followed by the migration and concentration of those units as described above. This mechanism of formation suggests that the building of a short-range structure, an individual structural unit, is distinct from that of the long-range structure, the bulk crystal structure (Fig. 16a). Considering silicate minerals as typical examples of inorganic minerals, the coexistence of structural units such as monomer, dimer, chain, and sheet species is confirmed in quenched silicate melts (Mysen *et al.* 1980, Mysen & Frantz 1993). This structure of silicate melt suggests that short-range and long-range structures of silicate minerals are formed progressively (Fig. 16b). This difference results from the chemical bonding of the structural units: those in organic minerals polym-

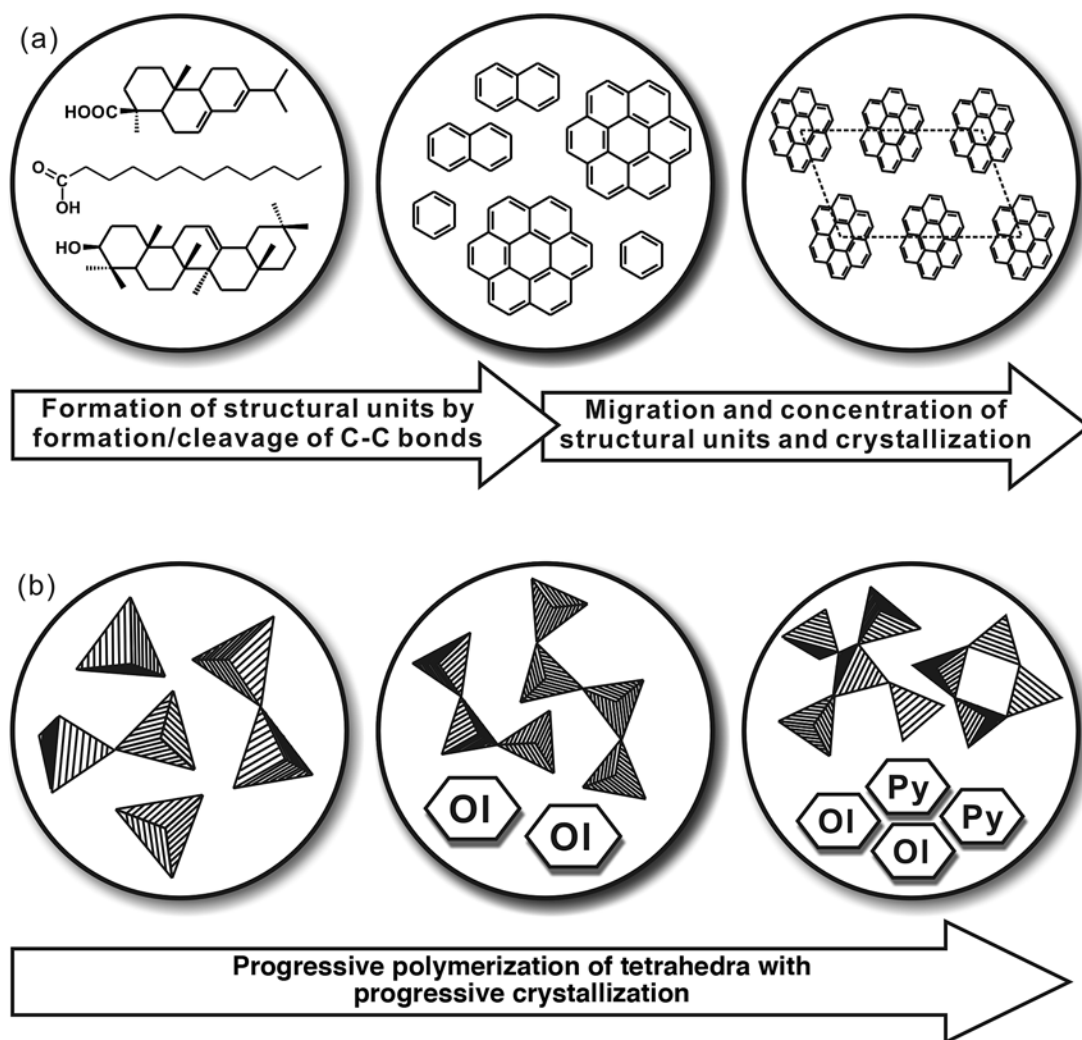


FIG. 16. Comparison between the mechanisms of formation of (a) organic minerals and (b) silicate minerals. (a) Schematic representation of the two stages in the formation of organic minerals. The first stage is the formation of structural units, *e.g.*, coronene molecules for karpatite, from biomolecules with formation or cleavage of C–C bonds. The second stage is the migration and concentration of structural units and subsequent crystallization of the mineral on cooling. (b) Schematic representation of part of Bowen's discontinuous reaction series. The SiO_4 tetrahedra in melt polymerize progressively, and mineral crystallization occurs simultaneously (Ol: olivine, Py: pyroxene).

erize by the formation of a carbon–carbon direct bond, whereas, on the other hand, those in silicate minerals require bridging oxygen atoms for their polymerization. In other words, the two stages in the process of formation of organic minerals can be divided according to whether or not the formation or cleavage of carbon–carbon bonds occurs. To understand the mechanism of formation of organic minerals, we have to develop a

new model, different from that of inorganic minerals such as Bowen's reaction series, on account of the high variety of C–C bonding. Many organic geochemists are working on the formation or cleavage of abiotic C–C bonds in hydrothermal and diagenetic systems (Freeman *et al.* 1994, Cody *et al.* 2004, Rushdi & Simoneit 2005, McCollom & Seewald 2007); their efforts also will

give insights into the process of formation of organic minerals.

CONCLUDING REMARKS

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 H₂O 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 [Cu²⁺(C₂O₄)_nH₂O] and glushinskite [Mg(C₂O₄)•2H₂O], are products of the interaction (Wilson *et al.* 1980, Clarke & 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 & 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.

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REFERENCES

- ALLEN, F. (2002): The Cambridge structural database: a quarter of a million crystal structures and rising. *Acta Crystallogr.* **B58**, 380–388.
- ANDERSON, K.B. & CRELLING, J.C. (1995): *Amber, Resinite, and Fossil Resins*. American Chemical Society (ACS Symp. Ser. 617), Washington, D.C.
- ATENCIO, D., COUTINHO, J.M.V., GRAESER, S., MATIOLI, P.A. & MENEZES FILHO, L.A.D. (2004): Lindbergite, a new Mn oxalate dihydrate from Boca Rica mine, Galileia, Minas Gerais, Brazil, and other occurrences. *Am. Mineral.* **89**, 1087–1091.
- BAILEY, E.H. (1962): Mercury in the United States. *U.S. Geol. Surv., Mineral Resources Map* **30**.
- BANNISTER, F.A. & HEY, M.H. (1936): Report on some crystal-line components of the Weddell Sea deposits. *Disc. Rep.* **13**, 60–69.
- BARTH, T.F.W. & KSANDA, C.J. (1933): Crystallographic data on mellite. *Am. Mineral.* **18**, 8–13.
- BASSO, R., LUCCHETTI, G., ZEFIRO, L. & PALENZONA, A. (1997): Caoxite, Ca(H₂O)₃(C₂O₄), 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, N.E. & CARTER, W.D., JR. (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., WALTER, F., BAUMGARTNER, J., & FÄRBER, G. (2010): Ammineite, CuCl₂(NH₃)₂, a new mineral species with an ammine complex: mineral data and crystal structure. *Can. Mineral.* **48**, 1359–1371.
- BOUŠKA, V., ČISAŘOVA, I., SKÁLA, R., DVOŘÁK, Z., ZELINKA, J. & ŽÁK, K. (1998): Hartite from Bílina. *Am. Mineral.* **83**, 1340–1346.
- BOWEN, N.L. (1928): *The Evolution Of The Igneous Rocks*. Princeton University Press, Princeton, New Jersey.
- BREARLEY, A.J. & JONES, R.H. (1999): Chondritic meteorites. In *Planetary Materials* (J. J. Papike, ed.). *Rev. Mineral.* **36**, 3–1 – 3–398.
- BRIDGE, P.J. (1973): Urea, a new mineral, and neotype phosphammite from Western Australia. *Mineral. Mag.* **39**, 346–348.

- BRIDGE, P.J. (1974): Guanine and uricite, two new organic minerals from Peru and Western Australia. *Mineral. Mag.* **39**, 889-890.
- BROOKE, H.J. & MILLER, W.H. (1852): *An Elementary Introduction to Mineralogy* (6th ed.). London, U.K.
- BROWN, I.D. (1981): The bond-valence method: an empirical approach to chemical structure and bonding. In *Structure and Bonding in Crystals II* (M. O'Keeffe & A. Navrotsky, eds.). Academic Press, New York, N.Y. (1-30).
- BROWN, I.D. (1988): What factors determine cation coordination numbers? *Acta Crystallogr.* **B44**, 545-553.
- BROWN, I.D. (2002): *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*. Oxford University Press, New York, N.Y.
- BROWN, I.D. (2009): Recent developments in the methods and applications of the bond valence model. *Chem. Rev.* **109**, 6858-6919.
- BRUCE, P.Y. (2001): *Organic Chemistry*. Prentice Hall, Upper Saddle River, New Jersey.
- BUCHACHENKO, A.L. (2001): Magnetic isotope effect: nuclear spin control of chemical reactions. *J. Phys. Chem.* **A105**, 9995-10011.
- BURNS, R.G. (1993): *Mineralogical Applications of Crystal Field Theory* (2nd ed.). Cambridge University Press, Cambridge, U.K.
- CALATAYUD, M.L., CASTRO, I., SLETTEN, J., LLORET, F. & JULVE, M. (2000): Syntheses, crystal structures and magnetic properties of chromato-, sulfato-, and oxalato-bridged dinuclear copper (II) complexes. *Inorg. Chim. Acta* **300**, 846-854.
- CASTILLO, O., LUQUE, A., JULVE, M., LLORET, F. & ROMÁN, P. (2001): One-dimensional oxalato-bridged copper (II) complexes with 3-hydroxypyridine and 2-amino-4-methylpyridine. *Inorg. Chim. Acta* **315**, 9-17.
- CHEN, JIE, BLUME, H.-P. & BEYER, L. (2000): Weathering of rocks induced by lichen colonization – a review. *Catena* **39**, 121-146.
- CHEN, JUNHONG, WALTER, M.R., LOGAN, G.A., HINMAN, M.C. & SUMMONS, R.E. (2003): The Paleoproterozoic McArthur River (HYC) Pb/Zn/Ag deposit of northern Australia: organic geochemistry and ore genesis. *Earth Planet. Sci. Lett.* **210**, 467-479.
- CHUKANOV, N.V., BELAKOVSKII, D.I., MALINKO, S.V. & ORGANOVA, N.I. (2000): Dashkovaite $Mg(HCO_2)_2 \cdot 2H_2O$ – a new formate mineral. *Zap. Vser. Mineral. Obshchest.* **129**(6), 49-53 (in Russian).
- CHUKANOV, N.V., BELAKOVSKII, D.I., RASTSVETAeva, R.K., KARIMOVA, O.V. & ZADOV, A.E. (2001): Novgorodovaite $Ca_2(C_2O_4)Cl_2 \cdot 2H_2O$, a new mineral. *Zap. Vser. Mineral. Obshchest.* **130**(4), 32-35 (in Russian).
- CHUKANOV, N.V., MALINKO, S.V., LISITSYN, A.E., DUBINCHUK, V.T., KUZ'MINA, O.V. & ZADOV, A.E. (1999): Formicaite $Ca(HCO_2)_2$ – a new mineral. *Zap. Vser. Mineral. Obshchest.* **128**(2), 43-48 (in Russian).
- CHUKANOV, N.V., PEKOV, I.V., OLYSYCH, L.V., MASSA, W., YAKUVOBICH, O.V., ZADOV, A.E., RASTSVETAeva, R.K. & VIGASINA, M.F. (2009): Kyanoxalite – a new cancrinite-group mineral with an extra-framework oxalate anion, from Lovozero alkaline massif, Kola Peninsula. *Zap. Vser. Mineral. Obshchest.* **138**(6), 18-35 (in Russian).
- CLARKE, R.M. & WILLIAMS, I.R. (1986): Moolooite, a naturally occurring hydrated copper oxalate from western Australia. *Mineral. Mag.* **50**, 295-298.
- CODY, G.D., BOCTOR, N.Z., BRANDES, J.A., FILLEY, T.R., HAZEN, R.M. & YODER, H.S., JR. (2004): Assaying the catalytic potential of transition metal sulfides for abiotic carbon fixation. *Geochim. Cosmochim. Acta* **68**, 2185-2196.
- DANA, J.D. (1892): *System of Mineralogy* (6th ed.). J. Wiley & Sons, New York, N.Y.
- DE, A., GHOSH, R., ROYCHOWDHURY, S. & ROYCHOWDHURY, P. (1985): Structural analysis of picene, $C_{22}H_{14}$. *Acta Crystallogr.* **C41**, 907-909.
- DEGANELLO, S., KAMPF, A.R. & MOORE, P.B. (1981): The crystal structure of calcium oxalate trihydrate: $Ca(H_2O)_3(C_2O_4)$. *Am. Mineral.* **66**, 859-865.
- DEINES, P. (1980): The isotopic composition of reduced organic carbon. In *Handbook of Environmental Isotope Geochemistry. 1. The Terrestrial Environment*, A (P. Fritz & J. C. Fontes, eds.). Elsevier, Amsterdam, The Netherlands (329-406).
- DINNEBIER, R.E., VENSKY, S., PANTHÖFER, M. & JANSEN, M. (2003): Crystal and molecular structures of alkali oxalates: first proof of a staggered oxalate anion in the solid state. *Inorg. Chem.* **42**, 1499-1507.
- DISNAR, J.R. (1996): A comparison of mineralization histories for two MVT deposits, Trèves and Les Malines (Causses basin, France), based on the geochemistry of associated organic matter. *Ore Geol. Rev.* **11**, 133-156.
- DOHI, T., HAGA, N. & TAGAI, T. (2002): The crystallographic study of biomineral, calcium oxalate crystal in higher plants. *Japan Geoscience Union Meeting, Abstr.*, **B006-006**.
- DONDI, M. & PUGGIOLI, G. (1990): Minerali organici **1**. *Riv. Mineral. Ital.*, 189-206.
- DONDI, M. & PUGGIOLI, G. (1991): Minerali organici **2**. *Riv. Mineral. Ital.*, 35-57.
- DOWNS, A.J. (1993): *Chemistry of Aluminium, Gallium, Indium, and Thallium*. Chapman & Hall, London, U.K.

- DRESSELHAUS, M.S. & DRESSELHAUS, G. (2002): Intercalation compounds of graphite. *Adv. Phys.* **51**, 1-186.
- DUMAS, J. (1832): Ueber die Verbindungen von Wasserstoff und Kohlenstoff (Naphthalin, Paranaphthalin und Idrialin). *Annal. Physik* **102**, 517-530.
- ECHIGO, T. & KIMATA, M. (2006): The common role of water molecule and lone electron pair as a bond-valence mediator in oxalate complexes: the crystal structures of $\text{Rb}_2(\text{C}_2\text{O}_4)\cdot\text{H}_2\text{O}$ and $\text{Tl}_2(\text{C}_2\text{O}_4)$. *Z. Kristallogr.* **221**, 762-769.
- ECHIGO, T. & KIMATA, M. (2008): Single-crystal X-ray diffraction and spectroscopic studies on humboldtine and lindbergite: weak Jahn-Teller effect of Fe^{2+} ion. *Phys. Chem. Minerals* **35**, 467-475.
- ECHIGO, T. & KIMATA, M. (2009): Recent advances in crystal chemistry and isotope geochemistry of organic minerals: contribution of oxalate and polycyclic aromatic hydrocarbon minerals to new developments in mineralogy. *Japan. Mag. Mineral. Petrol. Sci.* **38**, 57-74 (in Japanese).
- ECHIGO, T., KIMATA, M., KYONO, A., SHIMIZU, M. & HATTA, T. (2005): Re-investigation of the crystal structure of whewellite [$\text{Ca}(\text{C}_2\text{O}_4)\cdot\text{H}_2\text{O}$] and the dehydration mechanism of caoxite [$\text{Ca}(\text{C}_2\text{O}_4)\cdot 3\text{H}_2\text{O}$]. *Mineral. Mag.* **69**, 77-88.
- ECHIGO, T., KIMATA, M., KYONO, A., TAKIZAWA, S. & SHIMIZU, M. (2004): Ammonia intercalated graphite from Tatarazawa, Fujioka, Japan. *Japan. Mag. Mineral. Petrol. Sci.* **33**, 77-84 (in Japanese).
- ECHIGO, T., KIMATA, M. & MARUOKA, T. (2007a): Crystal-chemical and carbon-isotopic characteristics of karpatite ($\text{C}_{24}\text{H}_{12}$) from the Picacho Peak area, San Benito County, California: evidences for the hydrothermal formation. *Am. Mineral.* **92**, 1262-1269.
- ECHIGO, T., KIMATA, M., MARUOKA, T., SHIMIZU, M. & NISHIDA, N. (2009): The crystal structure, origin, and formation of idrialite ($\text{C}_{22}\text{H}_{14}$): inferences from the micro-beam and bulk analyses. *Am. Mineral.* **94**, 1325-1332.
- ECHIGO, T., KIMATA, M. & SHIMIZU, M. (2007b): Crystalline adamantane ($\text{C}_{16}\text{H}_{10}$) co-existed with native mercury from Itomuka mine, Hokkaido, Japan. *Frontiers in Mineral Sciences 2007 Conf., Abstr.*, 55.
- FOMINA, M., HILLIER, S., CHARNOCK, J.M., MELVILLE, K., ALEXANDER, I.J. & GADD, G.M. (2005): Role of oxalic acid overexcretion in transformations of toxic metal minerals by *Beauveria caledonica*. *Appl. Environ. Microbiol.* **71**, 371-381.
- FORESTI, E. & RIVA DI SANSEVERINO, L. (1969): X-ray crystal and molecular structure of an organic mineral: simonellite, $\text{C}_{19}\text{H}_{24}$: 1, 1-dimethyl-7-isopropyl-1, 2, 3, 4-tetrahydrophenanthrene. *Atti. Accad. Naz. Lincei Cl. Sci. Fis. Mat., Nat. Rend.* **47**, 41-54.
- FRANCESCHI, V.R. & HORNER, H.T. (1980): Calcium oxalate crystals in plants. *Botanical Review* **46**, 361-427.
- FRANCESCHI, V.R. & NAKATA, P.A. (2005): Calcium oxalate in plants: formation and function. *Annu. Rev. Plant Biol.* **56**, 41-71.
- FRANK, O., JEHLIČKA, J. & EDWARDS, H.G.M. (2007): Raman spectroscopy as tool for the characterization of thiopolyaromatic hydrocarbons in organic minerals. *Spectrochim. Acta* **A68**, 1065-1069.
- FRANK-KAMENETSKII, V.A., FILATOV, S.K. & YA, L. (1967): Crystalline structure and chemical formula of carpathite. *Mineral. Sbornik* **21**, 275-278 (in Russian).
- FRANZINI, L., PASERO, M. & PERCHIAZZI, N. (1991): Re-discovery and re-definition of dinitite, $\text{C}_{20}\text{H}_{36}$, a forgotten organic mineral from Garfagnana, northern Tuscany, Italy. *Eur. J. Mineral.* **3**, 855-861.
- FREEMAN, K.H., BOREHAM, C.J., SUMMONS, R.E. & HAYES, J.M. (1994): The effect of aromatization on the isotopic compositions of hydrocarbons during early diagenesis. *Org. Geochem.* **21**, 1037-1049.
- FROST, R.L., ERICKSON, K. & WEIER, M. (2004): Thermal treatment of moolooite: a high resolution thermogravimetric and hot stage Raman spectroscopic study. *J. Therm. Anal. Calorimet.* **77**, 851-861.
- FROST, R.L. & WEIER, M.L. (2003): Thermal treatment of weddellite – a Raman and infrared emission spectroscopic study. *Thermochim. Acta* **406**, 221-232.
- FROST, R.L. & WEIER, M.L. (2004): Thermal treatment of whewellite – a thermal analysis and Raman spectroscopic study. *Thermochim. Acta* **409**, 79-85.
- FROST, R.L., YANG, JING & ZHE, DING (2003): Raman and FTIR spectroscopy of natural oxalates: implications for the evidence of life on Mars. *Chin. Sci. Bull.* **48**, 1844-1852.
- FUCHS, L.H., OLSEN, E. & JENSEN, K.J. (1973): Mineralogy, mineral-chemistry, and composition of the Murchison (C2) meteorite. *Smithsonian Contrib. Earth Sci.* **10**, 1-39.
- GAINES, R.V., SKINNER, H.C.W., FOORD, E.E., MASON, B. & ROSENZWEIG, A. (1997): *Dana's New Mineralogy: the System of Mineralogy of James Dwight Dana and Edward Salisbury Dana* (8th ed.). John Wiley & Sons, New York, N.Y.
- GALIMOV, E.M. (1995): Fractionation of carbon isotopes on the way from living to fossil organic matter. In *Stable Isotope in Biosphere* (E. Wada, T. Yonegawa, M. Minagawa, T. Ando & B.D. Fry, eds.). Kyoto University Press, Kyoto, Japan (133-170).
- GALIMOV, E.M., TUGARINOV, A.I. & NIKITIN, A.A. (1975): Origin of whewellite in a hydrothermal uranium deposit. *Geochem. Int.* **5**, 31-37.
- GARAVELLI, C. (1955a): Discovery of oxalite among the secondary minerals of the Capo Calamita layer. *Rend. Soc. Ital. Mineral. Petrol.* **11**, 176-181.

- GARAVELLI, C.L. (1955b): A new mineral among the secondary products of the beds of Capo Calamita (Elba). *Atti. Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat., Rend.* **18**, 392-402.
- GARVIE, L.A.J. (2003): Decay-induced biomineralization of the saguaro cactus (*Carnegiea gigantea*). *Am. Mineral.* **88**, 1879-1888.
- GEIGER, C.A. (2001): Solid solutions in silicate and oxide systems. *Eur. Mineral. Union, Notes in Mineralogy* **3**.
- GEISSMAN, T.A., SIM, K.Y. & MURDOCH, J. (1967): Organic minerals. Picene and chrysene as constituents of the mineral curtisite (idrialite). *Cellular & Molecular Life Sciences* **23**, 793-794.
- GILLESPIE, R.J. (1972): *Molecular Geometry*. Van Nostrand Reinhold, New York, N.Y.
- GILLESPIE, R.J. & HARGITTAI, I. (1991): *The VSEPR Model of Molecular Geometry*. Allyn and Bacon, Boston, Massachusetts.
- GORCHAKOV, P.N., KHOMEYAKOV, A.P. & SHATSKAYA, N.S. (1981): Karpatite and idrialite as typomorphic minerals of tungsten-mercury ores in the Tamvatnei deposit (Chukchi). *Dokl. Akad. Nauk* **257**, 432-435 (in Russian).
- GUDE, A.J., 3D, YOUNG, E.J., KENNEDY, V.C. & RILEY, L.B. (1960): Whewellite and celestite from a fault opening in San Juan County, Utah. *Am. Mineral.* **45**, 1257-1265.
- GUILD, F.N. (1920): Flagstaffite, a new mineral from Arizona. *Am. Mineral.* **5**, 169-172.
- GUILD, F.N. (1921): The identity of flagstaffite and terpin hydrate. *Am. Mineral.* **6**, 133-135.
- HAWTHORNE, F.C. (1985): Towards a structural classification of minerals: the ${}^{\text{VI}}\text{M}^{\text{IV}}\text{T}_2\text{F}_n$ minerals. *Am. Mineral.* **70**, 455-473.
- HAWTHORNE, F.C. (1992a): Bond topology, bond-valence and structure stability. In *The Stability of Minerals* (G.D. Price & N.L. Ross, eds.). Chapman & Hall, New York, N.Y. (25-87).
- HAWTHORNE, F.C. (1992b): The role of OH and H₂O in oxide and oxysalt minerals. *Z. Kristallogr.* **201**, 183-206.
- HAWTHORNE, F.C. (1993): Minerals, mineralogy and mineralogists; past, present and future. *Can. Mineral.* **31**, 253-296.
- HAWTHORNE, F.C. (1994): Structural aspects of oxide and oxysalt crystals. *Acta Crystallogr.* **B50**, 481-510.
- HAWTHORNE, F.C. (1997): Structural aspects of oxide and oxysalt minerals. In *Modular Aspects of Minerals*. (S. Merlini, ed.). *Eur. Mineral. Union, Notes in Mineralogy* **1**, 373-429.
- HAWTHORNE, F.C. (1998): Structure and chemistry of phosphate minerals. *Mineral. Mag.* **62**, 141-164.
- HAYATSU, R., BOTTO, R.E., SCOTT, R.G., MCBETH, R.L. & WINANS, R.E. (1987): Thermal catalytic transformation of pentacyclic triterpenoids: alteration of geochemical fossils during coalification. *Org. Geochem.* **11**, 245-250.
- HIBBS, D.E., KOLITSCH, U., LEVERETT, P., SHARPE, J.L. & WILLIAMS, P.A. (2002): Hoganite and paceite, two new acetate minerals from the Potosi mine, Broken Hill, Australia. *Mineral. Mag.* **66**, 459-464.
- HOCHREIN, O., THOMAS, A. & KNIEP, R. (2008): Revealing the crystal structure of anhydrous calcium oxalate, Ca[C₂O₄], by a combination of atomistic simulation and Rietveld refinement. *Z. Anorg. Allgem. Chem.* **634**, 1826-1829.
- HOEFS, J. (1969): Natural calcium oxalate with heavy carbon. *Nature* **223**, 396.
- HOEFS, J. (2004): *Stable Isotope Geochemistry*. Springer, New York, N.Y.
- HOFMANN, B.A. (2004): Highly altered organic matters on Earth: biosignature relevance. In *Astrobiology: Future Perspectives* (P. Ehrenfreund, W. M. Irvine, T. Owen, L. Becker, J. Blank, J. R. Brucato, L. Colangeli, S. Derenne, A. Dutrey, D. Despois, A. Lazcano & F. Robert, eds.). Kluwer Academic Publishers, Dordrecht, The Netherlands (317-332).
- HOFMANN, B.A. & BERNASCONI, S.M. (1998): Review of occurrences and carbon isotope geochemistry of oxalate minerals: implications for the origin and fate of oxalate in diagenetic and hydrothermal fluids. *Chem. Geol.* **149**, 127-146.
- HUNT, J.M. (1995): *Petroleum Geochemistry and Geology* (2nd ed.). Freeman, New York, N.Y.
- HYDE, C. & LANDY, R.A. (1966): Whewellite from septarian concretions near Milan, Ohio. *Am. Mineral.* **51**, 228-229.
- IMAI, A., SHIKAZONO, N., SHIMIZU, M. & SHIMAZAKI, H. (2006): Sulfur isotope study on Hg and Sb deposits in Japan. *Resour. Geol.* **56**, 37-48.
- ISHIWATARI, R. (2004): Organic matters on Earth. In *Organic Geochemistry* (R. Ishiwatari & M. Yamamoto, eds.). Baifukan, Tokyo, Japan (6-10).
- JEFFREY, G.A. & PARRY, G.S. (1954): The crystal structure of sodium oxalate. *J. Am. Chem. Soc.* **76**, 5283-5286.
- JEHLIČKA, J. & EDWARDS, H.G.M. (2008): Raman spectroscopy as a tool for the non-destructive identification of organic minerals in the geological record. *Org. Geochem.* **39**, 371-386.
- JEHLIČKA, J., EDWARDS, H.G.M., JORGE VILLER, S.E. & FRANK, O. (2006): Raman spectroscopic study of the complex aromatic mineral idrialite. *J. Raman Spectrosc.* **37**, 771-776.
- JEHLIČKA, J., EDWARDS, H.G.M. & VÍTEK, P. (2009): Assessment of Raman spectroscopy as a tool for the non-destructive

- tive identification of organic minerals and biomolecules for Mars studies. *Planet. Space Sci.* **57**, 606-613.
- JORGENSEN, W.L. & SEVERANCE, D.L. (1990): Aromatic-aromatic interactions: free energy profiles for the benzene dimer in water, chloroform, and liquid benzene. *J. Am. Chem. Soc.* **112**, 4768-4774.
- KAWAMURA, K. & KAPLAN, I.R. (1987): Dicarboxylic acids generated by thermal alteration of kerogen and humic acids. *Geochim. Cosmochim. Acta* **51**, 3201-3207.
- KEMPE, S. (1979): Carbon in the rock cycle. In SCOPE 13, The Global Carbon Cycle (B. Bolin, E.T. Degens, S. Kempe & P. Ketner, eds.). John Wiley and Sons, Chichester, U.K. (343-377).
- KHOLODKOVSKAYA, L.N., TRUNOV, V.K. & TSKHELASHVILI, N.B. (1990): Crystal structures of cesium hydrogen oxalate and cesium oxalate dihydrate. *J. Struct. Chem.* **31**, 667-670.
- KHOMYAKOV, A.P. (1996): Natroxalate $\text{Na}_2\text{C}_2\text{O}_4$, a new mineral. *Zap. Vser. Mineral. Obshchest.* **125**(1), 126-132 (in Russian).
- KIM, E., PALIWAL, S. & WILCOX, C.S. (1998): Measurements of molecular electrostatic field effects in edge-to-face aromatic interactions and CH- π interactions with implications for protein folding and molecular recognition. *J. Am. Chem. Soc.* **120**, 11192-11193.
- KITAGAWA, S., OKUBO, T., KAWATA, S., KONDO, M., KATADA, M. & KOBAYASHI, H. (1995): An oxalate-linked copper (II) coordination polymer, $[\text{Cu}_2(\text{oxalate})_2(\text{pyrazine})_3]_n$, constructed with two different copper units: X-ray crystallographic and electronic structures. *Inorg. Chem.* **34**, 4790-4796.
- KLARUP, D.G. (1997): The influence of oxalic acid on release rates of metals from contaminated river sediment. *Sci. Total Environ.* **204**, 223-231.
- KLEIN, C. & DUTROW, B. (2008): *Manual of Mineral Science* (after James D. Dana) (23rd ed.). John Wiley & Sons, Inc., New York, N.Y.
- KLOPROGGE, J.T., BOSTRÖM, T.E. & WEIER, M.L. (2004): In situ observation of the thermal decomposition of weddellite by heating stage environmental scanning electron microscopy. *Am. Mineral.* **89**, 245-248.
- KNIPOVICH, Y.N., KOMKOV, A.I. & NEFEDOV, E.I. (1963): On stepanovite and the new mineral zhemchuzhnikovite. *Trudy Vses. Nauchno-Issled. Geol. Inst.* **96**, 131-135 (in Russian).
- KOLAY, A.K. (2007): *Soil Genesis, Classification Survey and Evaluation*. Atlantic Publishers & Distributors, New Delhi, India.
- KOTEL'NIKOVA, E.N., FILATOV, S.K. & CHUKANOV, N.B. (2004): Evenkite: symmetry, chemical composition, identification, and thermal behavior. *Zap. Vser. Mineral. Obshchest.* **133**(3), 80-92 (in Russian).
- KOTEL'NIKOVA, E.N., PLATONOVA, N.V. & FILATOV, S.K. (2007): Identification of biogenic paraffins and their thermal phase transitions. *Geol. Ore Deposits* **49**, 697-709.
- KOUKOZAS, N., WARD, C.R. & LI, ZHONGSHENG (2010): Mineralogy of lignites and associated strata in the Mavropigi field of the Ptolemais Basin, northern Greece. *Int. J. Coal Geol.* **81**, 182-190.
- KRISHNAMURTY, K.V. & HARRIS, G.M. (1961): The chemistry of the metal oxalato complexes. *Chem. Rev.* **61**, 213-246.
- KRZYSZOWSKA, A.J., VANCE, G.F., BAYLOCK, M.J. & DAVID, M.B. (1996): Ion-chromatographic analysis of low molecular weight organic acids in Spodosol forest floor solutions. *Soil Sci. Soc. Am. J.* **60**, 1565-1571.
- LEAVENS, P.B. (1968): New data on whewellite. *Am. Mineral.* **53**, 455-463.
- LEWIS, G.N. (1923): Valence and the electron. *Trans. Faraday Soc.* **19**, 452-458.
- LEWIS, G.N. (1966): *Valence and the Structure of Atoms and Molecules*. Dover Publications, New York, N.Y.
- LIBOWITZKY, E. (1999): Correlation of O-H stretching frequencies and O-H...O hydrogen bond lengths in minerals. *Monatsh. Chem.* **130**, 1047-1059.
- LOWENSTAM, H.A. & WEINER, S. (1989): *On Biomineralization*. Oxford University Press, New York, N.Y.
- MACE, H.A. & PETERSON, R.C. (1995): The crystal structure of fichtelite, a naturally occurring hydrocarbon. *Can. Mineral.* **33**, 7-11.
- MACKLEN, E.D. (1968): Influence of atmosphere on the thermal decomposition of some transition metal oxalates. *J. Inorg. Nucl. Chem.* **30**, 2689-2695.
- MANASSE, E. (1911): Oxalite (humboldtine) from Cape D'Arco (Elba). *Rend. Accad. Lincei* **19**, 138-145.
- MANNING, D.A.C., LOPEZ-CAPEL, E., WHITE, M.L. & BARKER, S. (2008): Carbon isotope determination for separate components of heterogeneous materials using coupled thermogravimetric analysis/isotope ratio mass spectrometry. *Rap. Comm. Mass Spectr.* **22**, 1187-1195.
- MASON, B. & BERRY, L.G. (1968): *Elements of Mineralogy*. W.H. Freeman, San Francisco, California.
- MASON, G.M., TRUDELL, L.G. & BRANTHAVER, J.F. (1989): Review of the stratigraphic distribution and diagenetic history of abelsonite. *Org. Geochem.* **14**, 585-594.
- MATIOLI, P.A., ATENCIO, D., COUTINHO, J.M.V. & MENEZES FILHO, L.A.D. (1997): Humboldtina de Santa Maria de Itabira, Minas Gerais: primeira ocorrência brasileira e

- primeira ocorrência mundial em fraturas de pegmatito. *An. Acad. Brasil. Ciênc.* **69**, 431-432.
- MATSUBARA, S. & ICHIKURA, M. (1975): Weddellite in bottom sediments from the sea of Japan. *J. Geol. Soc. Japan* **81**, 199-201.
- MCCOLLOM, T.M. & SEEWALD, J.S. (2007): Abiotic synthesis of organic compounds in deep-sea hydrothermal environments. *Chem. Rev.* **107**, 382-401.
- MIEDANER, M.M., MIGDISOV, A.A. & WILLIAMS-JONES, A.E. (2005): Solubility of metallic mercury in octane, dodecane and toluene at temperatures between 100°C and 200°C. *Geochim. Cosmochim. Acta* **69**, 5511-5516.
- MILLS, S.J., HATERT, F., NICKEL, E.H. & FERRARIS, G. (2009): The standardisation of mineral group hierarchies: application to recent nomenclature proposals. *Eur. J. Mineral.* **21**, 1073-1080.
- MILTON, C., DWORNIK, E.J., ESTEP-BARNES, P.A., FINKELMAN, R.B., PABST, A. & PALMER, S. (1978): Abelsonite, nickel porphyrin, a new mineral from the Green River Formation, Utah. *Am. Mineral.* **63**, 930-937.
- MOORE, P.B. (1973): Pegmatite phosphates: descriptive mineralogy and crystal chemistry. *Mineral. Rec.* **4**, 103-130.
- MUEHLDORF, A.V., VAN ENGEN, D., WARNER, J.C. & HAMILTON, A.D. (1988): Aromatic-aromatic interactions in molecular recognition: a family of artificial receptors for thymine that shows both face-to-face and edge-to-face orientations. *J. Am. Chem. Soc.* **110**, 6561-6562.
- MURDOCH, J. & GEISSMAN, T.A. (1967): Pendletonite, a new hydrocarbon mineral from California. *Am. Mineral.* **52**, 611-616.
- MYERS, R. (2003): *The Basics of Chemistry*. Greenwood Publishing Group, Westport, Connecticut.
- MYSEN, B.O. & FRANTZ, J.D. (1993): Structure of silicate melts at high temperature: in-situ measurements in the system BaO-SiO₂ to 1669°C. *Am. Mineral.* **78**, 699-709.
- MYSEN, B.O., VIRGO, D. & SCARFE, C.M. (1980): Relations between the anionic structure and viscosity of silicate melts – a Raman spectroscopic study. *Am. Mineral.* **65**, 690-710.
- NAGY, P., FISCHER, A., GLASER, J., ILYUKHIN, A., MALIARIK, M. & TÓTH, I. (2005): Solubility, complex formation, and redox reactions in the Ti₂O₃ – HCN/CN – H₂O system. Crystal structures of the cyano compounds Ti(CN)₃•H₂O, Na[Ti(CN)₄]•3H₂O, K[Ti(CN)₄], and Ti^{III}[Ti^{III}(CN)₄] and of Ti₂C₂O₄. *Inorg. Chem.* **44**, 2347-2357.
- NAKAMOTO, K., MARGOSHES, M. & RUNDLE, R.E. (1955): Stretching frequencies as a function of distances in hydrogen bonds. *J. Am. Chem. Soc.* **77**, 6480-6486.
- NASDALA, L. & PEKOV, I.V. (1993): Ravatite, C₁₄H₁₀, a new organic mineral species from Ravat, Tadzhikistan. *Eur. J. Mineral.* **5**, 699-705.
- NICKEL, E.H. & GRICE, J.D. (1998): The IMA Commission on New Minerals and Mineral Names: procedures and guidelines on mineral nomenclature, 1998. *Can. Mineral.* **36**, 913-926.
- NICKEL, E.H. & NICHOLS, M.C. (2008): IMA/CNMNC list of mineral names. <http://pubsites.uws.edu.au/ima-cnmc/MINERALlist.pdf>
- OFTEDAL, I. (1922): Minerals from the burning coal seam at Mt. Pyramide, Spitsbergen. *Res. Nors. Stat. Spits. Kristian.* **1**, 9-14.
- PAUTOV, L.A., KARPENKO, V.Y., SOKOLOVA, E.V. & IGNATENKO, K.I. (1993): Tsaregorodtsevitse, N(CH₃)₄[Si₂(Si_{0.5}Al_{0.5})O₆]₂: a new mineral. *Zap. Vser. Mineral. Obshchest.* **122**(1), 128-135.
- PEABODY, C.E. & EINAUDI, M.T. (1992): Origin of petroleum and mercury in the Culver-Baer cinnabar deposit, Mayacamas District, California. *Econ. Geol.* **87**, 1078-1103.
- PEACOR, D.R., ROUSE, R.C., ESSENE, E.J. & LAUF, R.J. (1999): Coskrenite-(Ce), (Ce,Nd,La)₂(SO₄)₂(C₂O₄)•8H₂O, a new rare-earth oxalate mineral from Alum Cave Bluff, Tennessee: characterization and crystal structure. *Can. Mineral.* **37**, 1453-1462.
- PEMBERTON, H.E. (1983): *Minerals of California*. Van Nostrand Reinhold, New York, N.Y.
- PIOTROVSKII, G.L. (1955): Karpatite (Carpathite) – a new organic mineral from Trans-Carpathia. *Mineral. Sbornik* **9**, 120-127.
- PLATONOVA, N.V. & KOTEL'NIKOVA, E.N. (2006): Synthesis of the organic mineral evenkite. *Zap. Vser. Mineral. Obshchest.* **135**(4), 87-91 (in Russian).
- POVARENENYKH, A.S. & RUSAKOVA, L.D. (1973): The new mineral kafehydrocyanite. *Int. Geol. Rev.* **15**, 1095-1100.
- RENNER, B. & LEHMANN, G. (1986): Correlation of angular and bond length distortions in TO₄ units in crystals. *Z. Kristallogr.* **175**, 43-59.
- ROST, R. (1937): The minerals in the burning shafts at Kladno. *Rozpravy Česká Akademie, Kl II*, **47**, 1-19.
- ROST, R. (1942): Supplements to the mineralogy of the burning (coal) heaps in the region of Kladno. *Rozpravy České Akademie* **52**, 4.
- ROUSE, R.C., PEACOR, D.R., DUNN, P.J., SIMMONS, W.B. & NEWBURY, D. (1986): Wheatleyite, Na₂Cu(C₂O₄)₂•2H₂O, a natural sodium copper salt of oxalic acid. *Am. Mineral.* **71**, 1240-1242.
- ROUSE, R.C., PEACOR, D.R., ESSENE, E.J., COSKREN, T.D. & LAUF, R.J. (2001): The new minerals levinsonite-(Y) [(Y, Nd, Ce)Al(SO₄)₂(C₂O₄)•12H₂O] and zugshunsite-(Ce) [(Ce, Nd, La)Al(SO₄)₂(C₂O₄)•12H₂O]: coexisting oxalates with different structures and differentiation of LREE and HREE. *Geochim. Cosmochim. Acta* **65**, 1101-1115.

- RUSHDI, A.I. & SIMONEIT, B.R.T. (2005): Abiotic synthesis of organic compounds from carbon disulfide under hydrothermal conditions. *Astrobiology* **5**, 749-769.
- SASAKI, A. & ISHIHARA, S. (1979): Sulfur isotopic composition of the magnetite-series and ilmenite-series granitoids in Japan. *Contrib. Mineral. Petrol.* **68**, 107-115.
- SCHINDLER, M. & HAWTHORNE, F.C. (2001a): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. I. Theory. *Can. Mineral.* **39**, 1225-1242.
- SCHINDLER, M. & HAWTHORNE, F.C. (2001b): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. II. Crystal structure and chemical composition of borate minerals. *Can. Mineral.* **39**, 1243-1256.
- SCHINDLER, M. & HAWTHORNE, F.C. (2004): A bond-valence approach to the uranyl-oxide hydroxy-hydrate minerals: chemical composition and occurrence. *Can. Mineral.* **42**, 1601-1627.
- SCHOEP, A. (1928): Julienite. *Natuurwetenschappelijk Tijdschrift (Ghent)* **10**, 58-59.
- SEPE, M.P. (1997): *Thermal Analysis of Polymers*. Rapra Technology, Shrewsbury, U.K.
- SHANNON, R. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.
- SHERLOCK, R. (2000): The association of gold-mercury mineralization and hydrocarbons in the coast ranges of northern California. In *Organic Matter and Mineralization: Thermal Alteration, Hydrocarbon Generation and Role of Metallogenesis* (M. Glikson & M. Mastalerz, eds.). Kluwer Academic Publications, Dordrecht, The Netherlands (378-399).
- SIMONEIT, B.R.T. (1986): Cyclic terpenoids of the geosphere. In *Biological Markers In The Sedimentary Record* (R.B. Johns, ed.). Elsevier, New York, N.Y. (43-99).
- SIMONEIT, B.R.T. (1993): Hydrothermal alteration of organic matter in marine and terrestrial systems. In *Organic Geochemistry: Principles and Applications* (M.H. Engel & S.A. Macko, eds.). Springer, Heidelberg, Germany (397-418).
- SIMONEIT, B.R.T. & FETZER, J.C. (1996): High molecular weight polycyclic aromatic hydrocarbons in hydrothermal petroleum from the Gulf of California and northeast Pacific Ocean. *Org. Geochem.* **24**, 1065-1077.
- SIMONEIT, B.R.T. & LONSDALE, P.F. (1982): Hydrothermal petroleum in mineralized mounds at the seabed of Guaymas Basin. *Nature* **295**, 198-202.
- SIMONEIT, B.R.T. & SCHOELL, M. (1995): Carbon isotope systematics of individual hydrocarbons in hydrothermal petroleum from the Guaymas Basin, Gulf of California. *Org. Geochem.* **23**, 857-863.
- SIMONEIT, B.R.T., SCHOELL, M. & KVENVOLDEN, K.A. (1997): Carbon isotope systematics of individual hydrocarbons in hydrothermal petroleum from Escanaba Trough, northeastern Pacific Ocean. *Org. Geochem.* **26**, 511-515.
- SKROPYSHEV, A.V. (1953): A paraffin in a polymetallic vein. *Dokl. Akad. Nauk* **88**, 717-719 (in Russian).
- ŚLEDZIŃSKA, I., MURASIK, A. & FISCHER, P. (1987): Magnetic ordering of the linear chain system manganese oxalate dihydrate investigated by means of neutron diffraction and bulk magnetic measurements. *J. Phys. C* **20**, 2247-2259.
- ŚLEDZIŃSKA, I., MURASIK, A. & PIOTROWSKI, M. (1986): Neutron diffraction study of crystal and magnetic structures of α -FeC₂O₄•2D₂O. *Physica B* **138**, 315-322.
- SOLEIMANNEJAD, J., AGHABOZORG, H., HOOSHMAND, S., GHADERMAZI, M. & GHARAMALEKI, J.A. (2007): The monoclinic polymorph of catena-poly [[diaquamanganese (II)]- μ -oxalato- κ O¹,O²:O¹,O²]. *Acta Crystallogr.* **E63**, m2389-m2390.
- SREBRODOL'SKII, B.I. (1975): Acetamide, CH₃CONH₂, a new mineral. *Zap. Vses. Mineral. Obshchest.* **104**, 326-328.
- STEIN, S.E. (1978): On the high temperature chemical equilibria of polycyclic aromatic hydrocarbons. *J. Phys. Chem.* **82**, 566-571.
- STEIN, S.E. & FAHR, A. (1985): High-temperature stabilities of hydrocarbons. *J. Phys. Chem.* **89**, 3714-3725.
- STIEFEL, E.I. & BROWN, G.F. (1972): Detailed nature of the six-coordinate polyhedra in tris (bidentate ligand) complexes. *Inorg. Chem.* **11**, 434-436.
- STRUNZ, H. (1962): Fichtelit, dimethyl-isopropyl-perhydrophenanthren. *Naturwiss.* **49**, 9-10.
- STRUNZ, H. & CONTAG, B. (1965): Evenkite, flagstaffite, idrialite, and refikite. *Neues Jahrb. Mineral., Monatsh.*, 19-25.
- TAZZOLI, V. & DOMENEGHETTI, C. (1980): The crystal structures of whewellite and weddellite: re-examination and comparison. *Am. Mineral.* **65**, 327-334.
- TYRA, M.A., FARQUHAR, J., WING, B.A., BENEDIX, G.K., JULL, A.J.T., JACKSON, T. & THIEMENS, M.H. (2007): Terrestrial alteration of carbonate in a suite of Antarctic CM chondrites: evidence from oxygen and carbon isotopes. *Geochim. Cosmochim. Acta* **71**, 782-795.
- VAN TASSEL, R. (1945): Une efflorescence d'acétachlorure de calcium sur des roches calcaires dans des collections. *Bull. Musée Royal d' Histoire Naturelle de Belgique* **21**(26), 1-11.
- VOLLHARDT, K.P.C. & SCHORE, N.E. (2002): *Organic Chemistry: Structure and Function* (4th ed.). W.H. Freeman and Company, New York, N.Y.

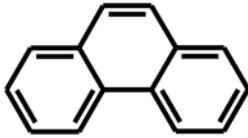
- WEINER, S. & DOVE, P.M. (2003): An overview of biomineralization processes and the problem of the vital effect. In Biomineralization (P.M. Dove, J.J. De Yoreo & S. Weiner, eds.). *Rev. Mineral. Geochem.* **54**, 1-29.
- WELLER, M.T., HENRY, P.F. & LIGHT, M.E. (2007): Rapid structure determination of the hydrogen-containing compound $\text{Cs}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ by joint single-crystal X-ray and powder neutron diffraction. *Acta Crystallogr.* **B63**, 426-432.
- WESSON, J.A. & WARD, M.D. (2007): Pathological biomineralization of kidney stones. *Elements* **3**, 415-421.
- WEST, A.R. (1988): *Basic Solid State Chemistry*. John Wiley & Sons Inc., New York, N.Y.
- WIEDEMANN, G. & BAYER, G. (1988): Kinetics of the formation of whewellite and weddellite by displacement reactions. *J. Therm. Anal. Calorimet.* **33**, 707-718.
- WILHELM, S.M. & BLOOM, N. (2000): Mercury in petroleum. *Fuel Process. Technol.* **63**, 1-27.
- WILLS, B.A. & NAPIER-MUNN, T. (2006): *Wills' Mineral Processing Technology: An Introduction to The Practical Aspects of Ore Treatment and Mineral Recovery*. Butterworth-Heinemann, Oxford. U.K.
- WILSON, M.J., JONES, D. & RUSSELL, J.D. (1980): Glushinskite, a naturally occurring magnesium oxalate. *Mineral. Mag.* **43**, 837-840.
- WINCHELL, H. & BENOIT, R.J. (1951): Taylorite, mascagnite, aphthitalite, lecontite, and oxammite from guano. *Am. Mineral.* **36**, 590-602.
- WISE, S.A., CAMPBELL, R.M., WEST, W.R., LEE, M.L. & BARTLE, K.D. (1986): Characterization of polycyclic aromatic hydrocarbon minerals curtisite, idrialite and pendletonite using high-performance liquid chromatography, gas chromatography, mass spectrometry and nuclear magnetic resonance spectroscopy. *Chem. Geol.* **54**, 339-357.
- WRIGHT, F.E. & ALLEN, E.T. (1930): Curtisite. A new organic mineral from Skaggs Springs, Sonoma County, California. *Am. Mineral.* **15**, 169-173.
- WRIGHT, J.D. (1995): *Molecular Crystals* (2nd ed.). Cambridge University Press, Cambridge, U.K.
- WUNDERLICH, B. (2005): *Thermal Analysis of Polymeric Materials*. Springer-Verlag, Berlin, Germany.
- YU, JIAN ZHEN, HUANG, XIAO-FENG, XU, JINHUI & HU, MIN (2005): When aerosol sulfate goes up, so does oxalate: implication for the formation mechanisms of oxalate. *Environ. Sci. Technol.* **39**, 128-133.
- ŽÁK, K. & SKÁLA, R. (1993): Carbon isotopic composition of whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) from different geological environments and its significance. *Chem. Geol.* **106**, 123-131.
- ŽÁK, L. (1972): A contribution to the crystal chemistry of melanophlogite. *Am. Mineral.* **57**, 779-796.

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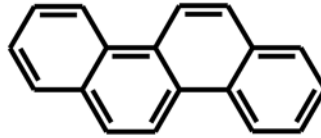
APPENDIX. THE STRUCTURES OF ORGANIC COMPOUNDS CITED IN THE TEXT



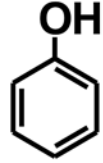
(I) benzene



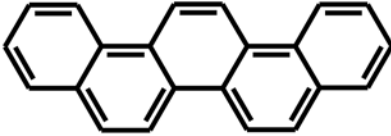
(II) phenanthrene



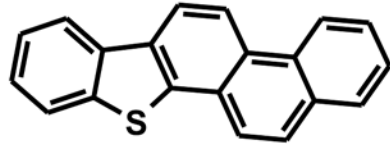
(III) chrysene



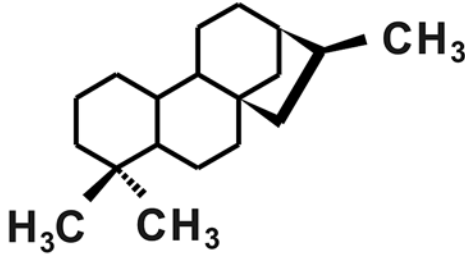
(IV) toluene



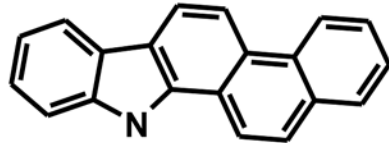
(V) picene



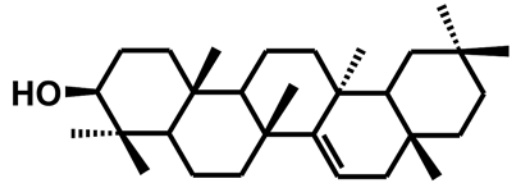
(VI) benzo-phenanthro-thiophene



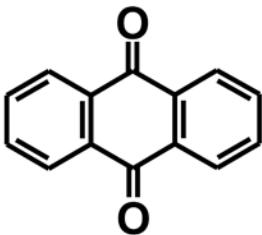
(VII) phyllocladane



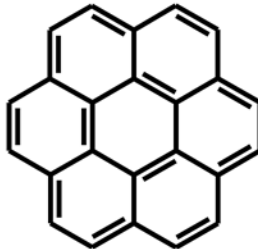
(VIII) dibenzo-carbazole

(IX) β -amylin

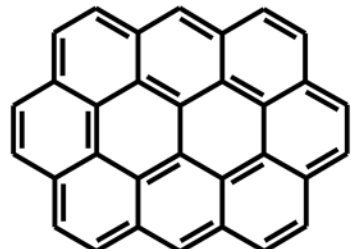
(X) taraxerol



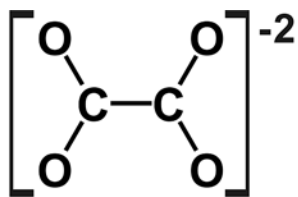
(XI) anthraquinone



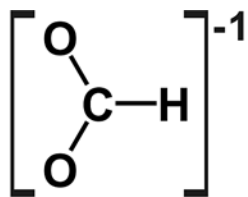
(XII) coronene



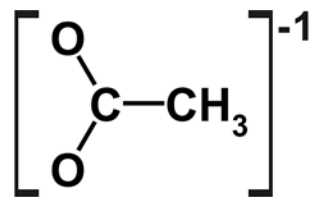
(XIII) ovalene



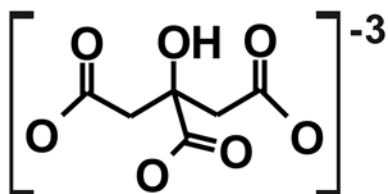
(XIV) oxalate ion



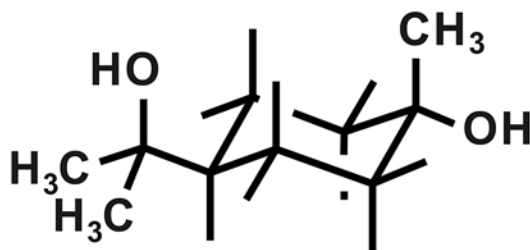
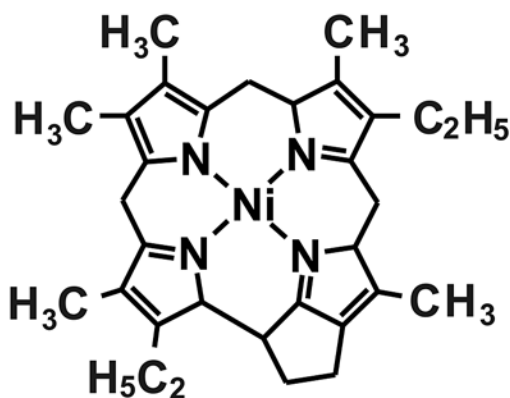
(XV) formate ion



(XVI) acetate ion



(XVII) citrate ion

(XVIII) *cis*-terpin

(XIX) Ni-porphyrin

