



Invited review

Natural iron oxalates and their analogous synthetic counterparts: A review



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ABSTRACT

Four iron-containing natural oxalates, usually classified as organic minerals, are known (humboldtine, minguzzite, stepanovite and zhemchuzhnikovite). Their occurrences and general properties are presented and briefly discussed. The subsequent part of the review is devoted to the discussion of synthetic oxalato-complexes, analogous to these natural species, including usual synthetic procedures and a thorough analysis of their crystallographic and structural peculiarities. The thermal, spectroscopic and magnetic properties of these complexes are also analyzed in detail and comparisons with other closely related complexes are also included in the discussions.

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1. Introduction

Metallic crystalline oxalates are widely distributed in nature and have been observed in rocks, soil, water bodies and among a variety of living organisms, including plants and animals. They constitute a group of relatively rare and scarce minerals which are usually classified as “organic crystals” or “organic minerals” (Strunz and Nickel, 2001; Weiner and Dove, 2003; Echigo and Kimata, 2010). Some of these crystals are found in living organisms (the so-called biominerals) and are generated through some of the well-known biomineral and physiological strategies used for the formation of such deposits (Lowenstam, 1981; Baran, 1995; Weiner and Dove, 2003; Franceschi and Nakata, 2005; He et al., 2014). Additionally, it was recently found that oxalic acid, mainly in the form of its Ca(II) and Zn(II) complexes, is also present in aerosol particles (Furukawa and Takahashi, 2011).

Since the recognition that organic acids are important constituents of some basinal fluids, their potential influence on diagenetic processes, especially porosity evolution and elemental mobilization through complexation, generated increasing research on the effects of these acids, their reactions in solution, and their thermal stability (Hofmann and Bernasconi, 1998). Among these dissolved acids, acetate is the most abundant one, constituting between 80–90% of total dissolved organic acid species. Propionate, butyrate and valerate constitute the greatest part of the remaining anions, whereas the concentration of dicarboxylic acids, including oxalate, is relatively low (Hofmann and Bernasconi, 1998). Notwithstanding, oxalates constitute the most abundant group of known organic minerals, with twenty one different species reported so far, which are presented in Table 1, whereas other carboxylate minerals (formates and acetates) are restricted to only a few examples (Echigo and Kimata, 2010).

Three main types of occurrences for oxalate minerals have been identified: near-surface environments, diagenetic or hydrothermal. The near-surface and biological occurrences are the most usual and have been reported from soils, lichen-soil interfaces, rock patinae, oxidized ores, marine sediments, guano and living organisms (Hofmann and Bernasconi, 1998; Baran and Monje, 2008). In all these cases, the association of oxalate phases with organic material providing a source of oxalate is obvious. The mineralogical variability of near-surface oxalates reflects the availability of this anion in various geochemical environments. Some interesting examples are the generation of moolooite, $\text{Cu}(\text{C}_2\text{O}_4) \cdot n\text{H}_2\text{O}$, formed by interaction of solutions derived from bird guano (the biological source) and weathering copper sulphides, as well as the appearance of oxammite, $(\text{NH}_4)_2(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ also in guano deposits (Baran and Monje, 2008). On the other hand, it was assumed that the generation of deveraite, $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$, occurs by interaction of an oxalate source provided by incomplete oxidation of organic material, such as decaying plant remains, and the cerium rich arsenosilicate cervandonite-(Ce) (Guastoni et al., 2013).

Hydrous oxalates are expected to form in incompletely oxidized surface environments such as plant material, sediments rich in organic materials, as well as coal and black shales, settings in which they are commonly reported (Hofmann and Bernasconi, 1998; Rouse et al., 2001).

The fact that whewellite, $\text{Ca}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$, seems to be the most common and widely distributed oxalate mineral, can surely be related to its extremely low water solubility (its solubility product is 1.45×10^{-9} (Streit et al., 1998)). It is also the thermodynamically

most stable form of the hydrates of calcium oxalate (Baran and Monje, 2008). This low water solubility is one of the main reasons for the rarity of other oxalate minerals; the formation of whewellite lowers the dissolved oxalate level to a point where other oxalates cannot form. Therefore, a low level of dissolved calcium is needed for the formation of other, more soluble oxalates, and calcium rich rocks should be unfavorable environments for the generation of oxalates, other than those of calcium (Rouse et al., 2001).

Oxalic acid, ethanedioic acid, is the simplest of the dicarboxylic acids. The acid and some of its salts have been known since more than two hundred years. The form usually used in the chemistry laboratories, obtained by water recrystallization, is the monoclinic dihydrate, usually referred as $\alpha\text{-(COOH)} \cdot 2\text{H}_2\text{O}$, space group $P2_1/n$ and $Z=2$ (Stevens and Coppens, 1980). Its protonation equilibria have often been investigated; the pK values obtained at 25 °C and at ionic strength of 0.1 M are $\text{pK}_1 = 1.04$ and $\text{pK}_2 = 3.82$ (Martell and Smith, 1977), indicating that oxalic acid is a strong organic acid.

The acid generates a great variety of salts and complexes with practically all the known metallic oxides or bases and the oxalate anion is a well-known and widely investigated ligand in coordination chemistry (Cotton et al., 1999). A recent survey of more than 800 oxalate-containing complexes for which structural information is available, has shown that the anion possesses 15 different coordination modes with respect to metal centers, and depending on the coordination mode, oxalate ions can form from one to eight metal-oxygen bonds (Serezhkin et al., 2005), confirming the wide versatility of this ligand. It is potentially a tetradentate ligand, but it can of course also act in a mono- bi- or tri-dentate fashion, forming mononuclear or polynuclear metal complexes.

Calcium oxalate minerals (the mono-, di- and tri-hydrates of $\text{Ca}(\text{C}_2\text{O}_4)$), are the most common family of organic minerals in natural environments, usually occurring in carbonate concretions, marine and lake sediments, hydrothermal veins and lignite (Echigo and Kimata, 2010). Other metallic oxalates, containing manganese, iron or copper and even some of the lanthanide cations are rarer and were found only sporadically.

Calcium oxalates are also the most common and abundant biominerals found in the plant kingdom (Webb, 1999; Nakata, 2003; Monje and Baran, 2004; Franceschi and Nakata, 2005; Baran and Monje, 2008; Echigo and Kimata, 2010) and they are also widely recognized in the life sciences due of their common association with kidney stone disease (urolithiasis) (Chaplin, 1977; Milliner, 1995; Baran and Monje, 2008). The presence of other metallic oxalates is extremely rare in biological systems, although the respective copper, magnesium and manganese complexes have sometimes been detected in rock-lichen interfaces (Monje and Baran, 2004; Baran and Monje, 2008), whereas natural ammonium oxalate (oxammite) has been found in guano deposits (Winchell and Benoit, 1951).

In the present review we will focus our attention on the four known natural iron oxalates, as well as to the analogous synthetic complexes, and to some closely related species, which chemical and physicochemical characterization allow a better and deeper understanding of the behavior of these interesting natural systems.

2. Natural iron oxalates

Only four from the twenty one mineral oxalates shown in Table 1 are iron compounds. These are humboldtine, $\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$, min-guzzite, $\text{K}_3[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, stepanovite, $\text{NaMg}[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3] \cdot 8\text{H}_2\text{O}$, and zhemchuzhnikovite, $\text{NaMg}[(\text{Al}, \text{Fe}^{\text{III}})(\text{C}_2\text{O}_4)_3] \cdot 8\text{H}_2\text{O}$. Only

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