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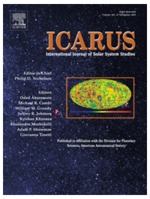

Reflectance spectroscopy of oxalate minerals and relevance to Solar System carbon inventories

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ABSTRACT

The diversity of oxalate formation mechanisms suggests that significant concentrations of oxalic acid and oxalate minerals could be widely distributed in the Solar System. We have carried out a systematic study of the reflectance spectra of oxalate minerals and oxalic acid, covering the 0.2–16 µm wavelength region. Our analyses show that oxalates exhibit unique spectral features that enable discrimination between oxalate phases and from other commonly occurring compounds, including carbonates, in all regions of the spectrum except for the visible. Using these spectral data, we consider the possible contribution of oxalate minerals to previously observed reflectance spectra of many objects throughout the Solar System, including satellites, comets, and asteroids. We find that polycarboxylic acid dimers and their salts may explain the reflectance spectra of many carbonaceous asteroids in the 3 µm spectral region. We suggest surface concentration of these compounds may be a type of space weathering from the photochemical and oxidative decomposition of the organic macromolecular material found in carbonaceous chondrites. The stability and ubiquity of these minerals on Earth, in extraterrestrial materials, and in association with biological processes make them useful for many applications in Earth and planetary sciences.

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1. Introduction

Oxalate minerals occur in many settings on Earth, and may be more widely distributed in the Solar System than has generally been recognized. In this paper we review the formation mechanisms of oxalate and its occurrence on Earth, in lunar samples, and in meteorites. This is followed by detailed analysis of the reflectance spectra of oxalates and a search for evidence of their presence in the Solar System.

1.1. Oxalates on Earth

Metal oxalates (most often $M_xC_2O_4{\bullet}nH_2O$) are the most commonly occurring ionic organic minerals on Earth (Gaines et al., 1997; Echigo and Kimata, 2010; Hazen et al., 2013), and are the only salts of any organic acid that are stable on geologic times scales (Hoffman and Bernasconi, 1998; Hofmann, 2004). Oxalic acid (in solid form, $H_2C_2O_4{\bullet}nH_2O$), forms through both biological and abiological mechanisms, most commonly from the decomposition of larger carbon-bearing compounds. With many formation mechanisms and greater residence time than all other organic salts, oxalates are present in a wide range of both naturally occurring and anthropogenic settings. Oxalates therefore bridge the gap between the inorganic and organic and are an important and unique class of minerals.

Oxalates are prevalent in desert rock 'varnish' accompanied by silica (Beazley et al, 2002). Oxalate desert coatings may form by the periodic flow of oxalate-bearing water over the rock surfaces or concentrated through evaporation of meteoric water (Dorn, 2007). The sources of this dilute oxalate are mostly biological (Del Monte et al., 1987; Whitney and Arnott, 1987; Russ et al., 1996; Bjelland et al., 2002; Bjelland and Thorseth, 2002; Souza-Egipsy et al., 2004), but can also be abiotic (Watchman, 1991). Most often, the varnish is associated with lichens, which commonly produce oxalates (Johnston and Vestal, 1993). The thickness of these coatings can range from a few microns to millimeters.

There are numerous occurrences of oxalate minerals (mostly whewellite - $CaC_2O_4{\bullet}H_2O$) in subsurface diagenetic and hydrothermal deposits dated as old as Ordovician, and they have been comprehensively reviewed by Hoffman (1999). Diagenetic oxalates are associated with organic-rich sediments, such as coal beds and black shales, with crystals reaching 23 cm in diameter. There has

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been at least one reported diagenetic occurrence of rock-forming oxalate (von Gaertner, 1958). In particular, oxalates are widely reported in organic-bearing uranium deposits; oxalate minerals appear highly resistant to radiation damage from coexisting uranium-bearing minerals and likely form from the radiolysis of organic matter. Indeed, metal oxalates have been shown to strongly resist decomposition by γ-radiolysis (Dougherty and Gottschall, 1976, 1977). Hydrothermal occurrences of oxalates are generally as late stage minerals in veins of paragenetic association, sometimes cogenetic with carbonates and sulfides. Oxalates are a predicted product of organic synthesis in hydrothermal systems (Shock and Schulte, 1998); carboxylic acid formation occurs in organic-rich basins, and oxalates form as precipitates in brine seepages (Kawamura and Nissenbaum, 1992). The review by Hoffman (1999) concludes that oxalates are a relatively common late phase in diagenetic and low-temperature hydrothermal environments, and are likely strongly underreported in analyses of such assemblages.

Oxalate is also present in Earth's atmosphere as the most abundant dicarboxylic acid, contributing significantly to organic aerosols (Crahan et al., 2004; Gierlus, 2011). The formation mechanisms of atmospheric oxalate have yet to be fully constrained, but it is thought to originate from biomass burning (Li et al., 2009), the photooxidation of heavier carboxylic acids (Carlton et al., 2007; Yang and Yu, 2008; Kundu et al., 2010), and cloud processing (Yu, et al., 2005; Yang et al., 2009). Investigations of Greenland ice core have shown that oxalic acid formation strongly correlates with solar irradiance (Kawamura et al., 2001). Oxalic acid is suggested to be the end product of photochemical oxidation of aromatic hydrocarbons in the Arctic atmosphere (Kawamura et al., 1996).

Oxalates minerals, particularly Ca-oxalate phases, are very strongly associated with life on Earth. Baran (2014) and references therein have comprehensively reviewed this phenomenon. The biosynthesis of oxalic acid occurs through a variety of different pathways which include the Krebbs citric acid cycle through glyoxalate oxidation (Gadd, 1999; Maxwell and Bateman, 1968; Balmorth and Thomas, 1984), oxidation of glycoaldehyde (Hammel et al., 1994), hydrolysis of oxalo-acetate (Lenz et al., 1976) Han et al., (2007), and metabolic degradation of glucose (Munir et al., 2001) and ascorbic acid (Kostman et al., 2001). While large amounts of oxalates are formed near Earth's surface, significant concentrations are not found in the rock record. This is due to enzymatically-catalyzed consumption of oxalates (oxalotrophy) by a large variety of organisms (e.g. Martin et al., 2012). Oxalates are ubiquitous in terrestrial endolithic communities, leading to numerous astrobiological studies (Appendix A).

1.2. Abiological oxalate formation mechanisms from Solar System-relevant materials

Abiological oxalate formation mechanisms typically involve oxidation or photodecomposition of carbon-bearing materials. Prominent among these processes are Fenton and Kolbe type reaction mechanisms. The Fenton mechanism involves the formation of hydroxyl radicals (OH^-) through the reaction of Fe^{2+} with H_2O_2. The OH^- radicals react with hydrocarbons, abstracting protons and progressively adding OH. Aromatic hydrocarbons can undergo such reactions, often yielding oxalate. Oxalic acid can be formed as the primary oxidation product of many aliphatic carboxylic acids, phenols, aromatic carboxylic acids, alicyclic, and heterocyclic compounds in NaOH solutions (Furuya et al., 1985). Oxalic acid is known to form via the ozonation, UV irradiation, and H_2O_2 treatment of polycyclic aromatic hydrocarbons (PAHs) in solution (Beltran et al., 1996a). Polycyclic Aromatic Hydrocarbons in the solid state can be oxidized to oxalic acid and other low molecular weight carboxylic acids by ozone (Seibel et al., 1995). Beltran et al. (1996b) shows that carboxylic acids, especially oxalic acid, are the main final products of some PAH treatments with UV and H_2O_2. The oxidation of phenols produces oxalic acid which are then refractory to Fenton's reagent (Zazo et al., 2007 and references therein). The oxidation of Murchison meteorite refractory organic fractions with ozone during tagging experiments formed large amounts of oxalic acid and oxalates as the only identifiable organic reaction products (Goodyear, 2013). The Kolbe and photo-Kolbe reactions are the electrolysis and photoassisted decarboxylation mechanisms of carboxylic acids; carbon dioxide and carbon-centered radicals can form, with the radicals forming oxalate.

Irradiation and aqueous alteration of common Solar System volatiles and carbon bearing compounds provide other avenues for oxalate production. Gamma-irradiation of aqueous urea can generate oxalic acid (Navarro-Gonzalez et al., 1989). Autoradiolysis of ^{14}C-bearing $CaCO_3$ can form oxalic acid (Albarran et al., 1987). Oxalic acid is the only observed decomposition product when (calcium and ammonium) bicarbonates and ammonium carbonate in aqueous solutions are exposed to β or γ radiation (Hasselstrom and Henry, 1956). Ennis et al. (2011) concluded oxalic acid could form in oxygen-rich Solar System ices by the interaction of carbonic acid molecules, which are strongly expected to form through the Solar System by the irradiation of H_2O and CO_2 assemblages.

Oxalic acid is formed in processes leading to HCN oligomers from HCN and was found to be the major hydrolysis product of HCN (Ferris et al., 1978), which is a major volatile in comets. Oxalic acid was formed as a significant component of γ-irradiated HCN solutions, frozen and liquid (Colin-Garcia et al., 2009). Hydrolysis of $(CN)_2$, which is also observed in comets, forms ammonium oxalate (Cataldo, 2002 and references therein). Oxalic acid was found to form from irradiated solutions of HCN, CH_3OH, CH_3CN, and C_2H_5CN (Draganic et al., 1985a). Irradiated aqueous solutions of HCN, NH_4CN, and CH_3CN were also shown to form oxalic acid as a byproduct (Negron-Mendoza et al., 1983). Very large doses of ^{60}Co γ radiation form oxalic acid as the most abundant byproduct from O_2-free aqueous solutions of HCN and NH_4CN, with concentration increasing with dose (Draganic et al., 1985b).

Oxalic acid formed in experiments with UV irradiation of the following mixtures: CH_3OH:pyrimidine, H_2O:CH_3OH:pyrimidine, CH_4:pyrimidine, H_2O:CH_4:pyrimidine, in vacuum at 15–25 K (Meterese et al., 2013). Photolysis of CO:NH_3:H_2O mixtures at 12 K formed oxalic acid as a component of a non-volatile residue, leading to the suggestion that oxalic acid could form in interstellar grains (Briggs et al., 1991). A similar experiment with a vacuum UV irradiated CO:NH_3:H_2O mixture on an Al block at 10 K also formed oxalic acid, and it was hypothesized that oxalic acid detected in the Murchison meteorite originates from photochemical reactions (Agarwal et al., 1985). Hydrolysis of other compounds formed in these photochemical reactions, oxamide and oxamic acid, forms oxalic acid. Oxalic acid is the major formation product from OH oxidation of the amino acid glycine in oxygen, while oxamic acid will form when no oxygen present (Berger, 1999). Oxalic acid is formed as a byproduct from the UV irradiation of acetylene in the presence of water (Menor-Salvan and Marin-Yaseli, 2013).

Lawless et al. (1974a) showed that electric discharge of a CH_4, N_2, and NH_4Cl solution formed oxalic acid amongst other dicarboxylic acids, and discussed this as a formation mechanism in Murchison. Oxalic acid is formed from glow discharge of formic acid in H_2O via the formation of carboxyl radicals (Jinzhang et al., 2008 and references therein). Arc discharge of graphite formed a variety of carboxylic acids, dominated by oxalic acid, and decreasing total yield with increased carbon chain length (Shimoyama and Shigematsu, 1994).

It has also been demonstrated that oxalic and formic acids, amongst other low-molecular weight C-O-H compounds, can be produced by photoreduction of CO_2 by Fe-rich clays, metal oxides, and transition metals in solution with ultraviolet-visible light

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