

# Review of occurrences and carbon isotope geochemistry of oxalate minerals: implications for the origin and fate of oxalate in diagenetic and hydrothermal fluids

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## Abstract

The known occurrences of oxalate minerals in deep diagenetic and hydrothermal environments are reviewed and new carbon isotope results are presented that cover, together with previously published data, 22 of 37 known diagenetic ( $n = 22$ ) and hydrothermal ( $n = 15$ ) oxalate occurrences. The very large range of observed  $\delta^{13}\text{C}$  compositions of solid oxalates,  $-31.7$  to  $33.7\text{‰}$  (VPDB), is largely independent of the carbon isotope signature of associated organic carbon and can be best explained by isotope fractionation processes during oxalate formation and breakdown. Within single deposits, the range in  $\delta^{13}\text{C}$  is rather limited. Diagenetic whewellites are, on the average, nearly 12‰ heavier than hydrothermal ones. Isotopically heavy oxalate minerals appear to be preferentially associated with Al-phases, possibly indicating Al deposition as a result of the destruction of oxalate complexant. Oxalates from near-surface and biological sources are enriched in  $^{13}\text{C}$  by 1 to 6‰ relative to the bulk organic matter. The heterogeneity of oxalate mineral  $\delta^{13}\text{C}$  reflects the low stability of dissolved oxalate due to thermal decarboxylation, oxidation and microbial degradation. The calcium oxalate whewellite is stable over geological periods of time at temperatures of at least 68°C (highest in situ temperature of whewellite occurrence) and provides easy access to the isotopic signature of an organic constituent of palaeofluids. The extreme variability of the C isotope signature of oxalate demonstrates that isotope fractionation during organic acid breakdown is a mechanism that must be taken into consideration in the interpretation of both very  $^{13}\text{C}$ -depleted and enriched natural carbon. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Since the recognition of organic acids as an important constituent in some basinal fluids, their po-

tential influence on diagenetic processes, especially porosity evolution and element mobilization through complexation, has led to numerous studies investigating the distribution of organic acid anions in formation waters (Carothers and Kharaka, 1978, 1980; Kharaka et al., 1986; MacGowan and Surdam, 1988, 1990; Means and Hubbard, 1987; Giordano and Kharaka, 1994) as well as experimental and theoretic-

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cal studies on their thermal stability (Crossey, 1991; Drummond and Palmer, 1986; Fein, 1991; Fein and Brady, 1995; Gestsdottir and Manning, 1992; Hajash et al., 1992; Harrison and Thyne, 1992; Hennes et al., 1988; Kawamura and Kaplan, 1987; Kharaka et al., 1983; Palmer and Drummond, 1986; Shock, 1995; Stoessell and Pittman, 1990; Surdam and Crossey, 1985; Surdam et al., 1989; Tait et al., 1992; Thyne et al., 1992; Welch and Ullman, 1992). The role of organic acids as potential ligands in diagenetic and low-temperature hydrothermal fluids is still debated (Giordano and Kharaka, 1994). Acetate, the most abundant organic acid species with concentrations of up to 10,000 ppm, constitutes 80 to 90% of total dissolved organic acid anions, the remainder consists mainly of propionate, butyrate and valerate. Difunctional carboxylic acid anions are less abundant and large variations in concentrations are reported even from individual wells (Giordano and Kharaka, 1994). The high oxalate concentrations of up to 494 ppm in oil field waters from California (MacGowan and Surdam, 1988, 1990) have not been confirmed by later studies. More recent analyses of the same wells resulted in low oxalate concentrations of 0.05 to 0.16 ppm (Kharaka et al., 1993).

Compared to the wealth of literature on dissolved organic acids, oxalate minerals such as whewellite  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and weddellite  $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  have received little attention by geochemists. While the presence of oxalate in present formation waters can be established by direct analysis, the presence of organic acids in palaeofluids is mostly based on circumstantial evidence such as mineral etching (e.g., Hansley, 1987). Only the presence of oxalate minerals can be taken as a direct proof that oxalate was a constituent of many types of fluids in the geological past. Knowledge of the mineralogical paragenesis and carbon isotope systematics of oxalate mineral may help to further constrain the geochemical influence of organic acids in diagenetic and hydrothermal processes. The stability of the crystalline oxalates of Zn, Cd, Hg and Pb has been evaluated experimentally by Kubacky-Beard et al. (1996) in order to assess the possible role as heavy metal carriers in soils.

This paper consists of two parts. The first section is a review of known Ca (and Na) oxalate mineral occurrences. We focus on these minerals because

available samples of other oxalate minerals (e.g., humboldtine  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , moolooite  $\text{CuC}_2\text{O}_4 \cdot 0.4\text{H}_2\text{O}$ ) are all from surface-related occurrences. The main part is a survey of the carbon isotope systematics of oxalate minerals from the majority of known occurrences, combined with some previously published results. These two types of information allow a more complete understanding of the geochemical role of oxalate otherwise based on formation water geochemistry and indirect evidence from diagenesis studies (Surdam and Crossey, 1985). Previous reports of carbon isotope data of oxalates from individual occurrences or districts (Hoefs, 1969; Galimov et al., 1975; Hoefs and Armbruster, 1978; Zak and Skala, 1993; Table 2) showed that carbon in some whewellites is unusually enriched in  $^{13}\text{C}$  compared with other organic materials. In this paper, we provide a broader data base for the understanding of the carbon isotope systematics of Ca (and one Na) oxalate minerals. We analyzed samples from 20 of 37 known occurrences (near-surface occurrences not counted). Including published data, carbon isotope ratios of oxalate minerals from 22 diagenetic/hydrothermal occurrences are presently available.

## 2. Samples and methods

Samples for the present study (Table 2) were obtained from museum collections and individuals (see acknowledgments). Pure oxalate mineral fractions were obtained by hand-picking and cleaning in dilute HCl to eliminate carbonate admixtures. All oxalate mineral fractions were checked for purity by XRD (Guinier-de Wolff Camera). For isotope analysis, 5 to 10 mg of oxalate mineral were mixed with 500 mg of copper oxide, filled in a quartz-tube, evacuated to a pressure of  $< 10^{-4}$  mbar and sealed with a torch. The tubes were combusted in a muffle furnace at 1000°C for 2 h. The evolved  $\text{CO}_2$  was cryogenically purified on a vacuum line and measured on a Fisons Instruments OPTIMA mass spectrometer calibrated with NBS 19, NBS 20 and NBS 22 standards. Replicate analyses of individual samples agree within  $\pm 0.2\%$ . Samples for isotopic analysis of organic matter were decarbonated with 10% HCl and thoroughly washed before analysis. Five to 20 mg of sample was measured using an elemental

analyzer coupled in continuous-flow mode with a Fisons Instruments OPTIMA mass spectrometer. Carbonates were measured with reaction in 100% phosphoric acid at 90°C in an automated VG-ISO-CARB coupled with a VG-PRISM mass spectrometer calibrated with NBS 19. All data are reported in the conventional delta notation with respect to VPDB for carbon and V-SMOW for oxygen.

### 3. Review of oxalate mineral occurrences

#### 3.1. Types of occurrences

Published occurrences of Ca oxalate minerals are quite numerous and have previously been reviewed by Quellmalz (1989) and Dondi and Puggioli (1990, 1991). The majority of reports consist of purely mineralogical descriptions with little genetic information. By far the most common Ca oxalate mineral in all environments is whewellite (calcium oxalate monohydrate) while weddellite (the dihydrate) is subordinate. The few other known oxalate minerals predominantly occur in near-surface environments. Since the first description (Brooke, 1840) a large number of papers dealt with paragenetic and morphological aspects of whewellite. Considering its simple composition, only few occurrences of this mineral are known. Based on the geological background information given, we identified three main types of occurrences: near-surface/biological (formed at the earth's surface in soils, unconsolidated sediments, caves, rock crusts, organisms); diagenetic (formed in consolidated sedimentary rocks, mainly in concretions, not in veins); and hydrothermal (mainly vein-type occurrences in any rock types). Our differentiation between diagenetic and hydrothermal occurrences is somewhat arbitrary and a considerable overlap of the respective temperature regimes may exist. Our hydrothermal occurrences only comprise vein-type mineralizations with evidence of large-scale fracture controlled fluid flow as well as all occurrences in crystalline rocks. Whewellite has also been recognized in the Murchison C2 carbonaceous chondrite (Fuchs et al., 1973) and organic acids in other carbonaceous chondrites (Briscoe and Moore, 1993). The most exotic occurrence investigated is natroxalate from apgaitic peg-

matites of the Kola peninsula (Khomyakov, 1996). The known 37 diagenetic and hydrothermal occurrences are summarized in Table 1 together with a selection of near-surface/biological occurrences.

#### 3.2. Near-surface and biological occurrences

Near-surface and biological occurrences of oxalate minerals are numerous and have been reported from soils (Graustein et al., 1977), lichens (Tirelli, 1977; Wilson et al., 1980; Mandarino, 1983), rock patinae (Cipriani and Franchi, 1958; Del Monte et al., 1987; Alaimo and Montana, 1993), calcretes (Verrecchia, 1990; Verrecchia et al., 1993), oxidized ores (Garavelli, 1955; Lebedev and Nikitina, 1983; Clarke and Williams, 1986; Rouse et al., 1986; Rust, 1991), recent marine and nonmarine sediments (Bannister and Hey, 1936; Marlowe, 1970; Gault, 1986; Griffin et al., 1984), guano (Frondel, 1950) and living organisms (e.g., Frondel and Prien, 1942; Lowenstam, 1968; Hoefs and Armbruster, 1978; Armbruster, 1981; Cowgill, 1989). In all these cases, the association of oxalate phases with organic material providing a source of oxalate is obvious. This type of occurrence is widely distributed reflecting the important role of oxalate in weathering, mineral dissolution and soil formation in surface environments (Graustein et al., 1977; Del Monte et al., 1987). A near-surface and biological origin for the oxalates found in late diagenetic and hydrothermal environments is unlikely because of the probable rapid microbial breakdown during weathering and early diagenesis. The mineralogical variability of near-surface oxalates reflects the availability of this anion in various geochemical environments. Old reports of the occurrence of the iron oxalate humboldtine in coal beds (summarized in Dondi and Puggioli, 1990, 1991) have not been confirmed more recently, one possibility being that these occurrences were restricted to relatively superficial areas where free iron was available as a result of pyrite oxidation.

#### 3.3. Diagenetic occurrences

In diagenetic environments oxalate minerals, typically whewellite, are closely associated with sediment sequences rich in organic matter such as coal beds and black shales. Calcium oxalate minerals

Table 1  
Occurrences of oxalate minerals

	Age/deposit type	Phase	References
<i>Meteorites</i>			
Murchison C2 carbonaceous chondrite	4.7 Ga	w	Fuchs et al. (1973)
<i>Near-surface occurrences</i>			
Modena, Appennines, Italy	recent lichen	w, wd	Tirelli (1977)
Capo Calamita, Isola d'Elba, Italy	recent	hu, min	Dondi and Puggioli (1991)
Täschental, Valais, Switzerland	recent lichen	w	This work
Pendarves Mine, Cornwall, UK	recent	hu	Ryback and Tandy (1992)
Milltown Quarry, Derbyshire, UK	recent	wd	Rust (1983, 1991)
Cheleken, Turkmenistan	recent	mo?	Lebedev and Nikitina (1983)
Florida, USA	recent peat	wd	Griffin et al. (1984)
Cochise County, AZ, USA	recent cave deposits	w	Williams, S.A., pers. comm. (1994)
Lower Pecos Region, Southwest TX, USA	0–6000 a, rock crust	w	Russ et al. (1996)
Haliburton County, Ontario, Canada	recent lichen	wd	Mandarino (1983)
St. Lawrence-Sagueney, Canada	recent stream sediment	wd	Marlowe (1970)
Bosanquet Township, Ontario, Canada	recent lichen	hu	Dondi and Puggioli (1991)
Weddell sea, Antarctica	deep sea sediment	wd	Lowenstam (1968)
<i>Diagenetic</i>			
Hoheleggelsen near Braunschweig, Germany	Cretaceous	w	Lippmann (1955); Hoefs (1969)
Etzel24 drillhole, NW Germany	L. Jurassic	w	von Gaertner (1958)
Zwickau, Saxony, Germany	Carboniferous	w	Frenzel (1889)
Döhlener Basin, Dresden, Saxony, Germany	Permian	w	Thalheim et al. (1991); Hofmann (1991)
Hannebach, Eifel, Germany	Quaternary	w	Hentschel (1986)
Kladno basin, WNW Prague, Czech Republic	Carboniferous	w	Rost (1942), Sarf (1981)
Northern Bohemian Basin, Czech Republic	Miocene	w,hu	Becke (1900); Zak and Skala (1993)
Cernin, Bohemia, Czech Republic	Ordovician	w	Povondra and Slansky (1964)
Cigel'ka, NE Slovakia (borehole VHC-1)	Palaeocene-Eocene	w	Baco and Pacindova (1993)
Csordakut, Tatabanya, Hungary		hu,w	Dondi and Puggioli (1990, 1991)
Condorcet, Drôme, France	Jurassic	w	Martin (1989, 1990)
Writhlington near Radstock, Avon, UK	Carboniferous	w	Morse (1994)
Mealbank, Ingleton, N Yorkshire, UK	Carboniferous	w	Ryback and Tandy (1992)
Kangilia, Nugsuak, Western Greenland	Tertiary	w	Bøggild (1953)
Milan, OH, USA	Upper Devonian	w	Hyde and Landy (1966); Leavens (1968)
Havre, MT, USA	Upper Cretaceous	w	Pecora and Kerr (1954)
Meade County, SD, USA	Cretaceous	w	Campbell and Roberts (1986)
Biggs, OR, USA	Miocene	wd	Mandarino and Witt (1983)
Radon Mine, San Juan, UT, USA	Triassic	w	Gude et al. (1960)
Majkop, Caucasus, Russia	Eocene	w	Vasseyevicz and Razumovsky (1928)
Kuznetsk Basin, W Siberia, Russia	U. Permian	w	Pel'dyakov and Karpenko (1984)
Wladiwostok area, Russia	'coal mine'	w	Weiner and Hochleitner (1996)
<i>Hydrothermal</i>			
Schlema-Hartenstein, Saxony, Germany	vein-type U-Ag-Co-As	w	Hofmann (1991)
Himmelsfürst Mine, Freiberg, Germany	vein-type base metal	w	Weisbach (1886)
Ronneburg, Thuringia, Germany	complex U deposit	w	Hofmann (1991)
Pribram, Czech Republic	vein-type U	w	Zak and Skala (1993)
Sailauf, Germany	veins in Permian volcanics	hu	Lorenz (1995)
Bois-Noirs-Limouzat U Mine, France	vein-type U	w	Cuney (1974, 1978)
St.Sylvestre Mine, Vosges, France	vein-type base metal	w	Ungemach (1909)
Cavnic, Maramures, Northern Rumania	vein-type base metal	w	Dondi and Puggioli (1990)
Recsk, Matra Mts, Hungary	vein-type base metal	w	Zsivny (1922)
Darnot U Mine, Northeast Mongolia	vein-type U	w	Kartashov, P.M., pers. comm. (1995)

Table 1 (continued)

	Age/deposit type	Phase	References
<i>Hydrothermal</i>			
Strel'tsovskoe, Transbaikalia, Russia	vein-type U	w	Galimov et al. (1975)
Klichka deposit, Transbaikalia, Russia	vein-type U	w	Naumov et al. (1971)
Yareg River, Timan Mts, Russia	calcite vein in Devonian sediments	w	Kalyuzhnyi (1948)
Slav'ansk, Ukraine	vein-type Hg-deposit	w	Zatsikha et al. (1985)
Chibiny, Kola, Russia	agpaitic pegmatite, Precambrian	nat	Khomyakov (1996)

Minerals: w: whewellite; wd: weddellite; hu: humboldtine; min: minguzzite; mo: moolooite; nat: natroxalate.

occur in druses, vugs and fissures within septarian concretions (Vasseyevicz and Razumovsky, 1928; Pecora and Kerr, 1954; Bøggild, 1953; Lippmann, 1955; Hyde and Landy, 1966; Leavens, 1968; Campbell and Roberts, 1986) from organic-rich sedimentary rocks indicating small-scale migration of oxalate. The occurrence of whewellite in coals ranging in rank from bituminous to semianthracitic is relatively common. In association with coals, whewellite most frequently occurs in fissures and siderite concretions close to the coal beds (Frenzel, 1889; Hibsch, 1934; Sarf, 1981; Thalheim et al., 1991; Morse, 1994). At least at two localities (Mandarino and Witt, 1983; Hentschel, 1986), flows of basaltic lava appear to have been responsible for the thermal degradation of sedimentary organic matter resulting in oxalate production. Based on general geological information, we judge that the thermal maturity of the host sediments where oxalates are found is very variable.

The size of diagenetic whewellite crystals often exceeds 1 cm and reaches maximum dimensions of 23 cm (Meade, South Dakota; Campbell and Roberts, 1986). The average maximum size of 12 occurrences is 5.1 cm.

With one exception (von Gaertner, 1958), all reported diagenetic occurrences are druse minerals and not rock-forming. This may be due to the difficult identification of microscopic grains of whewellite which has optical properties similar to calcite. Rock forming whewellite has been reported by von Gaertner (1958) from the bituminous Posidonia shale in Germany, based on microscopic identification and whole-rock oxalate assays. A survey of 44 randomly selected sedimentary rock samples analyzed for oxalate by HCl-extraction and ion chromatography showed detectable oxalate concentrations of up to

180 ppm in 16 samples (Hofmann, B.A., unpublished data). These data suggest that oxalate, either as rock-forming minerals or in adsorbed form, may be widely distributed.

### 3.4. Hydrothermal occurrences

In hydrothermal environments whewellite occurs as a late stage phase in hydrothermal veins of variable paragenetic associations (Weisbach, 1884; Ungemach, 1909; Zsivny, 1922; Chernykh and Pilyoyan, 1971; Naumov et al., 1971; Galimov et al., 1975; Cuney, 1978; Zatsikha et al., 1985; Schröder and Lipp, 1990; Hofmann, 1991). Well developed whewellite crystals occur in druses and appear to be one of the latest formed minerals, but sometimes are clearly cogenetic with carbonates and sulfides. Metallic elements in these veins comprise U, present as uraninite, native Ag, and sulfides of Fe, Cu, As, Sb, Pb, Zn, Hg (Table 4). Gangue minerals include Ca–Mg–Fe carbonates, quartz and fluorite. Host rocks of the veins are commonly organic-rich (meta)sediments. Organic matter (bitumen) is present in the veins in several cases in substantial amounts (Kribek, 1991). Humboldtine  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  from veins in a rhyolite in Germany (Lorenz, 1995) is the only reported occurrence of an oxalate other than whewellite from a hydrothermal environment.

The size of hydrothermal whewellite crystals often exceeds 1 cm and reaches maximum dimensions of 20 cm (Schlema-Hartenstein, Saxony, Hofmann, 1991). The average maximum size of nine occurrences is 5.2 cm.

A relatively large proportion of occurrences are related to uranium mineralizations, a fact that has been interpreted to indicate oxalate formation as a result of organic matter radiolysis (Buganenko et al., 1983). Probably the largest amount of hydrothermal

whewellite was found in the Schlema-Hartenstein uranium district in Saxony, eastern Germany. Crystals with a mass of up to 700 g have been reported from this locality (Hofmann, 1991). This vein-type

uranium district has a complex geologic history with main mineralization events in the Palaeozoic and in the Mesozoic. Ambient rock temperatures at the sites where the analyzed whewellites were found (1530 to

Table 2  
Carbon isotope data of oxalates and associated organic matter

Locality or sample type	Phase	Oxalate $\delta^{13}\text{C}$	<i>n</i>	Corg $\delta^{13}\text{C}$	Sample Nr/reference
<i>Near-surface and biological occurrences</i>					
Peloncillo Mts., AZ, USA (rock crust)	w	-11.8	1		NMBE B7748
Southwest TX, USA, (rock crust)	w	-9.4	10		Russ et al. (1996)
Täsch Valley, Valais, Switzerland (lichen)	w	-11.7	1	-17.4	NMBE 30514
Rhubarb	ox	-29.3; -26.0	2		Hoefs (1969); Hoefs and Armbruster (1978)
Spinach	ox	-19.5	1	-25.7	Rivera and Smith (1979)
Tomato	ox	-26.7	1		Hoefs and Armbruster (1978)
Cacti	ox	-8.1 ± 0.6	5	-13.2	Rivera and Smith (1979)
Human urinary concretions	w	-18.3 ± 0.7	19	-23.0	Hoefs and Armbruster (1978) human tissue: Lyon and Baxter (1978)
<i>Sediment-hosted, diagenetic</i>					
Hoheneggelsen, Germany	w	8.7	1		NMBE B7410
Hoheneggelsen, Germany	w	+7.7	2	-23.2	Hoefs (1969)
Milan-Monroeville, Erie County, OH, USA	w	1.9	1		NMNH 117755-1
Milan-Monroeville, Erie County OH, USA	w	0.6	1		Hoefs (1969)
Elm Springs, Meade County, SD, USA	w	-9.6	1		NMNH C7101
Kladno, 30 km WNW Prague, Czech Republic	w	11.2	1	-23.2	NMBE B2945
Kladno, 30 km WNW Prague, Czech Republic	w	10.1 ± 4.5	8		Zak and Skala (1993)
N Bohemian Basin, Czech Republic	w	-6.9; -14.2	2		Zak and Skala (1993)
Biggs, OR, USA	wd	-22.2	2	-29.9	NMBE B7751
Kangilia, Nugssuak, Umanak District, Greenland	w	4.5	1		GMK 1940.19
Burgk, Freital, near Dresden, Germany	w	-10.9	1		NMD 5794
Condorcet, Drôme, France (calcite vein)	w	31.3 ± 2.0	5		NMBE B8703
Condorcet, Drôme, France (septariae)	w	21.8 ± 1.3	11	-25.9	NMBE
Zwickau, Saxony, Germany	w	13.8	1	-23.2	NMBE B8022
Radon Mine, Lisbon Valley, UT, USA	w	-12.1	1		NMNH 114876
Cigel'ka, Slovakia (borehole VHC-1)	w	11.1	1		NMBE 30512
<i>Hydrothermal</i>					
St. Sylvestre Mine, Urbeis, Vosges, France	w	-17.9; -14.4	2	-25.4	NOS 6013; ULPS
Ronneburg, Thuringia, Germany	w	-11.8	1		NMBE B7663
Himmelsfürst Mine, Freiberg, Saxony, Germany	w	-8.4	1		TUBF 27157
Schlema-Hartenstein Mine, Saxony, Germany	w	-3.9 ± 2.6	6	-27.4	NMBE
Recsk, Hungary	w	8.6	1		HNHM
Boldut Mine, Cavnic, Rumania	w	-9.7; -7.1	2		NMBE 31206
Kola Peninsula, Russia	nat	1.5	1		NMBE B9417
Darnot U mine, NE Mongolia	w	-8.9	1		NMBE B8364
Pribram U deposit, Czech Republic	w	-30.2 ± 3.1	3	-32.0	Zak and Skala (1993), Corg: Kribek (1991)
Strel'tsovskoe, Krasnokamensk, Russia	w	-18.0 ± 3.1	4	-23.3	Galimov et al. (1975)
Strel'tsovskoe, Krasnokamensk, Russia	w	-15.1	1		NMBE 30477

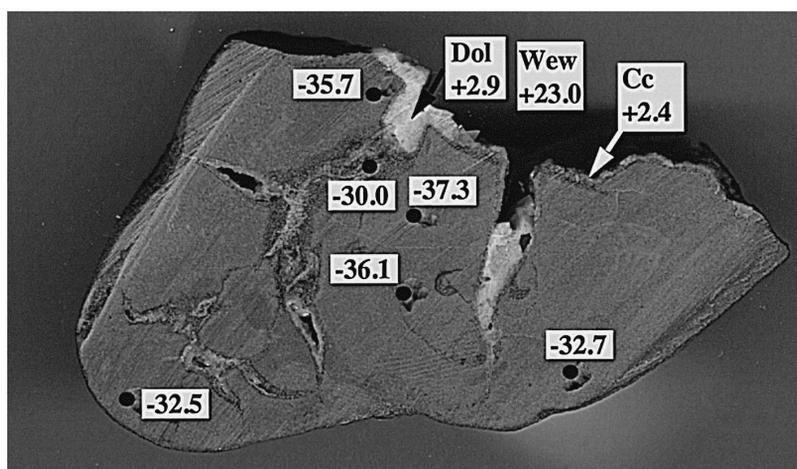


Fig. 1. Condorcet concretion NMBE B8017 with sampling sites demonstrating an extreme variability of  $\delta^{13}\text{C}$  from  $-37\text{‰}$  in matrix carbonate to  $23\text{‰}$  in druse whewellite. Maximum diameter of the concretion is 11 cm.

1665 m depth) range from  $62$  to  $68^\circ\text{C}$  (Schüler, S., pers. comm., 1991).

### 3.5. Systematics in the regional distribution of occurrences

Diagenetic and hydrothermal oxalate mineral occurrences show a pronounced concentration around the Erzgebirge ('Ore Mts.') in the German–Czech border area and are also common in Germany, eastern Europe, Russia and North America. Nine of the 37 known occurrences are located in the Erzgebirge area. Not a single non-surface related occurrence has been reported from the southern hemisphere, indicating a strong sampling bias. The known occurrences of oxalate minerals only represent a very minor fraction of geochemically and mineralogically very

similar environments. Whether the vast majority of these environments are really devoid of oxalate phases, or whether they just have not yet been recognized, is unclear. Geochemical analysis for mineral-bound oxalate would be a powerful tool to prospect for new occurrences of oxalate phases and to test whether both oxalate-bearing and oxalate-free mineral associations of low-temperature origin in suitable geochemical environments do exist. The age of oxalate mineral occurrences is most commonly Mesozoic or Tertiary. The Yareg River (Russia) and Milan, Ohio (USA) sites are Devonian, and the Kola natroxalate occurrence is of Precambrian age.

The available literature shows that oxalate minerals, eminently whewellite, are a relatively common phase in certain diagenetic and low-temperature hydrothermal environments. The presence of oxalate

#### Notes to Table 2:

NMNH: National Museum of Natural History, Washington DC, USA.

NMBE: Natural History Museum Bern, Switzerland.

NOS: Ecole des Mines, Paris, France.

ULPS: Université Louis Pasteur, Strasbourg, France.

NMD: Natural History Museum Dresden, Germany.

HNHM: Hungarian Natural History Museum, Budapest, Hungary.

GMK: Geologisk Museum København, Danmark.

TUBF: Technische Universität Bergakademie Freiberg, Germany.

w: whewellite.

wd: weddellite.

ox: oxalate unspecified.

nat: natroxalate.

minerals in these system is clear evidence that oxalate, and most likely other organic acids such as acetate in even higher amounts, were an important constituent in many palaeofluids.

## 4. Analytical results

### 4.1. Carbon isotope geochemistry

The carbon isotope compositions of all oxalate samples are given in Table 2 together with the carbon isotope compositions of associated organic carbon for selected samples compiled from the literature or obtained in our laboratory. The results for oxalates and associated minerals in the concretions from the Condorcet locality which has been studied most extensively are summarized in Fig. 1 and Table 3. This site will be discussed in more detail below.

Natural oxalate  $\delta^{13}\text{C}$  compositions range between  $-31.7\text{‰}$  to  $33.7\text{‰}$ . The isotopically heaviest samples represent one of the strongest enrichments of  $^{13}\text{C}$  ever found in terrestrial carbon of organic origin. The  $\delta^{13}\text{C}$  of oxalates from plants and human urinary

calculi range between  $-29.3$  and  $-11.75\text{‰}$ . This range in values reflects different controlling factors. For the plants, the type of photosynthetic mechanism is important: plants using the C3 photosynthetic pathway (rhubarb) have more negative  $\delta^{13}\text{C}$  compositions than those using the C4 pathway such as agave (e.g., O'Leary et al., 1992). The human urinary concretions have an intermediate composition (average  $-18.3\text{‰}$ ; Hoefs and Armbruster, 1978), which is approximately 5‰ heavier than the average isotope composition of human body tissue of  $-23\text{‰}$  (Lyon and Baxter, 1978). In general, oxalates from recent organisms are systematically enriched in  $^{13}\text{C}$  by 0.7 to 6.2‰ relative to the bulk organic matter (Fig. 2). The majority of the diagenetic oxalate occurrences are characterized by significantly more  $^{13}\text{C}$ -enriched carbon (mean  $2.8 \pm 15.3\text{‰}$ ) than near-surface and organic occurrences (mean  $-17.8 \pm 7.6\text{‰}$ ). Notably, very similar concretionary occurrences vary from  $-10$  to  $20\text{‰}$ . Compared with diagenetic occurrences, hydrothermal oxalates tend to be isotopically lighter ( $\delta^{13}\text{C} = 9.5 \pm 10.7\text{‰}$ ). For the occurrences where the isotopic composition of organic matter from host rocks are available (Table 2), it can be observed that the oxalate miner-

Table 3  
Oxygen and carbon isotope data for Condorcet samples

	$\delta^{18}\text{O}$ (VSMOW)	$\delta^{13}\text{C}$ (VPDB)
Concretion B8017 matrix calcite samples	31.23	$-35.69$
	31.33	$-37.30$
	31.18	$-36.15$
	31.21	$-36.27$
	31.29	$-32.67$
	31.32	$-32.46$
	31.51	$-29.96$
Organic matter in bulk concretion		$-25.89$
Druse calcite	28.78	2.36
Druse dolomite	32.20	2.94
Druse quartz	35.00	
Druse CO3 paraffinic hydrocarbon		$-28.94$
Druse CO4 paraffinic hydrocarbon		$-28.65$
Druse whewellite		$21.8 \pm 1.3$ ( $n = 11$ )
Vein-type calcite	30.57	3.15
Vein-type tunisite		$-6.08$
Vein-type whewellite		$31.3 \pm 2.0$ ( $n = 5$ )

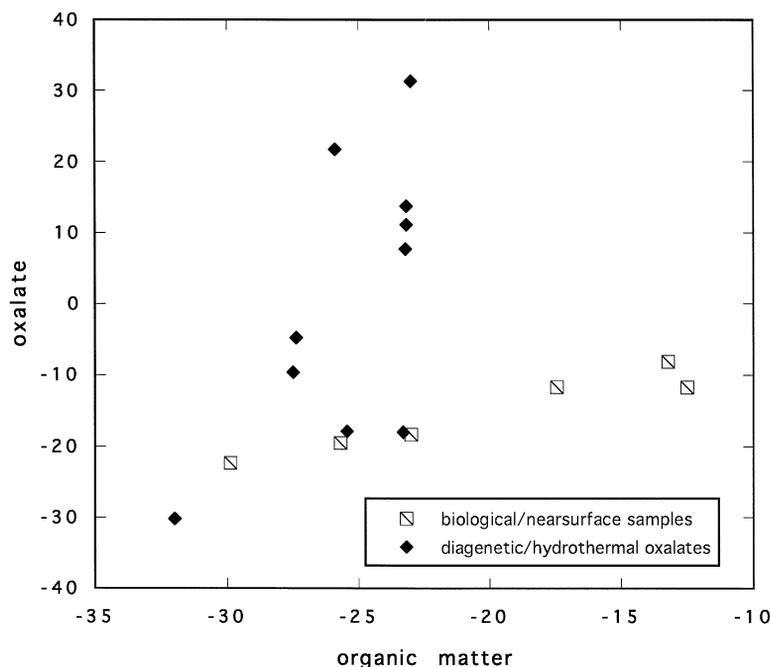


Fig. 2. Plot of  $\delta^{13}\text{C}$  of bulk organic matter vs.  $\delta^{13}\text{C}$  of associated oxalates for recent organisms (squares) and samples from diagenetic and hydrothermal occurrences (diamonds).

als are enriched in  $^{13}\text{C}$  by 5 to  $> 50\%$  relative to the organic matter from which they probably originate.

Four large crystals of whewellite (three from Condorcet, one from Schlemma-Hartenstein) have been investigated for carbon isotope zonation. Two large crystals from Condorcet concretions and the Schlemma sample show a slight increase of about 2‰ over a distance of 15 mm each from the center to the rim of the crystals, while the vein-type Condorcet crystals shows a decrease of 5‰. Compared with the large overall range of values, the C isotopic variability within single crystals appears to be rather limited.

In the Erzgebirge area, where data from eight relatively closely located occurrences are available, no regional trend of  $\delta^{13}\text{C}$  values is evident. Within individual deposits, both diagenetic and hydrothermal, we observed relatively small variations of oxalate  $\delta^{13}\text{C}$ . Most notably, whewellite from six concretions from different stratigraphic levels at Condorcet, France, yielded a relatively small variation of 19.8 to 23.6‰ ( $n = 11$ ). Where previously analyzed and published oxalate  $\delta^{13}\text{C}$  data were available, our results are consistently close to the formerly reported

values (Table 2). We are confident, therefore, that even single data from some occurrences yield a reasonably representative fingerprint of the overall isotopic composition of oxalate carbon in those occurrences.

#### 4.2. Whewellites from Condorcet, France

Whewellite is present at the locality Condorcet (Dept. Drôme, France) in veins and septarian concretions in the Callovian–Oxfordian organic carbon-rich Terres Noires formation. For a detailed description of the occurrences of concretions and bioherms, see Gaillard et al. (1985, 1992) and Rolin et al. (1990). The mineralogy and paragenetic sequence of minerals in veins and concretions has been described in detail by Martin et al. (1979, 1982) and Martin (1989, 1990). Minerals found in the concretions and veins include carbonates, sulfates, sulfides, hematite and quartz. The carbon isotope compositions of carbonates and oxalate from a single concretion from Condorcet are presented in Fig. 1 and all available carbon and oxygen isotope compositions are summa-

rized in Table 3.  $\delta^{13}\text{C}$  values of matrix calcite range from  $-30.0$  to  $-37.3\text{‰}$ , whereas drusy calcite and dolomite have  $\delta^{13}\text{C}$  of  $2.4$  and  $2.9\text{‰}$ , respectively. The whewellite in this concretion has a composition varying between  $19.9$  and  $23.6\text{‰}$  which is approximately  $60\text{‰}$  heavier than the matrix carbonate and  $50.5\text{‰}$  heavier than the solid paraffin-type material found in the concretions. The organic matter in the host rock has a  $\delta^{13}\text{C}$  of  $-23.2\text{‰}$ . The carbon isotope composition of whewellite from a tunisite-bearing vein has  $\delta^{13}\text{C}$  values of up to  $33.7\text{‰}$  (mean  $31.3 \pm 2.0$ ,  $n = 5$ ). The carbon isotope composition of the matrix calcite shows a trend of increasing  $\delta^{13}\text{C}$  towards the rim of the concretion. The sample at the interior with a  $\delta^{13}\text{C}$  of  $-30.0\text{‰}$  is from an alteration zone around the vein lined with drusy calcite. The heavier composition of this sample may be explained by partial recrystallization with the fluid that produced the drusy calcite. The oxygen isotope composition of the matrix carbonates varies in a narrow range of  $31.2$  to  $31.5\text{‰}$  (VSMOW). The drusy calcite has a more depleted  $\delta^{18}\text{O}$  of  $-28.8\text{‰}$

(VSMOW) and the dolomite a  $\delta^{18}\text{O}$  of  $33.9\text{‰}$  (VSMOW). An idiomorphic quartz crystal in this concretion shows a  $\delta^{18}\text{O}$  of  $35.0\text{‰}$  (VSMOW).

## 5. Discussion

### 5.1. Origin of the variability in $\delta^{13}\text{C}$ of oxalate minerals

In general, diagenetic oxalates are very enriched in  $^{13}\text{C}$  compared to common organic substances. This enrichment of  $^{13}\text{C}$  can occur during several different stages before oxalate is fixed in a mineral lattice (Fig. 3): (1) during formation of oxalic acid and/or oxalate during biosynthesis and/or through thermal decomposition of the precursor organic matter; (2) by degradation (decarboxylation, bacterial degradation) of oxalate as dissolved or adsorbed species in diagenetic and/or hydrothermal environments, (3) during mineral precipitation from solution. We will address these possible mechanisms in detail below.

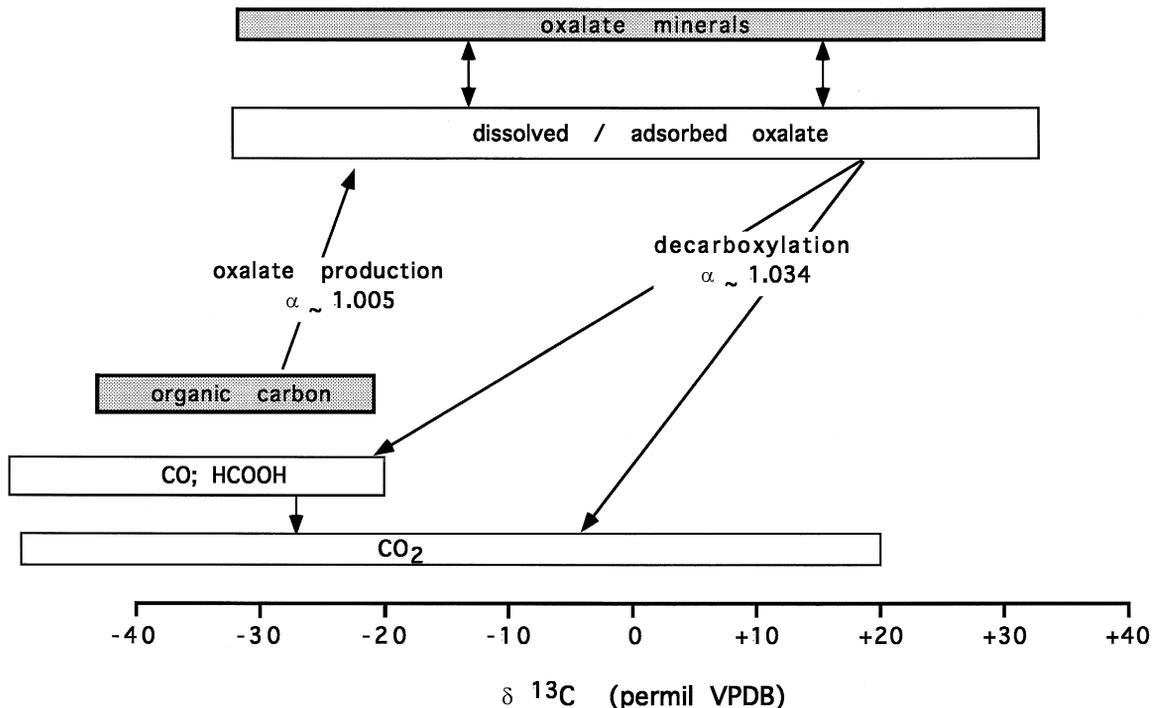


Fig. 3. Box model illustrating the carbon isotope evolution of oxalate. The main fractionating steps are oxalate production and decarboxylation of dissolved/adsorbed oxalate.

(1) Oxalate production from precursor organic matter: To our knowledge there are no measurements of the carbon isotope composition of dissolved oxalate in natural environments. The relation of the isotopic composition of dissolved oxalate to bulk organic matter is, therefore, unknown. It is now well established that different compound in organisms can have different carbon isotopic compositions (Galimov, 1985) and also large intramolecular carbon isotope variations have been observed. For example, Blair and Carter (1992) reported the isotopic composition of acetate in the pore waters of an anoxic marine sediment. While the isotopic composition of the total acetate is only approximately 2‰ heavier than the isotopic composition of the total organic carbon, the carboxyl group is 5‰ heavier than TOC and is 5 to 14‰ heavier than the methyl group. Meinschein et al. (1974) studied the isotopic composition of acetic acid extracted from vinegar and found that the carboxyl group is 18.4‰ more enriched in  $^{13}\text{C}$  than the methyl group. Blair et al. (1985) determined a difference in  $\delta^{13}\text{C}$  of 23.4 between the carboxyl and the methyl group in acetate formed as a metabolic product by *E. coli*. These intramolecular differences in  $\delta^{13}\text{C}$  can be attributed to the different oxidation state of carbon in methyl compared to the carboxyl group. The heavier isotope  $^{13}\text{C}$  is preferentially enriched in the more oxidized compounds (Craig, 1953). Alternatively, intramolecular isotopic inhomogeneities can be due to fractionations associated with the (bio)synthetic pathway (Meinschein et al., 1974) or due to the thermodynamic isotopic effects (Galimov, 1985). Assuming that oxalate is preferentially derived from carboxylic sites in the precursor, it is reasonable to assume that oxalic acid is enriched in  $^{13}\text{C}$  by at least a few permil relative to the bulk organic matter from which it is derived. The fractionation factor  $\alpha$  between organic matter and solid oxalate calculated with all data available for biological samples (Table 2) is  $1.005 \pm 0.002$ . Rivera and Smith (1979) found that the isotopic composition of oxalate in cacti is on the average 5‰ heavier than that of the woody fibers from the same plant. These data and the similarity of the isotopic composition of plant and human oxalates with the expected average composition of these organisms (Table 2, Fig. 2) indicate that intramolecular  $^{13}\text{C}$  enrichment may account for a 4–8‰ heavier

composition of oxalate than associated organic matter but probably not for more. These assumptions are consistent with our measurements of associated organic matter and oxalate in Swiss lichen (5.8‰ difference) and at the Biggs, Oregon, weddellite locality (7.7‰ difference).

(2) Isotope fractionation during decomposition of dissolved or adsorbed oxalate: The observed large variation of the carbon isotope composition of oxalate is most probably due to fractionation occurring during degradation of oxalic acid in the fluid. Data on the fractionation of carbon isotopes during oxalate breakdown reported by Lindsay et al. (1949) and Zielinski et al. (1994, 1995) indicate a fractionation factor  $\alpha$  of 1.034 for oxalate decarboxylation in concentrated sulfuric acid at 100°C. In close agreement with these data, Blair and Carter (1992) calculated a fractionation factor  $\alpha$  of 1.030 for the bacterial degradation of the carboxyl group of acetate. The large fractionations observed in these studies of oxalate breakdown indicate that the decomposition of oxalate prior to precipitation as solid phase is probably the most important process controlling its carbon isotope geochemistry. We are aware that because the experiments of Lindsay et al. (1949) and Zielinski et al. (1994) were conducted in concentrated acids and at 100°C only, their fractionation factors must be applied with care to natural environments. In particular the fractionation factor may be dependent on the temperature and on the reaction mechanism. However, because of the close agreement with  $\alpha$  values for microbial degradation of the carboxylic group of acetate determined by Blair and Carter (1992) we suggest that the fractionation factor will probably be at least close to 1.03.

The evolution of the isotopic composition of dissolved oxalic acid during progressive decarboxylation can be modeled with a Rayleigh distillation model (e.g., Taylor, 1986). Using a fractionation factor of 1.034 and assuming a  $\delta^{13}\text{C}$  of the starting oxalic acid of  $-20\text{‰}$ , the degradation of 80% of the original dissolved oxalate present in the system produces a residual oxalate with a carbon isotope composition of 33‰, the heaviest isotopic compositions observed in our data set.

The exact pathways of oxalate degradation leading to the enrichment of  $^{13}\text{C}$  in our samples is unknown, but we assume that decarboxylation to

CO<sub>2</sub> and CO and/or HCOOH is most likely. Microbial or thermogenic sulfate reduction cannot be excluded either. The carbon isotopic signature of the CO<sub>2</sub> formed strongly depends on whether an organic by-product, significantly depleted in <sup>13</sup>C is concomitantly formed, or whether all degraded oxalate is converted to CO<sub>2</sub>. In the former case δ<sup>13</sup>C values of CO<sub>2</sub> of -30 to 20 are possible depending on the relative amounts of the different reaction products. In the latter δ<sup>13</sup>C of the produced CO<sub>2</sub> will vary between -50 to 0‰ depending on the reaction progress. This CO<sub>2</sub> may then be available for the formation of isotopically exotic carbonates.

If decarboxylation controls the isotopic composition of oxalate, its δ<sup>13</sup>C is a measure of the product of residence time as dissolved species and temperature in individual hydrothermal and diagenetic systems. Small deviations in isotopic composition between sedimentary organic matter and the oxalates would indicate a relatively short dissolved residence time prior to precipitation. This may be the case in Biggs, Oregon occurrence where oxalates are found in an organic carbon-rich lacustrine sediment sandwiched between basalt flows (Mandarino and Witt, 1983). The difference in δ<sup>13</sup>C between organic matter and oxalate is only 7.7‰. In this case, it can be assumed that oxalic acid was produced by the short-lived heating event and underwent only minimal decomposition prior to precipitation because of the rapid cooling of the lava flow. A model considering limited decomposition of oxalic acid after its production in a hydrothermal environment may be valid for the Pribram occurrence studied by Zak and Skala (1993), but interpretation is uncertain because of the large variation of organic δ<sup>13</sup>C in this deposit (Kribek, 1991). The generally heavier signature of diagenetic oxalates compared with those from hydrothermal environments may indicate slower mass transfer and resulting longer residence times as dissolved species in diagenetic environments.

(3) Fractionation between solid and dissolved oxalate: No experimental data exists on the isotope fractionation between dissolved and solid oxalate. However, the composition of biological oxalates (Table 2, Fig. 3) again suggests that the isotope fractionation during solid oxalate precipitation cannot be very large. Otherwise, more pronounced enrichments of <sup>13</sup>C would be observed in biological samples. A

slight enrichment (in the order of 1‰) of <sup>13</sup>C in the solid phase during mineral precipitation can be assumed likely.

### 5.2. A case history of oxalate genesis: the Condorcet site

Gaillard et al. (1992) (and references therein) associated the formation of the pseudo-bioherms and the septarian nodules in the Terres Noires formation with methane-rich cold seeps active during the Oxfordian. This interpretation is supported by the very negative carbon isotope compositions of the nodule matrix indicating that these carbonates precipitated from a fluid containing a highly <sup>13</sup>C-depleted source of CO<sub>2</sub>. Carbonates found in modern active CH<sub>4</sub>-rich cold seeps are characterized by very negative δ<sup>13</sup>C compositions. These depletions in <sup>13</sup>C can be explained by the oxidation of methane by methanotrophic bacteria which form the base of the food chain in these environments (e.g., Paull et al., 1992). All of the oxygen isotope compositions would also be in agreement with such an interpretation even for the druse minerals present within the concretions. Using oxygen isotope thermometry, and assuming a seawater composition of 0‰, crystallization temperatures of the minerals are approximately 15°C for the matrix calcite, 25°C for the drusy calcite (using the revised O'Neil equation, see Friedman and O'Neil, 1977), 17°C for dolomite (using the equation of Fritz and Smith, 1970) and 40°C for quartz (using Sharp and Kirschner, 1994). Considering the complex mineralogy of the veins within the concretions and the fact that the region has been affected by low grade metamorphism and hydrothermal activity during Alpine nappe emplacement (Perthuisot and Guilhaumou, 1983; Guilhaumou et al., 1988) we consider a one-stage low temperature origin for the concretions and their mineralization unlikely. These temperature estimates, therefore, must be considered a minimum. If hydrothermal reactions were involved during late stage diagenesis or Alpine low grade metamorphism, fluid-rock interaction could have produced an <sup>18</sup>O enrichment in the formation waters which would lead to an increase in the temperature estimates.

To test a possibly high temperature origin for the vein minerals, we calculated the temperature of formation assuming that quartz and drusy calcite are

cogenetic and precipitated in isotopic equilibrium. Using the quartz–calcite isotope fractionation equations of Sharp and Kirschner (1994) a temperature of formation of approximately 100°C can be calculated for these minerals. The oxygen isotope composition of the water in equilibrium with these minerals would be 11.2‰ SMOW. These high values for the oxygen isotope composition of the water is not unrealistic as it is in the range observed in other sediment-hosted hydrothermal systems and in sedimentary basins (Sheppard, 1986). Moreover, in the region salt and gypsum-bearing Triassic rocks could provide the source of these  $^{18}\text{O}$ -enriched fluids. The presence of a high temperature hydrothermal event has been postulated by other authors based on mineralogical, organic geochemical and fluid inclusion studies. Perthuisot and Guilhaumou (1983) suggest that the hydrothermal activity leading to the mineralization in the carbonate nodules and associated veins could be related to other, more massif vein-type Ba, Pb, Zn mineralizations observed in the region of Condorcet, including a several meters thick celestite vein. Bellon and Perthuisot (1980) determined an age of 37 to 33 Ma for potassium feldspars in mineralized veins associated with the Triassic diapirs present in the region of Condorcet. Based on a detailed study of fluid inclusions, Guilhaumou et al. (1988) indicate that the temperature of fluid trapping in the region of Condorcet did not exceed 140–180°C. Based on the available data on stability of oxalic acids in natural environments (Crossey, 1991; Fein et al., 1994; Lundegard and Kharaka, 1994), the lower temperature estimates are probably more realistic, as it is not expected that oxalates can survive at high temperatures over prolonged periods of time. The  $\delta^{13}\text{C}$  values of the druse calcite and dolomite is similar to that of normal marine carbonates. However, because the host carbonates are strongly depleted in  $^{13}\text{C}$ , dissolved inorganic carbon in the fluids was not buffered by the surrounding carbonates. The strong enrichment of  $^{13}\text{C}$  in druse carbonates may be a result of relatively heavy carbon derived from oxalate breakdown.

In summary, we propose a two-phase model for the formation of these concretions and their mineral infilling. The formation of the concretions started in the Oxfordian as methane-rich fluids at low temperature were seeping out at the ocean floor. The location

of these seeps was controlled by synsedimentary faulting (Gaillard et al., 1992). During or before the major alpine thrusting event anomalous P-T conditions developed in the region (Guilhaumou et al., 1988). This increase in temperature led to maturation and migration of hydrocarbons which were channelled along the thrust faults. The development of the alpine thrust planes was probably at least partially controlled by the location of the Jurassic palaeo faults. The fluid circulating along these fault were rich in hydrocarbons and in dissolved organic acids. Partial oxidation of organic matter and oxalate production may be related to thermochemical sulfate reduction during the interaction of sulfate from the Triassic with the organic-rich shales of the Terres Noires formation. Celestite from four concretions yielded a  $\delta^{34}\text{S}$  (CDT) of  $20.38 \pm 0.61$  ( $n = 4$ ). These data are within the range of Triassic sulfates and provide no clear evidence of sulfate reduction.

Organic acids including oxalate were degraded by thermal decarboxylation leading to a  $^{13}\text{C}$  enrichment in the residual oxalate. The strong enrichment in  $^{13}\text{C}$  observed in the oxalates indicates that approximately 80% of the oxalic acid present in this system was decarboxylated.

The Condorcet site bears some resemblance with the Hoheneggelsen occurrence in terms of mineralogy and isotopic composition of carbonates and oxalate. Even though oxalate is not as heavy as at Condorcet (Hoefs, 1969; this paper), the carbonate concretions are also very light (Hoefs, 1970), yielding a similar overall picture.

### 5.3. Mineral associations and carbon isotopes

On Table 4 minerals associated with oxalates are listed together with the mean  $\delta^{13}\text{C}$  values of oxalates. Whewellite and weddellite belong to the paragenetically last minerals in all cases. While most minerals do not seem to be preferentially associated with either light or heavy oxalates, Al-phases (tunisite, dawsonite, kaolinite) are found only in association with isotopically heavy oxalates. Al-phases such as kaolinite/dickite (Povondra and Slansky, 1964; Rust, 1983; Morse, 1994) and tunisite (Zatsikha et al., 1985) also are commonly associated with whewellite at sites from where no samples were available to us. The relatively common paragenetic

Table 4  
Paragenetic association of oxalate minerals

	Average oxalate $\delta^{13}\text{C}$	Hydrothermal/ diagenetic	Sphalerite	Galena	Chalcopyrite	Pyrite	Uraninite	Tunisie (Al-carbonate)	Dawsonite (Al-carbonate)	Kaolinite	Hydrocarbons
Condorcet, Drôme, France (veins)	31.3	d						x			
Condorcet, Drôme, France (septariae)	21.8	d			x	x					x
Zwickau, Saxony, Germany	13.8	d	x		x	x				x	
Cigel'ka, NE Slovakia	11.1	d							x	x	
Kladno, Czech Republic	10.1	d	x	x	x	x				x	
Recsk, Matra Mts, Hungary	8.6	h				x					
Hoheneggelsen, Germany	8.0	d	x			x				x	
Kangilia, Western Greenland	4.5	d									
Milan, OH, USA	1.2	d	x			x					
Schlema-Hartenstein, Germany	-3.9	h			x	x	x				
Himmelsfürst Mine, Germany	-8.4	h					x				
Boldut Mine, Cavnic, Rumania	-8.4	h			x						
Darnot U Mine, Mongolia	-8.9	h					x				
Meade County, SD, USA	-9.6	d									
N Bohemian Basin, Czech Republic	-10.6	d									
Freital, Dresden, Saxony, Germany	-10.9	d	x	x	x	x	x				
Ronneburg, Thuringia, D	-11.8	h	x		x	x	x				
Radon Mine, San Juan County, UT	-12.1	d				x	x				x
Mine de St.Sylvestre, Vosges, France	-16.2	h	x		x	x					
Strel'tsovskoe, Transbaikalia, Russia	-17.5	h					x				
Biggs, OR, USA	-22.2	d									
Pribram, Czech Republic	-30.2	h					x				x

association with aluminium–minerals suggests that significant Al-transport occurred in the oxalate-containing fluids, possibly by oxalate complexation (Fein, 1991; Fein et al., 1994; Harrison and Thyne, 1992; Benezeth et al., 1994). The occurrence of these Al-phases associated with whewellite in carbonate rocks are true local Al-accumulations that can only be explained by Al-transport and not by in situ alteration of preexisting Al-phases (e.g., feldspars). Al–mineral precipitation could be explained as a result of oxalate decarboxylation processes leading to a reduced solubility of Al.

Another mineral frequently associated with oxalate phases is uraninite. Among the 22 diagenetic and hydrothermal occurrences from where  $\delta^{13}\text{C}$  values of oxalates are available now, eight (36%) are associated with uraninite or other U-phases. The average  $\delta^{13}\text{C}$  value of these occurrences is  $-12.0 \pm 9.5$ , lighter than either average diagenetic or average hydrothermal oxalates. There is no obvious reason why decarboxylation would be less effective in uraninite-containing deposits. It is possible, therefore, that oxalate production in a radioactive environment produces anomalous light oxalate. An origin of oxalate as a result of radiolysis has been postulated based on field (Bugaenko et al., 1983) and laboratory (Hasselstrom and Henry, 1956) evidence and must be taken as a viable possibility. Both inorganic (bicarbonate) and organic source materials must be taken into account.

#### 5.4. Growth and stability of oxalate phases

The reason for the growth of large whewellite crystals under conditions unfavourable for oxalate stability appears unclear at first.  $\text{CO}_2$  produced during oxalate decarboxylation may induce dissolution of calcite and cause whewellite to precipitate. The limited variation of oxalate  $\delta^{13}\text{C}$  within single crystals, compared with the large fractionation necessary to produce oxalate as heavy as 33‰, indicates that oxalate production and partial degradation did not take place at the site of oxalate mineral precipitation, or that production, degradation and mineral precipitation occurred at very steady rates. Oxalate of relatively constant isotopic composition must have been present at the site of crystallization over extended periods of time.

Once grown, oxalate mineral crystals may be destroyed by dissolution resulting from a change of chemical environment or by temperature increase leading to the decarboxylation of dissolved oxalate, resulting in undersaturation and dissolution. Geological evidence from the Schlemma-Hartenstein Mine in Saxony, where unetched whewellites were found under ambient temperature conditions of up to  $68^\circ\text{C}$ , indicates that decarboxylation is not important up to this temperature at least. Because the chemistry of the fluid (Ca, Al, pH) as well as adsorption to aluminosilicate minerals (Fein and Brady, 1995) will determine the amount of dissolved oxalate in equilibrium with whewellite, the most stable oxalate, the thermal stability of whewellite will depend on the equilibrium concentration of dissolved and adsorbed oxalate.

Alteration of whewellite under near-surface conditions resulting in the formation of a pink alteration product and aragonite both at Condorcet and at Havre, MT (Pecora and Kerr, 1954) indicates limited stability under oxidizing conditions, possibly due to microbial breakdown.

## 6. Conclusions

Oxalate minerals are relatively rare in nature. The diversity of the types of occurrences listed in this paper and the difficulty in identifying whewellite make it likely that oxalate minerals are more common than generally assumed. While the current paper deals only with relatively large crystals, data on the occurrence of rock-forming oxalates, especially whewellite, are nearly lacking.

This survey shows that oxalate minerals occur in a wide variety of biological, diagenetic and hydrothermal environments, often associated with organic matter. Whewellite is relatively common in diagenetic carbonate concretions and hydrothermal uranium and base metal mineralizations. The two most important factors controlling the occurrence and isotopic composition of oxalate minerals are (1) oxalic acid generation from kerogen or by partial oxidation of organic matter, (2) bacterial and/or thermal degradation of dissolved oxalate. An additional, less important factor is, isotopic fractionation occurring during oxalate mineral precipitation. The

large variability of carbon isotope composition of oxalates indicates that large isotope fractionations occur during decomposition of oxalate either by thermal decarboxylation or bacterial degradation leading to an enrichment in the heavy isotopes in the residual oxalate. The carbon isotope composition of oxalates may serve as a guide to determine the amount of organic acids present in a diagenetic and/or hydrothermal system.

It has become increasingly recognized that organic acids may play a significant role in diagenetic and hydrothermal systems, because of the possibility of enhancing mineral dissolution and as complexing agents for metal transport. However, their precise role in natural fluids remains to be more firmly established (Lewan and Pittman, 1994). Measurement of organic acids in fluid inclusions has been suggested as a possible way to determine their presence (Lewan and Pittman, 1994) because no organic acid except oxalate naturally forms solid phases. We suggest that a more focused search for rock-forming oxalates in combination with carbon isotope studies may be a promising tool to be used as indirect evidence for the presence and the extent of degradation of oxalic and other organic acids in hydrothermal and formation waters.

Highly  $^{13}\text{C}$ -enriched organic acids may be a common feature in many environments. This possibility should be taken into consideration in the interpretation of C isotope data from such settings where  $\text{CO}_2$  of extremely variable composition may be a product of decarboxylation. More detailed studies of the individual occurrences will be necessary to enable a more quantitative approach on the relation between oxalate  $\delta^{13}\text{C}$  and the role of oxalate in the formerly present fluid. Detailed petrographic, mineralogical, fluid inclusion and stable isotope studies of natural occurrences of oxalate minerals may lead to a better understanding of the role of oxalate in controlling the geochemistry and mineralogy of hydrocarbon-bearing systems. C isotope investigations of dissolved organic acids are likely to show similar large C isotope fractionations as observed in oxalate minerals, and may allow more detailed comparisons between active systems and 'organic acid fossils' such as whewellite.

The large isotopic fractionations occurring during oxalate decarboxylation indicate that the detection of

microbial activity in diagenetic and hydrothermal systems based on carbon isotope signatures alone may be misleading. Very  $^{13}\text{C}$ -depleted carbonates, indicating microbial methane oxidation, may instead form during decarboxylation of isotopically light oxalate. Oxidation of strongly  $^{13}\text{C}$ -enriched oxalate may produce extremely heavy carbonates that might be interpreted as evidence of methanogenesis.

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