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SULFATE CONTAMINATION IN GROUNDWATER FROM A CARBONATE-HOSTED MINE

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ABSTRACT

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Sulfide oxidation in a carbonate environment produces groundwater contamination with high sulfate making the water unsuitable for drinking supplies. The zinc-lead mines near Shullsburg, Wisconsin are located in the Galena-Platteville Formation, a carbonate aquifer that was dewatered during mining. Sulfate levels have reached as high as 40 mmol/l in some local wells and eleven wells were abandoned.

Geochemical modeling of chemical reactions and isotope effects using the USGS computer program PHREEQE showed the importance of dolomite, calcite, CO_2, and siderite or iron hydroxide in controlling the water chemistry. The decrease in sulfate levels with time indicated that dilution by incoming recharge water was an ongoing process. The results of carbon isotope reaction modeling are consistent with dilution of contaminated water. The evidence for localization of contamination and dilution means that area farmers have seen the worst of the contamination. The mechanism of contamination was further examined by microbiological sampling and sulfur isotope determinations, which indicated that bacteria of the *Thiobacillus* species that thrive under neutral pH conditions may have catalyzed sulfide oxidation.

Research into the chemical evolution of contamination in this environment not only explains how sulfide oxidation causes contamination despite buffering by carbonate rocks, but also suggests how oxidation is initiated in the case of acid mine drainage.

INTRODUCTION

Background

An understanding of the hydrogeologic and geochemical processes associated with dewatering and subsequent refilling of mines in areas of sulfide mineralization is needed to predict potential contamination. Oxidation of sulfide minerals in coal-mining districts and massive-sulfide mines is well

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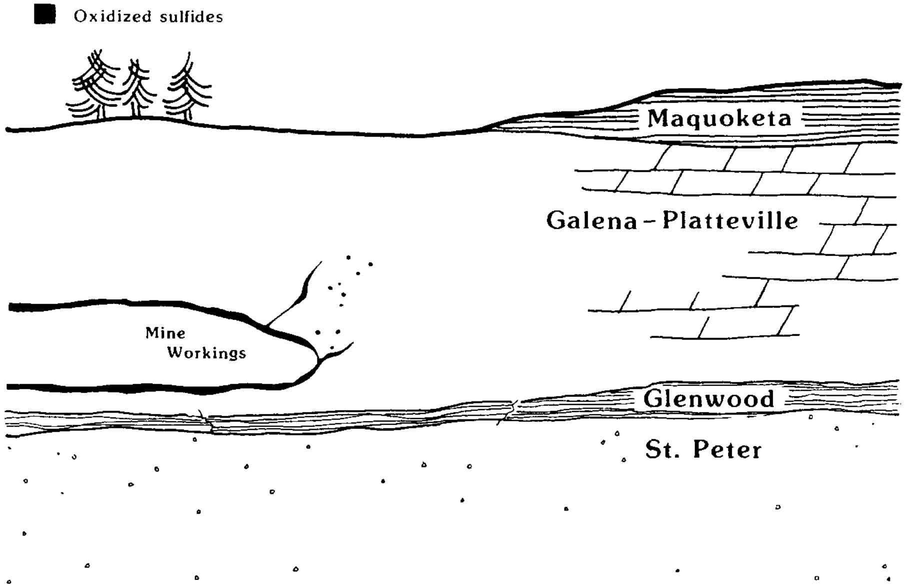
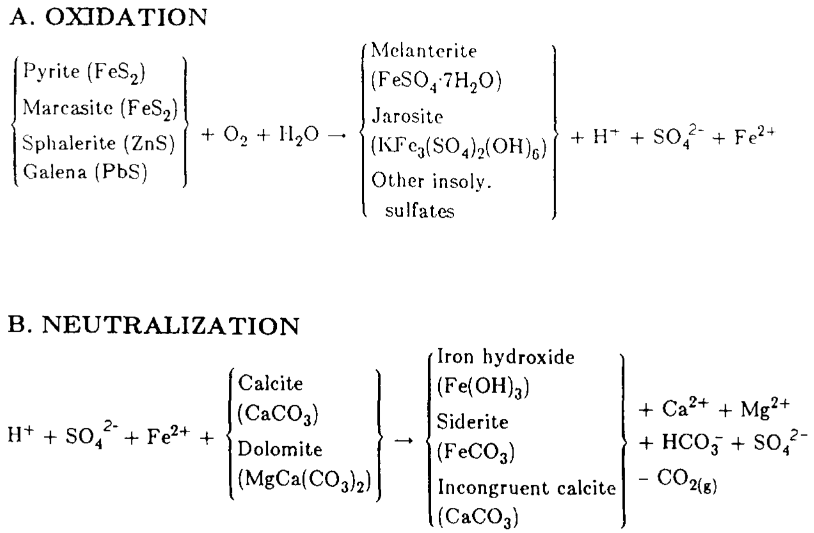


Fig. 1. Schematic cross section of Shullsburg geology (not to scale).

known. The resulting low-pH water, referred to as acid mine drainage, is caused by the formation of sulfuric acid and creates unacceptable levels of heavy metals. Neutralization of acidity has been studied where coals are associated with carbonates or mines are backfilled with gangue mixed with lime (Caruccio and Geidel, 1981). However, the effects of sulfide oxidation in water whose pH is buffered by carbonate host rocks has been little studied previously, and can be compared and contrasted with mechanisms that produce acid mine drainage. An example of a buffered environment was found in the zinc-lead mines near Shullsburg, Wisconsin.

The Shullsburg mines are part of the upper Mississippi Valley zinc-lead district of southwestern Wisconsin, northwestern Illinois, and northeastern Iowa (Heyl et al., 1959; Mullens, 1964). Approximately 57% of the ore was zinc from sphalerite (ZnS), 5% secondary lead from galena (PbS). In addition, pyrite and marcasite (polymorphs of FeS_2) each represented about 10% of the mineralization (McLimans, 1977). The ore was deposited along joints and bedding planes as thin veins varying from 0.4 to 2 km in length. The mines are located in the upper part of the Platteville Formation (Fig. 1). The Galena-Platteville Group is Ordovician in age and consists of dolomite, limestone and some shale units. It is approximately 100 m thick in the area (Heyl et al., 1959). The Galena-Platteville Group is separated from the underlying St. Peter Sandstone by a thin (approximately 1 m) layer of Glenwood Shale. The carbonate and sandstone aquifers are believed to be separate hydrologic units (Hindall and Skinner, 1973; Toran and Bradbury, in prep.).



A. OXIDATION

$$\left\{\begin{array}{l}\text{Pyrite } (FeS_2)\\ \text{Marcasite } (FeS_2)\\ \text{Sphalerite } (ZnS)\\ \text{Galena } (PbS)\end{array}\right\} + O_2 + H_2O \rightarrow \left\{\begin{array}{l}\text{Melanterite}\\ (FeSO_4 \cdot 7H_2O)\\ \text{Jarosite}\\ (KFe_3(SO_4)_2(OH)_6)\\ \text{Other insoly.}\\ \quad\text{sulfates}\end{array}\right\} + H^+ + SO_4^{2-} + Fe^{2+}$$

B. NEUTRALIZATION

$$H^+ + SO_4^{2-} + Fe^{2+} + \left\{\begin{array}{l}\text{Calcite}\\ (CaCO_3)\\ \text{Dolomite}\\ (MgCa(CO_3)_2)\end{array}\right\} \rightarrow \left\{\begin{array}{l}\text{Iron hydroxide}\\ (Fe(OH)_3)\\ \text{Siderite}\\ (FeCO_3)\\ \text{Incongruent calcite}\\ (CaCO_3)\end{array}\right\} \begin{array}{l}+ Ca^{2+} + Mg^{2+}\\ + HCO_3^- + SO_4^{2-}\\ - CO_{2(g)}\end{array}$$

Fig. 2. Possible reactants and products in: A. oxidation and B. neutralization. Solid phases shown in brackets.

The main mine workings operated from the 1920's until 1979 when they were shut down for economic reasons. While the mines were exposed to air, sulfide minerals in the surrounding rock oxidized to sulfate. When groundwater re-entered after the mines closed, the sulfate could spread to nearby wells. Shortly after the mines shut down, local well owners began complaining about poor water quality. A preliminary study (Evans et al., 1983) showed that sulfate had risen as high as 40 mmol/l in some wells near the mines. The EPA safe drinking water standard is 2.6 mmol/l (National Secondary Drinking Water Regulations, Federal Register, v. 44, July 19, 1979, p. 42198). Because elevated sulfate levels can cause diarrhea in humans and poor milk production in cows, eleven local wells were abandoned.

The pH of groundwater near the Shullsburg mines is usually around 7.0 and never below 6.0. In contrast, coal mines in the northeastern U.S. (Caruccio, 1968) or sulfide mines in the west (Wentz, 1974; Nordstrom, 1977) can have acidic pH values, as low as 0.8.

Mining-associated contamination problems have been documented in other carbonate-hosted mines, such as the Graham Mine in northern Illinois (Lindorff and Cartwright, 1977) and the Pitcher Field in Oklahoma (Playton et al., 1980). Tar Creek, which drains from the mine in Oklahoma, has a pH around 1.8 and high trace metals, and was declared a Superfund site by the EPA. Surface water contamination receives more attention because of visibility: streams move water faster than groundwater, and pollution can spread quickly. Although contamination of underlying aquifers is a concern in some cases (Emrich and Merritt, 1969; Playton et al., 1980), in Shullsburg the mined formation is used as an aquifer for water of domestic quality.

The Shullsburg mines present a water problem that is chemically different from previous investigations because it is in carbonate rock, and physically different because contamination has dispersed through groundwater not surface water.

Sulfide oxidation

When a mineralized formation is exposed to air, sulfide minerals can oxidize to sulfate (eqn. 1):

$$FeS_2 + \tfrac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-} \qquad (1)$$

The oxidation reaction may actually be incongruent with respect to sulfate minerals that become saturated and precipitate (Fig. 2). The oxidation reaction (eqn. 1) produces acidity that enables dissolution of potentially toxic trace metals associated with sulfide deposits, such as Cd^{2+} and Pb^{2+}.

However, in carbonate rocks the pH is buffered to around 7, and the trace metal concentrations are low. Thus, sulfide oxidation in a carbonate environment produces high sulfate by reactions analogous to acid mine drainage, while carbonate rocks such as dolomite neutralize the acidity generated by the reaction (eqn. 2):

$$2H^+ + 2SO_4^{2-} + MgCa(CO_3)_2 \rightarrow 2SO_4^{2-} + Mg^{2+} + Ca^{2+} + 2HCO_3^- \qquad (2)$$

The neutralization reaction may be incongruent with respect to calcite, iron hydroxide, or siderite (Fig. 2). The pH of a system will influence reaction paths, stability of products, and survival of bacteria.

Electrons given up by sulfide (eqn. 3) when it is oxidized to sulfate must be accepted by another reactant:

$$S^{2-} \rightarrow SO_4^{2-} + 8e^- \qquad (3)$$

Oxygen gas can be an electron acceptor in the reaction. Oxidation is unlikely to be extensive in a water-saturated system because oxygen diffusion through water is slow. Thus, the relationship of mining to sulfide oxidation is the exposure of a large volume of rock to air. Although the reaction (eqn. 1) is roughly proportional to oxygen concentration (Smith and Shumate, 1970; Nriagu and Hem, 1978) oxygen is not necessarily the oxidizing agent for sulfur.

An alternative oxidizing agent is Fe^{3+} (eqn. 4):

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (4)$$

$$\underline{14Fe^{2+} + \tfrac{7}{2}O_2 + 14H^+ \rightarrow 14Fe^{3+} + 7H_2O} \qquad (5)$$

$$FeS_2 + \tfrac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-} \qquad (1)$$

The Fe^{2+} on the product side of eqn. (4) is replenished by oxidation to Fe^{3+} (eqn. 5). The overall reaction (eqn. 4 plus eqn. 5) is identical to the previous oxidation equation (eqn. 1) because oxygen is the electron acceptor for Fe^{2+}.

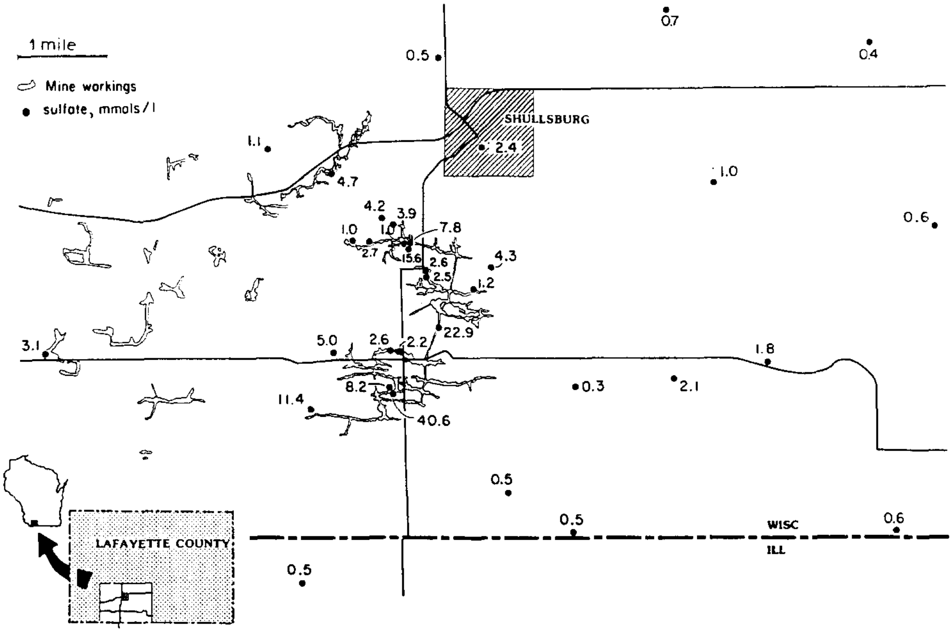


Fig. 3. Map of average sulfate concentrations in the Galena-Platteville aquifer, 1983–1985.

Rates of these three oxidation reactions (Nordstrom, 1982) show that oxidation by Fe^{3+} is faster than oxygen as an electron acceptor. However, production of Fe^{3+} can be limiting. At low pH oxidation of Fe^{2+} is slow; at high pH precipitation of ferric hydroxide removes Fe^{3+}. Singer and Stumm (1970) identify eqn. (5) as the rate-limiting step. Unless this pathway is catalyzed, it will not oxidize significant quantities of sulfides.

The bacterium *Thiobacillus ferrooxidans* is known to catalyze oxidation of Fe^{2+} to Fe^{3+}. *Thiobacilli* are sulfur-oxidizers that primarily use CO_2 as their carbon source. *Thiobacillus ferrooxidans* not only oxidizes sulfur, but iron as well. Transfer of electrons is used to obtain energy through the electron transport system (Ehrlich, 1981). Oxidation of Fe^{3+} by bacterial catalysis is the favored mechanism at low pH (Singer and Stumm, 1970; Nordstrom, 1982).

The extent of bacterial activity in underground mines is not well known (Smith and Shumate, 1970; Nordstrom, 1982; McNabb and Mallard, 1984) although *T. ferrooxidans* has been found in acid mine drainage (Nordstrom, 1977) and in mines (Beck, 1967). Different species of *Thiobacillus* survive over a range of pH conditions. Laboratory studies (Arkesteyn, 1979, 1980; Kleinmann and Crerar, 1979; LeRoux et al., 1980; Moses, 1982; Goldhaber, 1983) have examined the question of how oxidation occurs before pH drops, and have suggested both biological and abiological mechanisms. However, the role of 'neutrophilic' *Thiobacillus* in sulfide oxidation in a natural environment has not been previously addressed and will be examined here.

Problem statement

Chemical pathways of sulfide oxidation are complex and intermediate products are often unstable. Thus, one cannot examine effluent water composition to deduce all of the reactions that have taken place. Reaction models for sulfide oxidation can be hypothesized based on laboratory experiments and theoretical pathways. In this study, chemical equilibrium modeling and isotope measurements were used to provide constraints for extrapolation from hypothetical reaction models to conditions in the field.

This study will address two questions. First, what is the extent and duration of contamination? Local well owners want to know whether contamination is spreading or dissipating. Second, what is the mechanism of contamination? Comparisons with acid mine drainage may suggest how oxidation is initiated before the pH drops, and why contamination occurred despite the buffering effect of carbonate rocks. Understanding the mechanism will help prediction of contamination in other areas and prevention by understanding effective abatement techniques.

METHODS

Groundwater flow

Over 150 measurements of total head in the Galena-Platteville and St. Peter aquifers were made over a 180 km^2 area in the summer of 1983. From these data, potentiometric maps were constructed giving approximate flow directions in both the Galena-Platteville and St. Peter Formations (Toran and Bradbury, 1985). These maps were compared with historic data collected before and during mining (Holt, 1958). Results of digital computer modeling using the code developed by McDonald and Harbaugh (1984) to predict future groundwater flow paths will be reported elsewhere (Toran and Bradbury, in prep.).

Chemical sampling

Fifty-nine samples were collected from contaminated and uncontaminated areas near the Shullsburg mines (Fig. 3). Near the mine workings, samples were collected from wells, prospect holes, a mine shaft and springs. Samples were collected from prospect holes and the mine shaft using either a point-source bailer or a submersible nitrogen-powered bladder pump to limit degassing and oxidation during sampling. It was not possible to flush prospect holes because of their size and depth, and the lack of permanent pumps. In uncontaminated areas domestic wells were the primary source of water. Domestic wells were sampled using the homeowners' pumps and were flushed for at least 20 minutes before sampling. Nonetheless, unstable species such as carbon isotopes and trace elements were not measured in domestic well samples because of the possibility of alteration by contact with atmospheric oxygen in pressure tanks.

All water samples were filtered immediately using a maximum of 0.45 μm porosity filter paper, and the aliquot for cations was acidified with nitric acid. Unstable parameters (temperature, pH, Eh and conductivity) were measured in the field and alkalinity was measured in the lab within two days. Samples were analyzed for cations by flame atomic absorption or inductively coupled plasma spectroscopy; for anions with Dionex ion chromatography or titration for alkalinity. A limited number of samples were analyzed for trace metals using graphite furnace methodology.

Isotope analyses

Selected samples were analyzed for $\delta^{34}S$, $\delta^{18}O$ in sulfate, $\delta^{18}O$ in water, and $\delta^{13}C$ in dissolved inorganic carbon.* Except for $\delta^{18}O$ in sulfate, all isotope analyses were done on a triple collector Finnigan/Mat 251 mass spectrometer at the Department of Geology and Geophysics, University of Wisconsin. Oxygen in sulfate analyses were done under contract at Northern Illinois University.

Sulfate and carbonate were precipitated by $BaCl_2$. Sulfur in precipitated $BaSO_4$ was converted to Ag_2S then burned with cuprous oxide to form SO_2 gas for input to the mass spectrometer according to the method of Robinson and Kusakabe (1975). The average deviation of replicate runs for sulfur isotopic analysis of 17 different samples and standards was ± 0.2‰ and reached as high as ± 0.5‰. Carbon from precipitated $BaCO_3$ was converted to CO_2 by acidification with 100% phosphoric acid in a vacuum. The CO_2 was input to the mass spectrometer for analysis of carbon only. Precision on two duplicate analyses of carbon isotopes was better than 0.1‰. Water was stored in tightly sealed bottles, then equilibrated with CO_2 at 25°C for 2 days as described in Epstein and Mayeda (1953). The CO_2 was analyzed in the mass spectrometer for oxygen only. Five analyses of the University of Wisconsin water standard deviated by ± 0.2‰. Oxygen in sulfate analyses were done by heating barite with graphite to produce CO_2. Lab precision for analysis of $\delta^{18}O$ in sulfate at Northern Illinois University was reported as ± 0.5‰.

Microbiological sampling

Bacteria were cultured from weathered rock samples collected aseptically from mineralized rock piles near the mine complex; from the Badger Mine, a shallow mine in the town of Shullsburg; and from the Young Mine, an analogous Mississippi Valley-Type deposit near Knoxville, TN. Underground sam-

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[*] δ of the heavy isotope = $(R_{sample}/R_{standard} - 1) \times 1000$ in units of ‰ where R = (heavy isotope/light isotope) and the conventional standards are as follows: sulfur - Canyon Diablo Troilite (CDT); oxygen - Standard Mean Ocean Water (SMOW); and carbon - Peedee Belemite (PDB)

ples were collected from depths of 20 m and 305 m, respectively. Samples were collected with a sterilized spatula then placed in sterile Whirl Pak bags, and refrigerated until culturing. The media for culturing bacteria (Kuenen and Tuovinen, 1981) selected for the following species: *Thiobacillus neopolitanus*, *T. intermedius*, and *T. ferrooxidans*. The media for *T. intermedius* may support several different species of *Thiobacillus*. No quantitative measure of bacterial activity was made since rock sample size is highly variable and none of the environments currently available are identical to the now-flooded Shullsburg mine.

RESULTS AND DISCUSSION

Four approaches were taken to understand the distribution and mechanisms of contamination:

(1) Groundwater flow was mapped to determine the physical forces driving contaminant movement.

(2) Chemical samples of groundwater were collected from contaminated and uncontaminated sites to find the distribution of contamination and measure total water chemistry for input to reaction models.

(3) The role of *Thiobacilli* was examined because these bacteria can catalyze sulfide oxidation and have been implicated in acid mine drainage.

(4) Computer modeling of chemical reactions and isotope effects demonstrated a thermodynamically valid reaction path. Stable isotopes provided additional information by acting as tracers of chemical reactions.

Groundwater movement

Groundwater flow was examined to determine the potential for downward movement that would contaminate the underlying aquifer, as well as movement of contaminated water within the Galena-Platteville Formation.

Because hydraulic heads near the mine were higher in the Galena-Platteville aquifer than in the underlying St. Peter aquifer (Toran and Bradbury, 1985) potential existed for contaminated Galena-Platteville water to move downward, contaminating the St. Peter aquifer. It is important to reiterate the findings of Evans et al. (1983) that deep wells drilled during mining became contaminated because they were not cased through the mined formation. After contamination was discovered, failure to abandon the wells that were open to both the Galena-Platteville and St. Peter aquifers provided a further conduit for migration of contaminants. These casing problems need to be taken into account in future remedies for mine dewatering and groundwater contamination.

No evidence of natural leakage between the two aquifers was found although the thin shale layer separating the two aquifers (Fig. 1) may not be impervious everywhere. Water in the St. Peter aquifer near the mines was almost universally low in sulfate (Table 1). The only exceptions were wells S-38

TABLE 1

Chemical analyses

Sample I.D.	Date collected	pH	Major ions, mmol/liter					Isotopes, δ (‰)			
			SO_4^{2-}	Alk	Ca^{2+}	Mg^{2+}	Fe^{2+}	$^{34}S_{CDT}$	$^{18}O_{SMOW}$-SO_4	$^{13}C_{PDB}$	$^{18}O_{SMOW}$-H_2O
S-1	6/21/83	7.1	40.72	9.7	10.97	38.44	0.006	12.2	−0.9		
	6/22/83	6.8	39.67	9.85	11.34	27.44	0.04				
S-2a	6/27/83	7.9	7.60	6.78	5.38	6.49	–	12.1			
	6/27/84	7.9	7.40	5.4	5.64	4.09	–				
	6/12/85	7.7	7.31	5.53	5.27	5.01	0.0005	12.7	−3.2	−10.7	
S-2b	6/27/83	6.9	21.09	6.78	7.16	14.36	0.43	9.1			
S-2c	6/27/83	6.8	21.51	6.52	9.61	14.07	0.43	9.8	−1.9		
	6/27/84	7.0	36.38	7.8	11.08	27.03	0.83	9.4	−2.4		
	6/12/85	6.9	10.77	5.89	7.49	8.86	0.018	11.9		−7.3	−8.2
S-3	8/18/83	6.4	16.35	9.11	9.73	10.52	0.003	13.1	−2.8		
S-4	8/18/83	7.0	7.81	9.84	5.93	4.70	0.07	15.0	3.0		
S-5	8/18/83	7.85	4.10	8.28	4.18	3.98	0.009	13.5	1.4		
S-6	8/18/83	7.0	3.88	7.25	4.08	3.96	0.008	11.6			
S-7	9/24/83	7.2	3.24	7.90	3.98	3.20	0.006	12.6	−2.2		
S-8	12/ 5/83	8.0	1.83	5.12	2.21	1.74	0.0007	14.0	−2.5		
S-9	6/ 1/84	6.6	12.38	7.4	8.61	6.41	0.10	11.4	−2.0		−8.3
	6/18/85	6.55	10.38	7.08	8.01	5.29	0.092	11.4	−1.6		
S-10	6/ 4/84	7.3	4.34	5.9	4.02	3.12	0.022	12.0			
S-11	6/ 4/84	6.85	5.00	9.0	4.87	4.06	–	7.4	−0.9		
S-12	6/12/84	7.2	2.08	6.7	2.73	2.34	0.0002	10.1			
S-13	8/10/84	7.1	1.08	6.54	2.33	1.81	0.001	11.2		−10.7	
S-14	8/10/84	7.1	2.67	6.99	3.07	2.21	0.03	13.7			
S-15	8/13/84	7.3	2.58	5.10	2.78	2.04	0.0014	12.2	−2.7	−14.7	
S-16	8/13/84	7.29	2.52	5.81	2.81	2.32	0.0004	12.7		−14.0	
S-17	8/14/84	7.24	1.21	8.71	2.81	2.21	0.0029	3.5			
S-18	8/14/84	7.35	8.18	5.90	5.96	4.65	0.012	11.0	−1.1	−8.8	−8.3
S-19	8/15/84	7.19	4.70	6.76	4.13	2.96	0.0002	11.5	−2.6	−9.5	−7.9
S-20	8/15/84	7.7	2.20	5.10	1.85	2.25	–	8.6	−1.3	−6.4	
S-21	8/15/84	7.95	2.64	5.80	2.54	2.76	–	9.7		−10.3	−7.4
S-22	8/16/84	7.1	2.41	6.36	3.25	2.41	–	11.9		−13.0	
S-23	9/24/83	7.0	1.07	7.53	2.96	2.64	0.0007	10.5			
	6/26/84	7.1	0.99	7.2	2.83	1.94	0.0004				
S-24	9/24/83	7.6	0.28	6.10	2.19	1.62	0.0007	5.1			
	8/ 9/84	7.2	0.85	5.69	2.00	1.59	0.002	−1.5		−4.6	−7.4
S-25	12/ 5/83	6.8	0.63	8.37	2.29	2.12	0.0005	9.35	2.4	−13.7	
S-26	6/ 1/84	7.3	0.72	6.1	1.78	1.75	0.0003	9.0			
S-27	6/ 8/84	7.1	0.40	6.7	1.90	1.72	–	4.6			
S-28	6/12/84	7.47	0.61	6.2	1.85	1.74	–	0.9	−2.0		−7.4
S-29	6/12/84	7.2	0.51	5.5	0.98	3.11	–	7.2	0.4		−7.7
S-30	6/22/84	7.3	0.49	6.5	1.84	1.56	0.0004	2.8			
S-31	6/26/84	7.11	0.59	7.9	2.22	1.94	–	7.5			−7.4
S-32	6/26/84	7.3	0.30	6.0	1.74	1.37	0.0002	1.6			
S-33	8/16/84	7.25	1.08	6.86	2.50	2.29	–	11.9	−0.5	−8.6	−7.7
S-34	6/18/85	7.04	1.04	4.80	2.03	1.57	0.0005			−13.3	
S-35	6/12/84	7.3	1.10	7.2	2.66	2.30	0.001	5.8			
S-36	5/31/84	7.18	0.18	6.3	1.44	1.30	0.005	8.9			
S-37	5/31/84	7.15	0.14	5.8	1.43	1.28	0.01	5.2			
S-38	5/31/84	7.15	2.94	7.2	3.47	2.82	0.002	12.2			
S-39	6/ 1/84	7.3	0.24	5.7	1.50	1.26	0.03	9.0			
S-40	6/13/84	7.1	0.17	6.7	1.58	1.42	0.0026	2.7			
S-41	6/13/84	7.2	0.18	5.6	1.54	1.29	0.011	9.6			
S-42	6/13/84	7.2	0.26	5.6	1.52	1.32	0.0004	8.6			
S-43	6/22/84	7.3	0.11	5.6	1.44	1.26	0.0046	6.5			
S-44	8/16/84	7.3	5.48	6.14	3.48	4.18	0.046	7.9			

Notes: S-1 through S-34 from Galena-Platteville aquifer. Contaminated samples through S-22, based on sulfate concentration > 1 mmol/l and proximity to mine working for samples ≃ 1 mmol/l. S-35 from Maquoketa Shale. S-36 through S-44 from St. Peter aquifer. S-2 is mine shaft: (a) 50 m below land surface; (b) 80 m; (c) 100 m. Alkalinity measured as meq/l. Blank is not measured, –– is below detection.

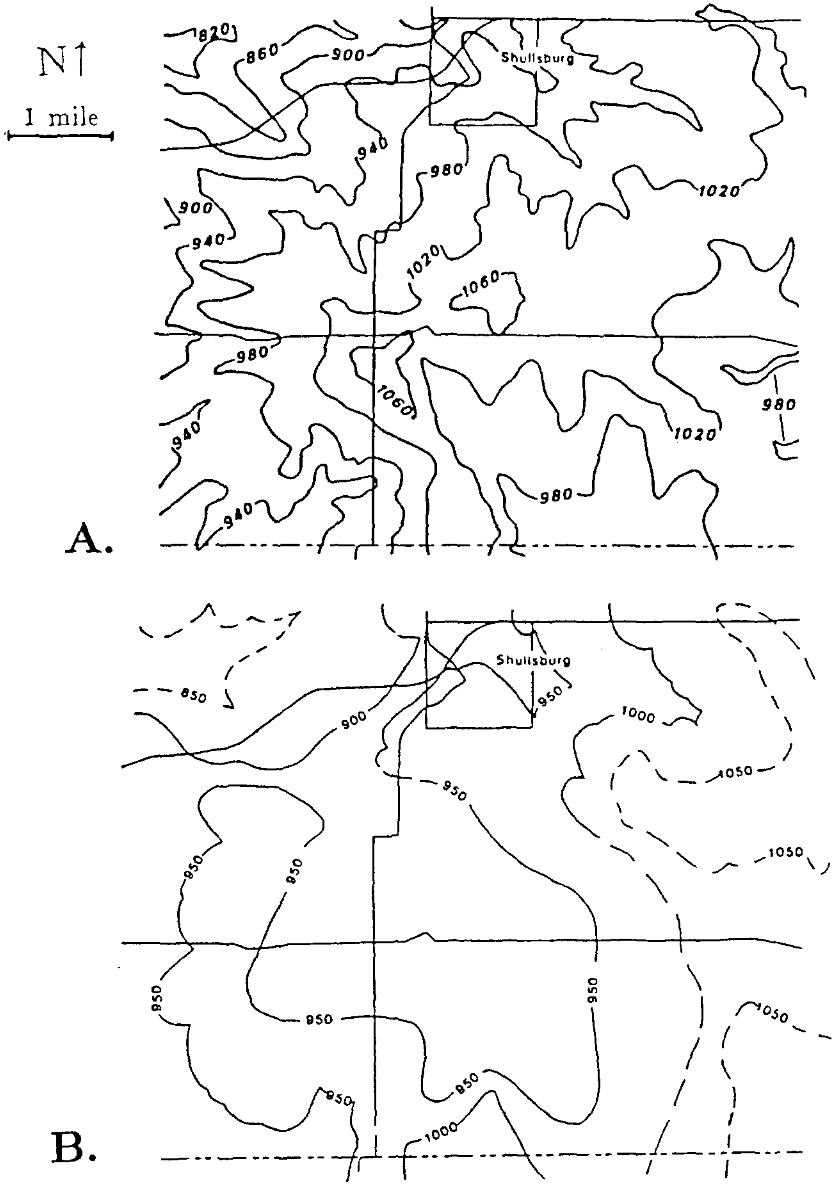

Fig. 4. Maps of the potentiometric surface in the Galena-Platteville aquifer. A. Before mining (Holt, 1958); B. Summer 1983. Contour intervals in feet above sea level.

and S-44 which were near wells open to both formations. Thus, the chemistry of these waters was used to establish lack of mixing between the formations.

Groundwater in the Galena-Platteville aquifer flowed radially toward the center of the relict cone of depression in 1983 (Fig. 4b). Consequently, contamination in the Galena-Platteville aquifer was localized near the main mine workings (Fig. 3) and did not spread laterally. Furthermore, contamination levels near the mine should decrease as uncontaminated water flows inward to dilute contaminated water.

When the cone of depression fills, the groundwater flow direction will reverse and water should move away from the mines again as it did in the pre-mining era (Fig. 4a). Groundwater flow modeling (Toran and Bradbury, in prep.) suggested flow will begin moving away from the mines as early as 1990. It is important to predict the quality of this water as well as flow paths. Prediction requires an understanding of the development of contamination and the present water chemistry.

Change in water chemistry and distribution of contamination

Using sulfate concentrations greater than 1 mmol/l as the indicator of contamination (Table 1), contaminated water had higher Ca^{2+} and Mg^{2+} than uncontaminated water, but was similar in pH and HCO_3^- (alkalinity). The correlation (R = 0.99) between sulfate concentration and calcium plus magnesium is a consequence of the dissolution of dolomite [$MgCa(CO_3)_2$] to neutralize acidity produced by sulfate (eqn. 2). Although the reaction also produces carbonate ions, there was no relationship between alkalinity (primarily HCO_3^-) and sulfate.

High heavy-metal concentration was not a problem in Shullsburg groundwater. One sample (S-1) had a lead concentration of 0.19 μmol/l, but was below the EPA safe drinking water standard (SDWS) of 0.24 μmol/l. Other metals were not significantly higher than background trace element concentrations determined by geochemical prospecting (DeGeoffroy, 1969; Hansen, 1979). Either trace elements have precipitated with iron hydroxides (Jenne, 1968) or they were not released by oxidation.

Sulfate contamination was localized within a half mile (0.8 km) of the mine workings around Shullsburg (Fig. 3). Sulfate concentration varied from 1.0 to 40 mmol/l in wells near the mine and from 0.3 to 2.1 mmol/l in wells more than half a mile away. The variability of sulfate concentrations may have been related to the fracture network that characterizes carbonate aquifers. Localization of contamination is consistent with the observed groundwater flow toward the mines.

Sulfate levels have declined (Fig. 5) during the past three years (1983–1985). The previous three years of sampling showed varying increases or decreases, with initial increases as the sulfate contamination spread. The declines observed were greater than seasonal or spatial variation and suggested that water quality near the mines is improving. Decline in sulfate concentration is caused by recharge and inflow of low sulfate water from the surrounding area.

Influence of bacteria

Members of the *Thiobacillus* genus that thrive under neutral pH might play a role in sulfide oxidation in a carbonate environment. Two of these species

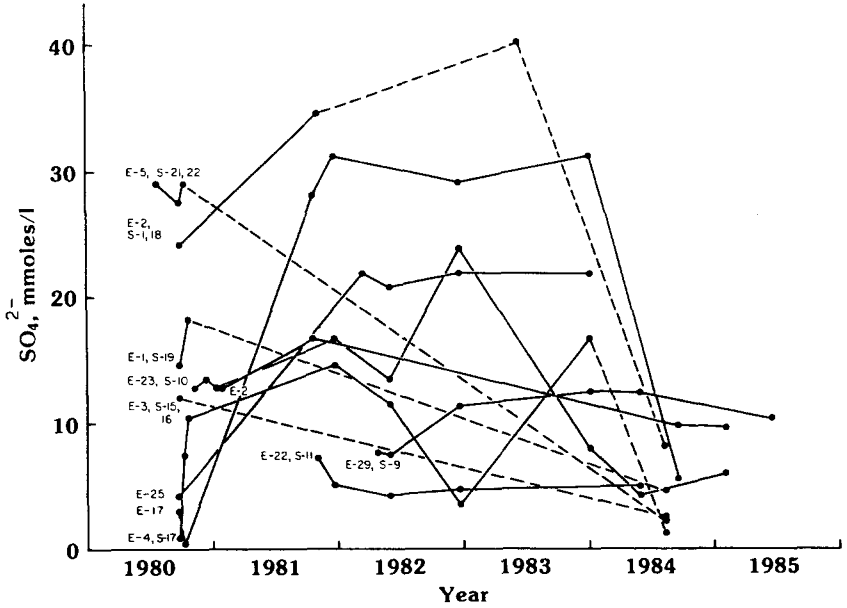

Fig. 5. Sulfate concentration changes with time: graph showing recent decline in sulfate levels. Where dashed lines are present, original well was abandoned and a nearby prospect hole was selected to continue the record. Samples prior to 1984 were collected by Evans et al. (1983) and are labeled E. Recent samples are from this study except where no S identification is given. Lines connecting sample points do not necessarily reflect sulfate concentration at intermediate times. Mine shaft has been omitted.

were selected to check the viability of bacteria growing in underground mines and tailings piles: *T. intermedius* and *T. neopolitanus.*

All samples produced positive results for the presence of *T. intermedius* and *T. neopolitanus.* Some samples collected from the Badger Mine (this study) and from Shullsburg tailings piles (Brock, 1975), also contained acidophilic *T. ferrooxidans* despite buffering of pH by carbonate rocks. No doubt, there is likely to be an active *Thiobacillus* population in the sulfide mine. Presence of bacteria in this environment provided necessary if not sufficient evidence for bacterial catalysis of reactions. Isotope ratios of sulfur and oxygen in sulfate further suggested bacterial catalysis, although quantitative analysis was not possible.

Reaction path modeling

Geochemical modeling can help explain how contamination occurred. By examining what minerals and phases control the present water chemistry, a thermodynamically valid reaction path to produce sulfate contamination and carbonate buffering can be developed. Carbon and sulfur isotope signatures can act as tracers of chemical reactions and suggest additional processes such as dilution and microbial oxidation.

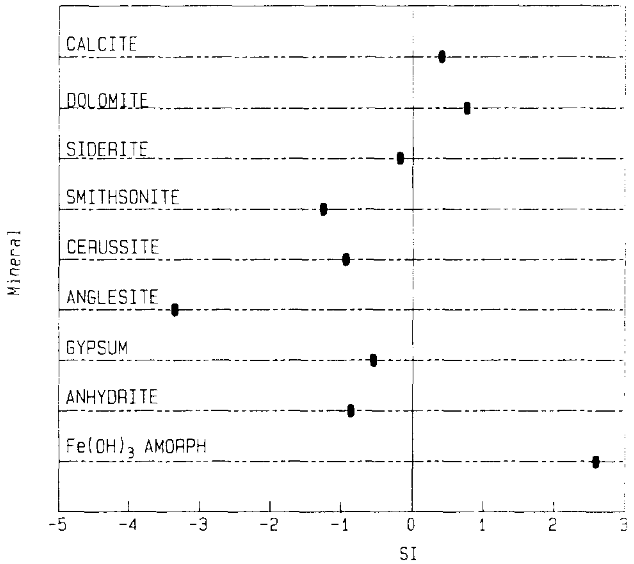

Fig. 6. Mineral saturation indices for a contaminated sample (S-18). SI = log(IAP/K), where IAP is the ion activity product and K is the equilibrium constant for the mineral in PHREEQE.

The computer program PHREEQE (Parkhurst et al., 1980) was used for chemical equilibrium and reaction path modeling. PHREEQE does speciation and mass transfer calculations to find the distribution of aqueous complexes and the saturation indices of potential mineral phases present. Thermodynamic properties of aqueous species and minerals from WATEQ2 (Ball et al., 1980) were added to the data base to include trace metals.

The first step was to examine present water chemistry to determine minerals and reactions to include in the reaction path model. Saturation indices of contaminated water calculated by PHREEQE suggested mineral phases likely to be involved in chemical reactions (Fig. 6). The groundwater samples were saturated with respect to calcite, dolomite, iron hydroxide and in some cases siderite. Gypsum and anhydrite were undersaturated in most samples despite the high calcium and sulfate concentrations. In addition, trace-metal measurements indicated that lead and zinc carbonates and lead sulfate were undersaturated and unlikely to be controlling phases.

Aside from mineral equilibria, another consideration in selecting appropriate reactions for the water was adjusting the carbon balance by CO_2 outgassing. Increasing amounts of sulfide oxidation imply increasing amounts of carbonate dissolution in a 1:1 stoichiometric ratio (eqn. 2). When calcite precipitation, driven by dolomite dissolution, is included in reaction modeling the relationship between sulfate and carbon becomes nonlinear (Fig. 7). Nonetheless, the amount of carbon produced in a system closed to the atmosphere was more than the measured carbon in most Shullsburg samples. Loss of carbon could be accounted for by CO_2 outgassing.

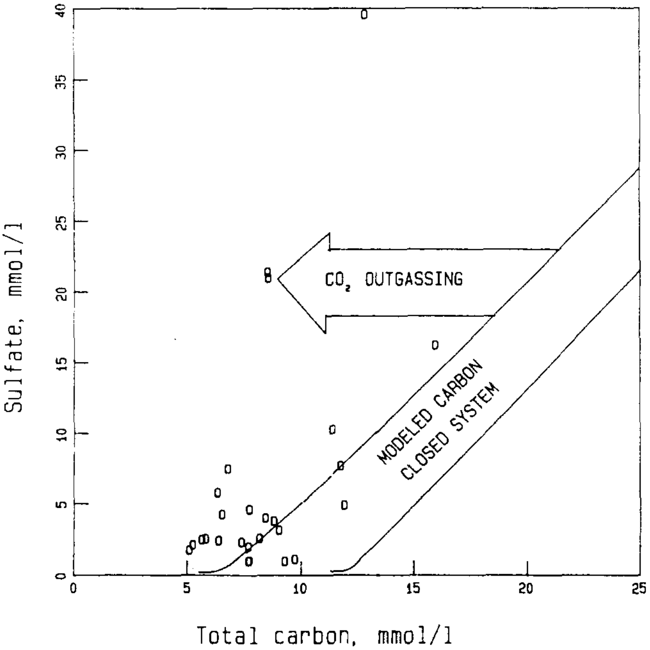

Fig. 7. Sulfate versus total inorganic carbon (calculated by PHREEQE). Diagonal lines show closed system oxidation for the range of different starting waters. Shullsburg samples (o) have undergone CO_2 outgassing to reduce total carbon.

Loss of CO_2 would be evidence that contamination occurred in an open system. Outgassing might occur when the mines were dewatered and open to the atmosphere. Hence, the carbon balance supported the fact that dewatering the mines was a factor in development of contamination. By way of analogy to cave systems, this process is similar to exposure of saturated solutions to a cave atmosphere as described by Hendy (1971) and Wigley et al. (1978, example 5).

Using the reactions and mineral equilibria discussed above as input to PHREEQE, contaminated water near the Shullsburg mines was modeled by five chemical changes (Table 2). The reactions were modeled in PHREEQE using one step, implying nothing about the sequence of reactions or reaction path.

(1) From an initial uncontaminated water, sulfide oxidation increases SO_4^{2-} and H^+ producing the acidity of acid mine drainage (eqn. 1). Sulfate oxidation was modeled by adding iron and sulfuric acid as reactants using the stoichiometry in eqn. (1). This acidity may be important if microenvironments exist around oxidizing minerals.

(2) Then dolomite plus or minus calcite dissolution buffers pH and increases Ca^{2+}, Mg^{2+} and HCO_3^- in the water. Calcite dissolves faster than dolomite and may create the higher Ca/Mg ratios seen in some samples.

(3) Calcite precipitation occurs subsequently when the dissolution of dolomite is incongruent with respect to calcite.

TABLE 2

Example of PHREEQE calculations for contaminated water S-18

a. Chemical composition

		Model 1	Model 2	S-18 Obs
Ca^{2+}	mmol/l	4.85	4.98	5.96
Mg^{2+}		5.61	5.76	4.65
Fe^{2+}		0.3	0.005	0.01
SO_4^{2-}		8.18	8.18	8.18
TIC		6.42	6.48	6.42
pH		7.12	7.10	7.35
$\delta^{13}C$ ‰		−6.0	−9.4	−8.8

b. Mass transfer

		Model 1	Model 2
(1) Δ SO_4 Reaction	mmol/l	3.890	3.890
(2) Δ Calcite		−0.937	−0.958
(3) Δ Dolomite		3.893	4.041
(4) Δ Iron Mineral		−1.730	−1.715
(5) Δ CO_2		−8.449	−4.828
log P_{CO_2}		−1.4	−1.5

Model 1 = $Fe(OH)_3$ precipitation
Model 2 = Siderite ($FeCO_3$) precipitation
TIC = total inorganic carbon
(1–5) reaction number described in text
positive mass transfer indicates dissolution
negative mass transfer indicates precipitation or outgassing

(4) Iron concentration can be reduced by precipitation of an iron mineral such as siderite or amorphous iron hydroxide. It was unclear what mineral or phase controls iron concentration, especially since precipitation was sensitive to oxidation potential (pe) which was assumed to be constant in the reaction model.

(5) To reduce the total carbon concentration, CO_2 outgassing must occur. Carbon concentration was matched by arbitrarily selecting a log P_{CO_2}, different for each model. Fixing the log P_{CO_2} effectively converted the PHREEQE model to a mass balance calculation for carbon since this constraint is not based on equilibration with a known phase. Although the physical control on outgassing was not known, alkalinity seemed to have an upper limit of around 10 mmol/l (Table 1).

Cation concentrations could be matched closely (Table 2) by equilibration with the appropriate mineral phase: calcite, dolomite and iron hydroxide or siderite. Differences between observed and calculated concentrations can be attributed to differences in starting water, mixing, or lack of information about the controlling iron phase.

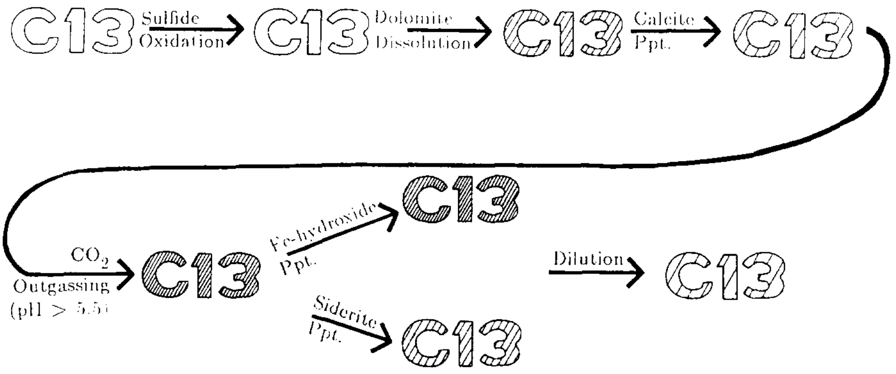

Fig. 8. Carbon isotope effects for the five reactions modeled in PHREEQE plus dilution. The degree of shading of C13 indicates the relative $\delta^{13}C$ value.

Carbon isotope modeling

Carbon isotope effects of outgassing and carbonate dissolution and precipitation can be modeled to gain more insight to the reaction mechanism and environment of oxidation (Deines et al., 1974; Reardon and Fritz, 1978; Wigley et al., 1978). The stable ^{13}C isotope may behave differently, yet predictably, in reactions and leave an isotopic signature. The carbon isotope effects of the reactions modeled for Shullsburg waters are as follows (Fig. 8). For sulfide oxidation, there is no change in $\delta^{13}C$. Dolomite dissolution introduces heavier carbon ($\delta^{13}C = -1‰$) to dissolved inorganic carbon in the water. Incongruent calcite precipitation will reverse this trend by preferentially removing ^{13}C ($\varepsilon_{ps} = 11.8$ to 2.0‰ at 10°C)*, but mass transfer for this step was small. Finally, CO_2 outgassing preferentially removes lighter carbon above pH = 5.5 ($\varepsilon_{gs} = 0.5$ to -9.0‰ at 10°C), and enriches the remaining dissolved inorganic carbon in ^{13}C.

These effects were modeled using an integrated form of Rayleigh distillation developed by Wigley et al. (1978). Their equation for one input (dolomite in this case) and two outputs (CO_2 and calcite) was rearranged to solve for $\delta^{13}C$ of the final water. The input parameters included: fractionation factors, determined as a function of pH (Wigley et al., 1978); pH during oxidation and fractionation; the isotope values of rocks, determined by field measurements (Hall and Friedman, 1969); mass transfer of carbon, derived from the PHREEQE model; initial and final total carbon, from PHREEQE; and initial $\delta^{13}C$. The basic carbon isotope model consists of typical values for these parameters (see Appendix and Table 3 for values selected).

The basic model calculated carbon isotopes heavier than observed for all but one sample (Table 3). Furthermore, all of the samples would be even lighter

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*Isotopic fractionation between calcite precipitation (p) or CO_2 gas (g) and the solution (s) = $\varepsilon_{ps,gs} = (\alpha - 1)10^3 \simeq \Delta_{ps,gs}$, where $\alpha = R_{p,g}/R_s$ and $\Delta = \delta_{p,g} - \delta_s$.

TABLE 3

Calculated and observed $\delta^{13}C$ ‰ for contaminated samples. Calculated using the "basic model"[†] parameter values. Observed carbon isotope ratios are typically lighter than calculated

ID	Calc	Obs
S-2c	−4.9	−7.3
S-18	−6.0	−8.8
S-2a	−6.3	−10.7
S-19	−7.9	−9.5
S-20	−9.6	−6.4
S-22	−9.9	−13.0
S-16	−10.0	−14.0
S-21	−10.2	−10.3
S-15	−10.3	−14.7

[†] Starting water S-27, pH = 5 ($\varepsilon_{gs} = 0.5$; $\varepsilon_{ps} = 11.8$), initial $\delta^{13}C = -12$‰, dolomite = −1‰, pe = 2.8.

than predicted if the model included dilution and additional outgassing. It may be more appropriate to consider higher sulfate water in modeling oxidation for these samples because dilution occurred as the mines flooded and sulfate minerals dissolved from surrounding rock. The amount of dilution is unknown, but the effect of ignoring dilution was to make modeled $\delta^{13}C$'s minimum calculations.

What makes measured $\delta^{13}C$ lighter than predicted? Two sources of isotopically light carbon are organic matter and background water with unaltered $\delta^{13}C$. Additional carbon from oxidation of organic matter would disrupt the mass balance of carbon. However, the amount of carbon in isotopically light background water was similar to contaminated water. Therefore, mixing of these two waters would have a small effect on the carbon balance while affecting a change in the carbon isotope composition.

Based on these observations, it was hypothesized that carbon isotopes showed contaminated water was diluted by background water, which obscured the isotope signature of chemical reactions. It was not possible to quantify the amount of dilution since the composition of incoming groundwater was variable and not well-determined.

The carbon isotope modeling pointed out some important aspects of tracing chemical reactions, although the information gained was not quantitative. Note that it was difficult to obtain the appropriate background samples after contamination developed, particularly since the mines are now flooded and inaccessible. There is a need to develop baseline data on natural water chemistry. Also, the observed water chemistry could be matched to a thermodynamic model using PHREEQE while ignoring the possibility that dilution occurred (Table 2). The effort to match observed and predicted carbon isotopes pointed to additional processes in development of contamination.

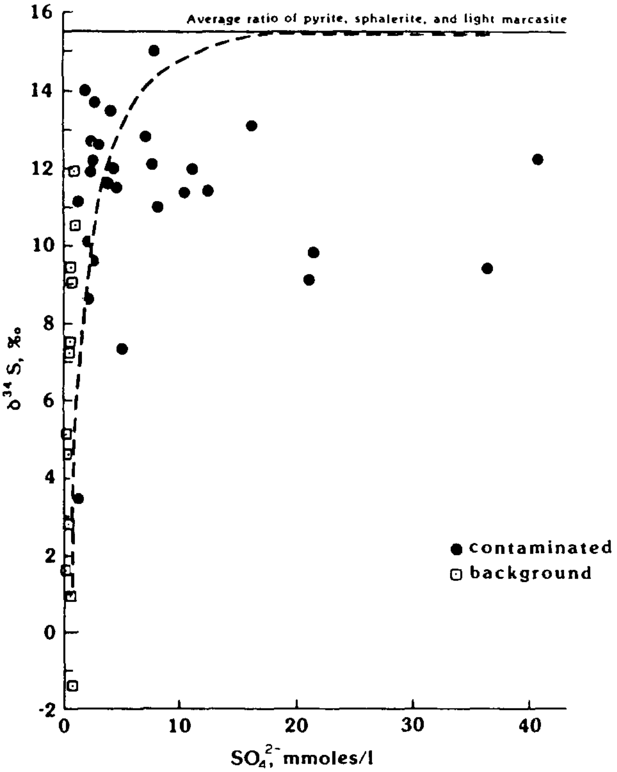

Fig. 9. Relationship between sulfate concentration and sulfur isotope ratio in Shullsburg groundwater. Contaminated samples, sulfate > 1 mmol/l; background samples, sulfate < 1 mmol/l. Dashed line shows schematic mixing path.

Since dilution was added to the reaction path model, it was necessary to consider how much dilution would be necessary to change the saturation indices of minerals from saturated to undersaturated. In other words, if the concentrated predecessor of the contaminated water was modeled, would additional minerals need to be considered as controls on observed chemistry?

Equilibration with each of the undersaturated minerals using PHREEQE provided an estimate of the amount of dilution necessary to reach present saturation indices. Sample S-18 was used as an example of calculation of dilution factors. The groundwater samples were only slightly undersaturated with respect to gypsum and anhydrite, and dilution factors of 2.5 and 4.5 would be sufficient to undersaturate sample S-18 with respect to these two minerals. Dilution of 10 times and 16 times would produce the present state of saturation with respect to cerussite ($PbCO_3$) and smithsonite ($ZnCO_3$). If the water was originally saturated with respect to anglesite ($PbSO_4$), then it has been diluted 2000 times. Gypsum may have been saturated in the water during sulfide oxidation, but anglesite was unlikely to be a limit to lead concentrations. The $\delta^{13}C$ effects of equilibration with respect to gypsum, cerussite or smithsonite were not calculated, but the change in carbon mass transfer is likely to be small compared to the additional outgassing corresponding to higher sulfate, undiluted waters.

Sulfur isotopes

The isotope dilution suggested by carbon isotopes raised another question. What was the effect of mixing on sulfur isotopes? Also, what factors influenced the sulfur isotope signature?

Several sources of sulfur existed in the Shullsburg area. The primary source of sulfate in contaminated water was sulfides in the Shullsburg mines with an average sulfur isotope ratio of 15.5‰ (McLimans, 1977). Background water was lighter (Fig. 9), but ranged from − 2 to 12‰. The range was probably owing to variable sources of sulfur in the system: heavy sulfide from the Galena-Platteville Formation, light sulfide from the Maquoketa Shale above, and meteoric sulfur.

The sulfur isotope ratio of contaminated water from Shullsburg with > 2 mmol/l sulfate ranged between 0.5 and 8‰ below the average sulfides. The mean isotopic ratio of these contaminated samples was 11.7‰ ($n = 21$) with a standard deviation of 1.8‰. The contaminated sulfate mean was about 4‰ lighter than the mean for area sulfides.

Isotope dilution can explain some of the observed light sulfur isotope ratios, but not all. Contaminated samples with sulfate less than 5 mmol/l may have been diluted by lighter background sulfur (Fig. 9). Sample S-17 is a notable candidate for the dilution hypothesis, and thus was omitted from the statistical calculation above. The extent of dilution was not determined because there was a wide range of values for background sulfur isotopes in both the Galena-Platteville Formation and the St. Peter Sandstone. Because of this variability, sulfur isotopes were not a good tracer for incipient contamination in either formation.

However, the most contaminated sulfate samples had far too much light sulfur to be explained by mixing (Fig. 9). The concentration of sulfate in background water was low enough that mixing with sulfate produced by oxidation would have little effect on sulfur isotopes containing high sulfate concentration.

The light sulfur isotopes in contaminated samples cannot be explained by mineralogy since pyrite, main stage marcasite and sphalerite each average 15.5‰ with standard deviations of only 1.7 ($n = 20$), 2 ($n = 10$), and 1.5 ($n \simeq 220$), respectively (McLimans, 1977). Galena is lighter, averaging 10.3‰, but it is unlikely to control the sulfur isotope composition of sulfate because it oxidizes slowly. Late-stage marcasite is heavier, averaging 25.5‰ ($n = 5$). There was no observed relationship between the spatial variability of sulfides and sulfates. However, the standard deviation of the sulfate and sulfides is similar, which may indicate a chemical process fractionated the sulfate and caused a shift in the sulfur isotope ratio.

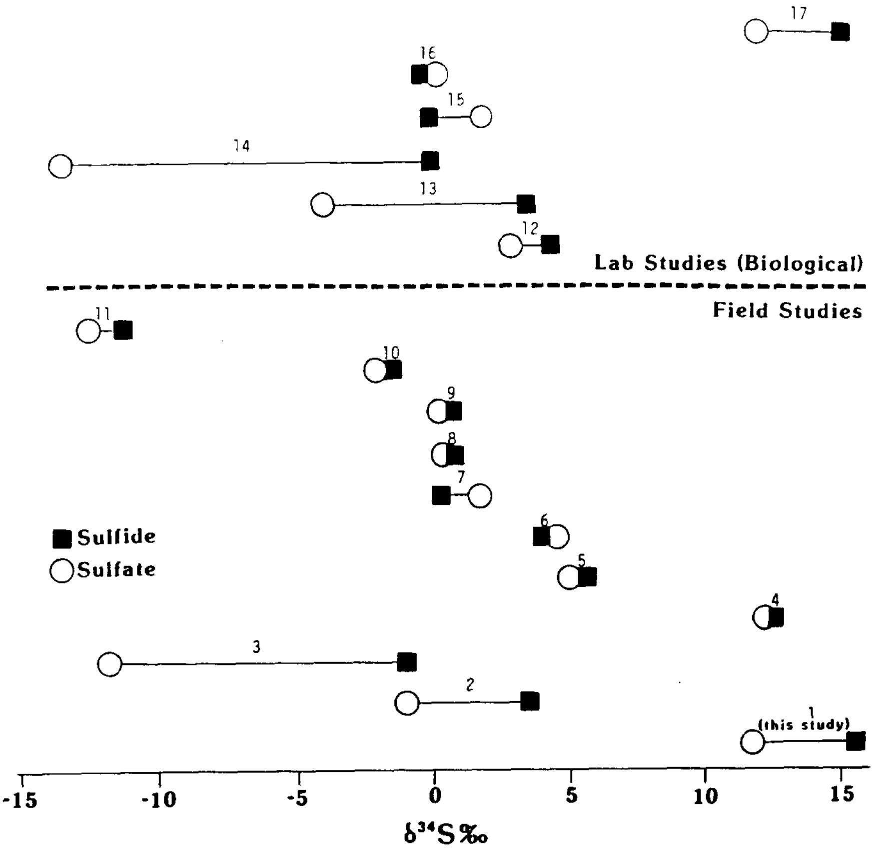

Fig. 10. Mean δ^{34}S of sulfide-sulfate reaction pairs reported in the literature. Initial sulfide listed for laboratory experiments. References: 1. this study; 2. Sakai, 1957; 3. Nissenbaum and Rafter, 1967; 4. Dechow, 1960; 5. Steiner and Rafter, 1966; 6. Taylor et al., 1984a; 7. Gavrishin and Rabinovich, 1971; 8. Lawrence and Rafter, 1962; 9. Vinogradov and Stepanov, 1964; 10. Gavelin et al., 1960; 11. Field, 1966; 12. Nakai and Jensen, 1964 (S°); 13. Kaplan and Rafter, 1958 (H_2S); 14. Kaplan and Rittenberg, 1964 (H_2S); 15. Taylor et al., 1984a (FeS_2); 16. Fry et al., 1986 (NaS_2O_3); 17. Toran, 1986 (FeS_2 and ZnS).

Several processes can be considered which would influence the sulfur isotope ratio. One process which produces isotopically light products is bacterial activity. Bacteria preferentially select light isotopes, and some of the largest fractionation effects observed in nature are the result of bacterial activity (Hoefs, 1980). Laboratory experiments suggest that *Thiobacilli* can fractionate dissolved sulfide during oxidation, producing sulfate as much as 13‰ lighter (Kaplan and Rittenberg, 1964). Fractionation (sulfate 0 to 5‰ lighter) has also been observed in microbially mediated experiments using solid sulfides (Toran, 1986). However, Taylor et al. (1984a, b) found no fractionation of pyrite by *T. ferrooxidans* under acidic conditions. Fractionation is unlikely to occur by inorganic oxidation because the reaction tends to occur over a complete layer and is irreversible so that no isotope exchange can take place

(Field, 1966; Pearson and Rightmire, 1980; Taylor et al., 1984a, b). Moreover, equilibrium fractionation would produce an isotope shift in the direction opposite to that observed (Friedman and O'Neil, 1977).

Other chemical reactions to consider are sulfate precipitation and sulfate reduction. If precipitation of sulfate minerals such as gypsum or jarosite caused fractionation (effect unknown), it should no longer be a factor since the waters are presently undersaturated with respect to these minerals. They would have dissolved and the isotopes re-mixed. Sulfate adsorption preferentially selects the light isotope, leaving associated solutions heavier; however, this process would cause significant fractionation only at dilute concentrations (Nriagu, 1974). Sulfate reduction is probably not extensive since the waters are well oxygenated (> 1 ppm O_2). Furthermore, if the reaction was catalyzed by sulfate reducing bacteria, the sulfur isotope effect would leave the remaining sulfate in solution heavier, not lighter. Thus, most of the alternatives to biological oxidation are unfavorable to produce the observed sulfur isotope fractionation.

The range of fractionation between sulfide minerals and coexisting sulfates reported in the literature (Fig. 10) may reflect the variety of environments and pathways available for sulfide oxidation. It is difficult to classify the field data into categories of biological oxidation where fractionation occurred versus inorganic or acidophilic bacterial oxidation where there is no fractionation, because there is little information to distinguish the difference between environments in the reported cases. However, bacterial activity is a feasible explanation for light sulfates, and in the Shullsburg mines biological sampling suggests there was likely to be an active bacteria population, including species that have been shown (Toran, 1986) to produce fractionation.

Oxygen isotopes in sulfate

An additional isotope that may help to understand these reactions is $\delta^{18}O$ in sulfate. Oxygen in the sulfate molecule can come from two sources: light groundwater or heavy oxygen from the atmosphere.

For an inorganic mechanism, Goldhaber (1983) suggested a model which would incorporate 87.5% oxygen from O_2. Experiments conducted at high P_{O_2} by Lloyd (1967, 1968) using dissolved sulfide and Schwarcz and Cortecci (1974) using pyrite showed about 60% of sulfate oxygen comes from water while 40% comes from air. However, recent experiments under normal P_{O_2} (Taylor et al., 1984a, b; Toran, 1986) indicated as little as 10% of the oxygen may come from O_2 through inorganic pathways. Thus, the oxygen isotope signature for inorganic oxidation is unclear.

On the other hand, one might expect micro-organisms to produce isotopically lighter sulfate oxygen. Unfortunately, the kinetics of uptake of oxygen by *Thiobacilli* are poorly understood (Roy and Trudinger, 1970; Kelly, 1982; Ehrlich, 1981). However, energy production for bacteria in this reaction comes through the electron transport system, a path that transfers oxygen from water

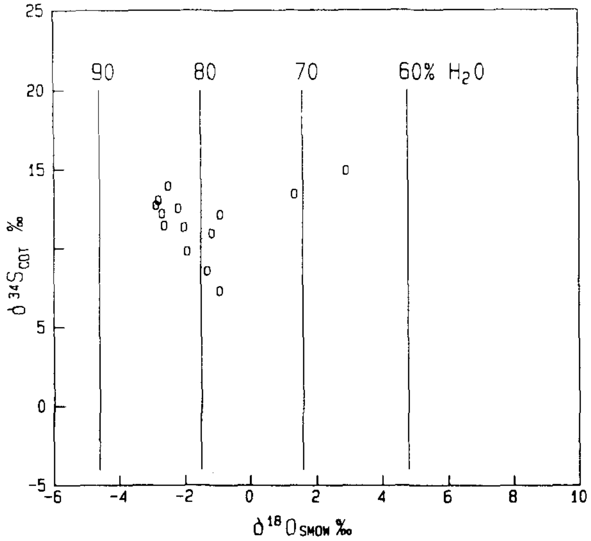

Fig. 11. Oxygen versus sulfur isotopes for contaminated Shullsburg groundwater. Vertical bars show % from water in sulfate oxygen assuming no fractionation.

to the sulfate molecule. This interpretation predicts that light oxygen isotope data will be produced by bacterial catalysis. Microbially-mediated oxidation experiments (Toran, 1986) showed 60–75% oxygen from water (ignoring fractionation). However, it was not possible to distinguish inorganic and biological pathways with oxygen isotopes at neutral pH.

The mole fraction of atmospheric O_2 and water (f_a and f_w) in sulfate can be calculated by the following equation:

$$\delta^{18}O_s = (f_w)(\delta^{18}O_w + \varepsilon_w) + (f_a)(\delta^{18}O_a + \varepsilon_a) \tag{8}$$

The average $\delta^{18}O$ value of Shullsburg water was $-7.8‰$. The average value for atmospheric oxygen is 23.5‰ (Kroopnick and Craig, 1972). Isotopic fractionation, ε_w for water and ε_a for air, has been ignored since they differ for each mechanism. Ignoring fractionation adds ± 10% uncertainty to calculation of percent water in sulfate (Toran and Harris, in prep.).

A plot of oxygen and sulfur isotope data from Shullsburg groundwater (Fig. 11) showed no obvious trends. Shullsburg samples showed between 65 and 85% contribution of oxygen from water, with most of the samples centering around 80%. Thus, the Shullsburg oxygen isotope data do not prohibit bacterial catalysis as a mechanism. The variability of oxygen isotopes suggests sulfide oxidation can occur by multiple pathways. The mechanism of oxidation may be a complex mixture of biological and abiological processes in this and other environments.

CONCLUSIONS

The Shullsburg mines present a case of sulfate contamination in the presence of carbonate buffered water. The amount of sulfate produced contradicts the notion that sulfide oxidation in a carbonate system occurs at negligible rates, whether because of biological or inorganic processes at neutral pH or in acidic microenvironments.

Contamination was localized because groundwater presently flows toward the mine workings. When groundwater begins flowing away from the mines, sulfate levels should remain low in areas distant from the mines because of dilution of sulfate. Incoming groundwater from the surrounding area diluted contaminated mine water as shown by the decline in sulfate concentration since 1983. Evidence for localization of contamination and dilution means that area farmers have probably seen the worst of contamination, and mining will not necessarily lead to long term pollution in the Shullsburg area.

The recovery of water supplies from mine-water contamination near Shullsburg was dependent on the particular physical system. That is, the gradual filling of the cone of depression by uncontaminated water, the availability of a second water supply and the size and location of the source sulfides lent the system to dissipation of contamination. This prognosis assumes new problems will not develop, such as:

(1) Pockets of sulfate presently above the water table will not introduce additional contamination. The mines and large ore deposits are now flooded, but near surface mineralization exists. However, the shallow mines around Shullsburg contain primarily galena, which is unlikely to oxidize and produce sulfate.

(2) The tailings pile will not leach sulfate to the underlying aquifer. The tailings pile is unlined and the mine shaft nearby is a potential conduit, but sulfate concentrations have been too high in the mine shaft to monitor input from the tailings pile.

(3) Contamination in the Galena-Platteville aquifer will not breach the Glenwood Shale and spread to the St. Peter aquifer. Most St. Peter wells near the mines presently have low concentrations of sulfate (Table 1).

Modeling of chemical reactions and carbon isotope effects was used to explore the mechanism of contamination. The reactions to produce contaminated water were sulfide oxidation, carbonate dissolution, CO_2 outgassing, and dilution. The mineral phases controlling water chemistry were calcite, dolomite, and siderite or iron hydroxide. Gypsum was often undersaturated in the groundwater despite high SO_4^{2-} and Ca^{2+} concentrations.

Furthermore, the presence of *T. ferrooxidans* as well as neutrophilic *Thiobacillus* species in environments similar to the Shullsburg mines was evidence for bacterial catalysis of oxidation of sulfides. Sulfur isotopes in sulfate were 0–8‰ lighter than the average area sulfides; this fractionation is typical of a bacterial isotope effect (Toran, 1986). The oxygen in sulfate showed 65–85% contribution from water assuming no fractionation. The large contribution of oxygen from water is consistent with microbial energetics, but does not exclude inorganic oxidation pathways.

Thus, sulfides can be oxidized by inorganic processes, by acidophilic *Thiobacillus* species, or by species that thrive in neutral pH. To prevent oxidation, a method must be devised to block all three processes. Acid mine drainage can be initiated by both biological and abiological mechanisms. Therefore, adding lime to neutralize pH during or after mining will not prevent oxidation of sulfides and development of high sulfate water.

Understanding of groundwater contamination requires an interdisciplinary approach, and consideration of isotope effects and microbiological activity should be an important addition to future research.

ACKNOWLEDGEMENTS

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APPENDIX

Sensitivity analysis for carbon isotope modeling

Sample S-18 was selected as a typical groundwater with intermediate sulfate contamination to do a sensitivity analysis of carbon isotope calculations. The sensitivity to a change in parameters was tested because of uncertainties in the values selected. For example, composition of the starting water and pH during oxidation can no longer be measured directly because the mines are flooded. The sensitivity analysis started with a basic model containing mean or typical values for parameters. Each parameter was varied, holding the others constant. Selection of these parameters is discussed below.

Total carbon of starting water ranged from 6.4 (S-29) to 11.4 (S-25) mmol/l total carbon with an average value of 8.0 (S-27). The typical $\delta^{13}C$ of dissolved inorganic carbon from this aquifer was believed to be − 12‰ (Siegel, in prep.) based on mixing between carbon from soil gas and carbonate rocks. The $\delta^{13}C$ of background water was difficult to measure because $\delta^{13}C$ may not be preserved in water from domestic wells that has been stored in pressure tanks. Only four samples with low sulfate might be considered background for $\delta^{13}C$: observation well S-24, spring S-25, and vent holes S-33 and S-34. The spring and one vent hole had a $\delta^{13}C$ around − 13‰, while the other vent hole was − 8.6‰. The observation well was anomalously heavy ($\delta^{13}C$ = − 4.6‰). There could have been a sampling error in S-24 since outgassing during sampling will result in heavier $\delta^{13}C$. Initial $\delta^{13}C$ of − 18 and − 6‰ were tested, with the basic model value at − 12‰.

The $\delta^{13}C$ of the carbonate host rock in the mines varied between − 2 and 0‰ (Hall and Friedman, 1969), so a mean of − 1‰ was used in the basic model. In addition, calculations were made using 1 and − 3‰.

TABLE 4

Sensitivity analysis for $\delta^{13}C$ calculations, sample S-18

Model	$\delta^{13}C$ ‰
Basic[†]	− 6.0
Starting water S-25	− 7.3
Starting water S-29*	− 7.0
Siderite ppt.	− 9.4
pH = 7 (ε_{gs} = − 7.5; ε_{ps} = 3.5)	0.4
Initial $\delta^{13}C$ = − 18‰	− 8.0
Initial $\delta^{13}C$ = − 6‰	− 4.0
Dolomite $\delta^{13}C$ = − 3‰	− 7.3
Dolomite $\delta^{13}C$ = 1‰	− 4.7
pe = 4	− 5.9
pe = 2	− 6.5
Observed	− 8.8

[†] See Table 3 for parameter values.
*Based on modified equation for $C \simeq C_0$ (Wigley et al., 1979).

Another poorly constrained parameter was the pH during oxidation. Oxidation experiments (Toran, 1986) suggested pH can be as low as 5 even with a carbonate buffer. Microenvironments of low pH may also exist. Below pH of 5, fractionation is relatively constant (ε_{gs} = 0.5; ε_{ps} = 11.8 at 10°C). The pH of Shullsburg groundwater can be at least 7 based on the sampled water. The higher pH made calculations heavier since ε_{gs} = − 7.5 and ε_{ps} = 3.5. The lower pH was selected in the basic model.

In addition carbon mass transfer differed for siderite versus iron hydroxide as the control on iron concentrations. For lack of experimental data, siderite was assumed to fractionate as calcite, which introduces uncertainty in these calculations. The basic model used iron hydroxide precipitation. The amount of iron hydroxide precipitation was affected by oxidation potential input as pe during reactions, so pe was varied in models as well. The sensitive range for pe was between 2 and 4. The measured value of S-27 (pe = 2.8) was used in the basic model.

The basic model calculated a $\delta^{13}C$ of − 6.0‰ which is heavier than the measured value of − 8.8‰. The sensitivity analysis gives a range of values between 0.4 and − 9.4‰ (Table 4). The lightest values calculated were for an initial $\delta^{13}C$ of − 18‰ and for siderite precipitation. All other predictions were heavier than the observed value. The heaviest value was obtained for pH = 7.

How typical was the basic model? The basic model fell in the middle of the range of parameters tested except for pH = 7. The effect of raising pH was to make calculated values heavier, so the basic model represents minimum values of $\delta^{13}C$ based on pH constraints. Considering the range of values selected for S-18, calculations were not sensitive to $\delta^{13}C$ of the starting water. Nor were there large changes for different pe's or starting water concentrations. Dolomite would have to be much lighter than any measured value to lower the $\delta^{13}C$ of calculations to observed values. The pH of oxidation and siderite precipitation had the biggest effect on calculation of $\delta^{13}C$. Given the uncertainty in the siderite fractionation factor little can be said about that model.

The sensitivity analysis shows there are many uncertainties in calculating $\delta^{13}C$, but nonetheless nearly all of the calculations predicted heavier $\delta^{13}C$ than observed.

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