

## Caminite: A new magnesium-hydroxide-sulfate-hydrate mineral found in a submarine hydrothermal deposit, East Pacific Rise, 21°N

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### ABSTRACT

As laboratory experiments predict, a Mg-hydroxide-sulfate-hydrate mineral, here named *caminite*, precipitates in nature from seawater heated in an active submarine hydrothermal system. Caminite is found intergrown with anhydrite in the wall of a black-smoker chimney precipitated around hydrothermal fluids discharging on the East Pacific Rise axis at 21°N latitude. Caminite is tetragonal (space group  $I4_1/amd$ ) with  $a = 5.239$  Å and  $c = 12.988$  Å. The five strongest lines appearing in X-ray powder diffraction patterns (CuK $\alpha$  radiation) are 3.345 ( $I/I_0 = 100$ ;  $hkl = 103$ ); 3.220 (80; 112); 1.871 (50; 116); 1.620 (25; 303); 1.609 (20; 224). Bond-strength calculations and experimental results predict that the caminite structure accommodates a range of compositions described by a general formula:  $MgSO_4 \cdot xMg(OH)_2 \cdot (1 - 2x)H_2O$ , where  $0 \leq x \leq 0.5$ . The caminite in our sample has a composition corresponding to a stoichiometry of  $MgSO_4 \cdot 0.4Mg(OH)_2 \cdot 0.2H_2O$ . It is soft ( $H = 2.5$ ) and apparently colorless. Caminite is uniaxial negative and has low birefringence (0.002). Its indices of refraction are  $\omega = 1.534$  and  $\epsilon = 1.532$ . In the recharge zones of submarine hydrothermal systems, large volumes of convecting seawater heated above approximately 240°C may precipitate abundant caminite and anhydrite. Formation of abundant caminite can drastically lower the pH of downwelling seawater in such systems, and rapid removal of sulfate into caminite and anhydrite may prevent the reduction of much seawater sulfate to sulfide within the hydrothermal system. Incorporation of seawater sulfate into caminite and anhydrite at elevated temperatures and subsequent recycling of this sulfate into the oceans by dissolution at low temperatures should affect the oxygen-isotope composition of seawater sulfate and may play a part in maintaining the oxygen-isotope values of oceanic sulfate in disequilibrium with  $\delta^{18}O$  of seawater.

### INTRODUCTION

On the axis of the East Pacific Rise (EPR) at 21°N latitude, 350°C hot springs discharge onto the seafloor through chimney-like mineral structures and abruptly precipitate black, sooty plumes of fine sulfide particles (Spiess et al., 1980). The chimneys formed at these “black-smoker” hydrothermal vents are composed predominantly of sulfate minerals, precipitated from heated seawater, and sulfide minerals, crystallized from cooled hydrothermal fluid (Haymon and Kastner, 1981; Styrts et al., 1981; Haymon, 1983; Oudin, 1983). We have identified one of the chimney sulfate minerals as a Mg-hydroxide-sulfate-hydrate compound that was synthesized experimentally from seawater heated to temperatures above 250°C and that has been referred to as “Mg-oxy-sulfate” or “MHSH” in publications describing these experiments (Bischoff and

Seyfried, 1978; Keefer et al., 1980, 1981; Janecky and Seyfried, 1980, 1983; Hochella et al., 1983). The identification of this phase in a seafloor hydrothermal system marks its first recognition in nature and qualifies this compound as a new mineral. The name *caminite* has been selected for the new mineral after the Latin word for chimney, *caminus*.

Although caminite is not abundant in hydrothermal vent deposits studied to date, its occurrence in a seafloor hydrothermal system may be geochemically important. As Bischoff and Seyfried (1978) originally pointed out, the formation of caminite from heated seawater removes  $OH^-$  ions from solution and transforms slightly alkaline seawater into an acidic hydrothermal fluid capable of leaching and transporting components from igneous rocks. The formation of caminite in midocean ridge hydrothermal systems is therefore a potentially important mecha-

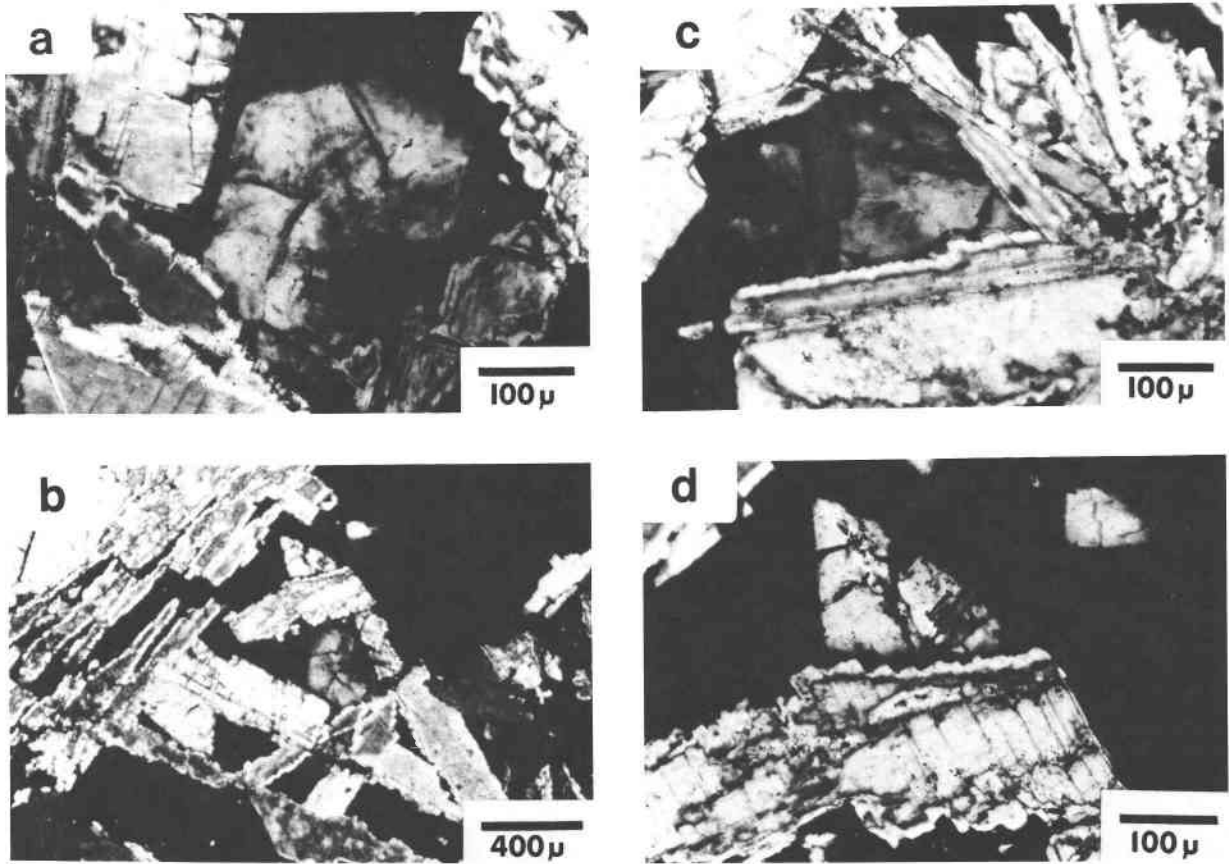


Fig. 1. Photomicrographs illustrating optical properties and textural characteristics of caminite. The four photomicrographs (a–d) shown here, taken with cross-polarized light, depict intergrowths of caminite (dark) and anhydrite (bright) in thin sections from a black-smoker chimney sample. Caminite grains are centered; (a) and (b) show the same grain at different magnifications. Note the absence of good cleavage and the lower birefringence of caminite relative to anhydrite. Caminite typically exhibits irregular cracks.

nism for mobilizing metals and other chemical species from oceanic crust into hydrothermally convecting seawater.

#### ANALYTICAL METHODS

Caminite was identified in a black-smoker chimney sample by X-ray diffractometry, using a Norelco X-ray diffractometer and  $\text{CuK}\alpha$  radiation. Cell parameters were computed from 13 reflections in the X-ray diffraction pattern using a Fortran IV program called CELLREF. The optic sign and indices of refraction for caminite were determined with a petrographic microscope on crystals immersed in oils of known refractive indices. Upon immersion, caminite grains settled with an orientation parallel to (001), and rotation of the crystals with a universal stage was necessary to measure  $\epsilon$ . Additional optical and textural characteristics of caminite were determined by microscopic study of caminite grains in thin sections. The habits and textures of caminite crystals were studied at high magnifications with a scanning electron microscope (SEM). Caminite was distinguished from anhydrite in the SEM by spot chemical analysis with an X-ray energy-dispersive system (EDS) attached to the SEM. The hardness of caminite was determined using a Reichert microhardness tester calibrated with minerals of known hardness.

Caminite grains in polished thin sections were quantitatively

analyzed for Mg, Ca, and S with an electron microprobe at an accelerating voltage of 10 kV. Anhydrite was used as a standard for analysis of S, and Ca and Mg were analyzed with a dolomite standard. To detect the presence of additional elements, an EDS attached to the microprobe was used to collect counts for 1000-s intervals at an accelerating voltage of 15 kV.

#### OCCURRENCE

Caminite was found intimately intergrown with anhydrite within the wall of a black-smoker chimney sample (see Fig. 3 in Haymon and Kastner, 1981). Both anhydrite and caminite apparently precipitate from ambient seawater heated by hydrothermal discharge rather than from hydrothermal fluids that have cooled and oxidized within chimneys. In the case of anhydrite, this assumption is substantiated by the sulfur-isotope composition of the anhydrite, which is essentially identical to that of seawater sulfate (Arnold and Sheppard, 1981; Kerridge et al., 1983; Styr et al., 1981). The  $\delta^{34}\text{S}$  value of caminite has not been measured, but this magnesian mineral must also precipitate from seawater, since no Mg was detected in black-smoker hydrothermal fluids at EPR, 21°N (Edmond et al., 1982; Von Damm et al., 1985). Both anhydrite and cam-

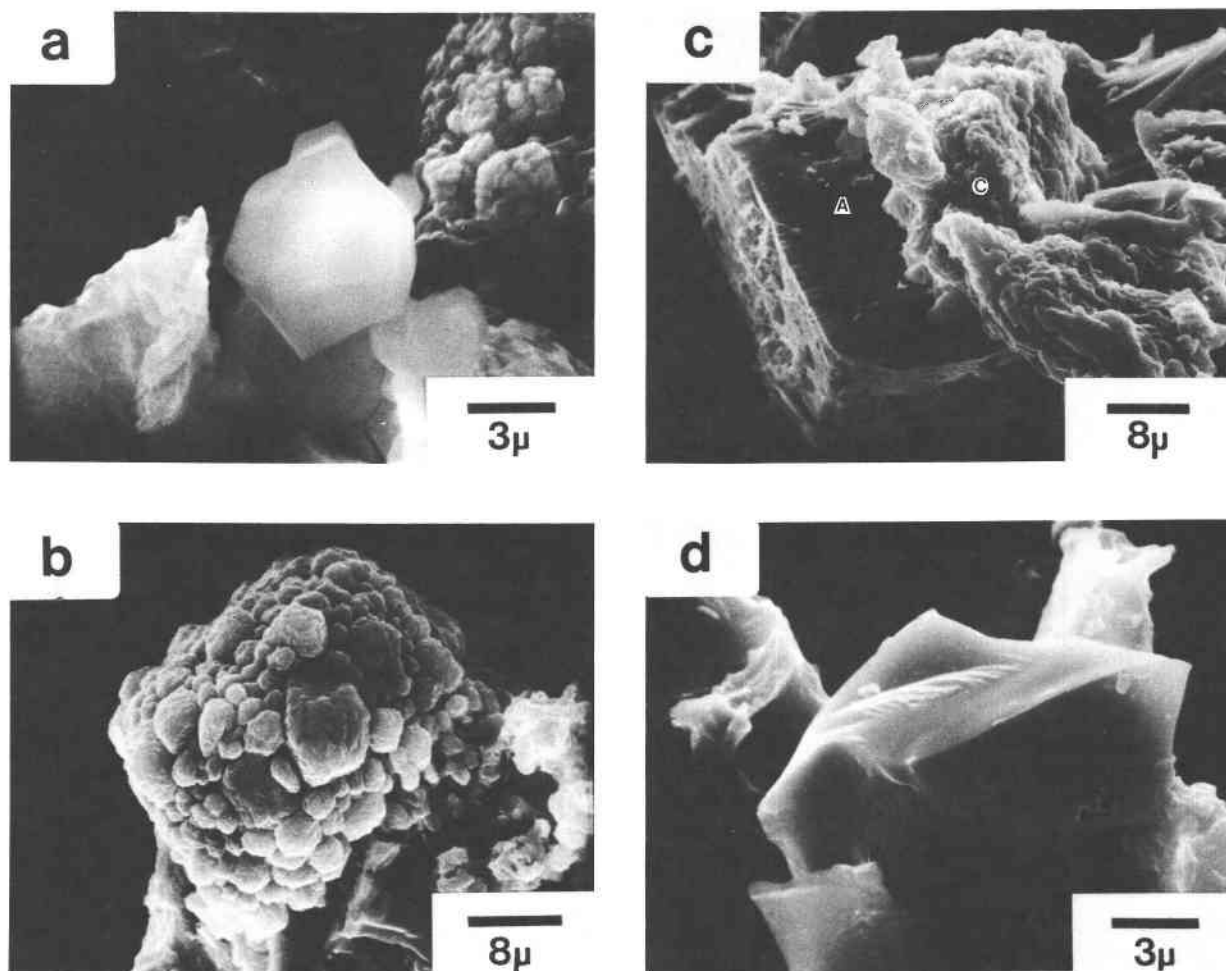


Fig. 2. SEM photomicrographs of caminite. (a) Caminite crystal with well-developed faces. (b) Botryoidal mass of caminite crystals. (c) Association of anhydrite (A) with caminite (C). (d) Caminite crystal fragment.

inite have been synthesized in the laboratory by heating of seawater (Bischoff and Seyfried, 1978; Janecky and Seyfried, 1980, 1983; Keefer et al., 1981). Precipitation of anhydrite in these experiments is due to a decrease in its solubility as temperature rises at a constant pressure (Blount and Dickson, 1969). For caminite, it is not clear whether crystallization results from heating, as for anhydrite, or from heating plus increasing  $Mg^{2+}:Ca^{2+}$  in solution, brought about by incorporation of  $Ca^{2+}$  into anhydrite.

The temperature of incipient caminite precipitation from seawater can be estimated on the basis of petrographic and experimental evidence. In thin sections, black-smoker caminite typically fills interstitial spaces between laths of anhydrite (Fig. 1), which implies that anhydrite precipitates before caminite as seawater heats. The water depth at EPR, 21°N is roughly 2600 m, corresponding to a hydrostatic pressure of approximately 260 bars. Linear interpolation between anhydrite solubilities determined in seawater experiments at vapor pressure (Glaser and Schwartz, 1976) and at 500 bars (Bischoff and Seyfried,

1978) indicates that a temperature of approximately 130°C is required to precipitate anhydrite from seawater at 260 bars. This establishes 130°C as a lower limit for the onset of caminite precipitation on the seafloor at 21°N. In seawater heating experiments at 500 bars, where synthetic caminite was first produced, significant removal of  $Mg^{2+}$  from solution was observed only above approximately 250°C (Bischoff and Seyfried, 1978). Thermodynamic model calculation of the equilibrium reaction pathway for heating of pure seawater suggests that caminite forms at temperatures  $\geq 240^\circ C$  (Janecky and Seyfried, 1984; McDuff and Edmond, 1982).

At low temperatures, caminite rapidly redissolves in water. Samples of active chimneys temporarily stored in seawater retain some anhydrite, but no traces of caminite are preserved in these samples. Neither anhydrite nor caminite are found in dead chimneys that have suffered low-temperature weathering on the seafloor. Caminite identified by X-ray diffraction in some samples disappeared when the samples were stored outside of a vacuum dessicator. In new X-ray diffraction patterns of these sam-

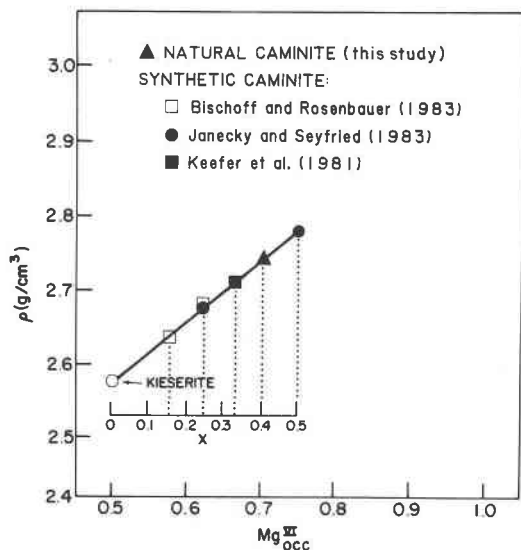


Fig. 3. Plot of density ( $\rho$ ) vs. Mg occupancy in the octahedral site of the caminite structure ( $Mg_{Occ}^{VI}$ ); modified from Hochella et al. (1983). The solid line illustrates the solid-solution range of possible compositions in the caminite structure, represented by the general formula  $MgSO_4 \cdot xMg(OH)_2 \cdot (1 - 2x)H_2O$ , where  $0 \leq x \leq 0.5$ . [See Hochella et al. (1983) for derivation of this formula.]

ples, caminite reflections had disappeared and reflections of epsomite, a hydrous magnesium sulfate, were found instead. The susceptibility of caminite to dissolution and hydration explains the belated discovery of this mineral in nature. Although caminite forms with ease from the common, widespread process of seawater heating, its life-span in the submarine environment is far too short to allow its preservation in the geologic record.

#### HABITS AND PHYSICAL PROPERTIES

Caminite in our sample is fine grained, displaying crystal sizes ranging from  $< 10 \mu m$  to  $200 \mu m$ , with rare grains as large as  $500 \mu m$ . Although synthetic caminite forms elegant bipyramidal crystals (Bischoff and Seyfried, 1978, Pl. 1), crystal faces in the natural material are poorly developed, as illustrated by the scanning electron photomicrographs in Figure 2. The fine grain size of caminite coupled with the difficulty of separating caminite from the more abundant anhydrite in the same sample has made it very difficult to determine directly properties such as luster, streak, color, or density for natural caminite. We assume, however, that the new mineral is either white or colorless since caminite cannot visibly be distinguished from intergrowths of white anhydrite, even when magnified by a binocular microscope. Grains of synthetic caminite are reported to be colorless except where affected by iron contamination from laboratory apparatus (Keefe et al., 1981). It has been determined by calculation from the crystal structure and by the flotation of crystals that the density of caminite varies from  $2.58$  to  $2.79 \pm (0.01) g/cm^3$  depending on composition (Hochella et al., 1983; Fig. 3). A diamond pyramid microhardness of approxi-

mately 10 was measured for natural caminite. This value corresponds to a hardness of 2.5 on Mohs hardness scale.

#### OPTICAL PROPERTIES

Examination of black-smoker caminite with a petrographic microscope establishes that caminite is transparent and colorless in transmitted light and is uniaxial negative. Its indices of refraction at surface temperatures are relatively low, near that of balsam ( $\omega = 1.534$ ;  $\epsilon = 1.532$ ). The birefringence of caminite is also low, 0.002 (first-order gray). Neither obvious twinning nor evidence of good cleavage is observed in thin sections, although the orientation of grains in immersion oils suggests a good cleavage parallel to (001). Irregular cracks are typical in natural caminite grains (Fig. 1). In thin section the appearance of caminite is similar to that of low quartz, but these two minerals are easily distinguished by their opposite optic signs and different indices of refraction. In Figure 1, caminite is readily identified from the adjacent anhydrite by its lower birefringence and absence of distinct cleavage.

#### STRUCTURE AND CHEMICAL COMPOSITION

The structure for synthetic caminite (or "MHSH") was determined using standard crystallographic techniques (Keefe et al., 1981; Hochella et al., 1983). Although structural analysis was based on data for synthetic rather than natural caminite, the excellent agreement of the calculated X-ray powder diffraction pattern for synthetic MHSH and the X-ray powder diffraction pattern for natural caminite (Table 1), along with the close correlation between the predicted composition calculated for MHSH and the measured chemical composition of natural caminite (Table 2), leaves little doubt that the synthetic and natural substances are the same.

Caminite crystallizes in the tetragonal space group  $I4_1/amd$  (Keefe et al., 1981). The cell dimensions calculated from X-ray diffraction data for natural caminite (Table 1) are  $a = 5.239 \text{ \AA}$  and  $c = 12.988 \text{ \AA}$ . Keefe et al. (1981) suggested that the structure of caminite consists of ribbons of face-sharing Mg-octahedra interconnected by sulfate tetrahedra. The fraction of octahedral sites occupied by  $Mg^{2+}$  in the MHSH studied by Keefe et al. (1981) was found to be 0.67, corresponding to a stoichiometry of  $MgSO_4 \cdot 0.33Mg(OH)_2 \cdot 0.33H_2O$ . Bond-strength calculations by Keefe et al. (1981) and Hochella et al. (1983) suggest, however, that the MHSH structure accommodates a range of compositions from  $MgSO_4 \cdot H_2O$  to  $2MgSO_4 \cdot Mg(OH)_2$  (Fig. 3). The latter composition is isochemical with kieserite. The general formula for the solid solution is given by Hochella et al. (1983) as  $MgSO_4 \cdot xMg(OH)_2 \cdot (1 - 2x)H_2O$ , where  $0 \leq x \leq 0.5$ . The existence of a caminite solid solution is supported by the apparent range of MHSH compositions indirectly determined in seawater-heating experiments from solution chemistry (Fig. 3), from  $x = 0.16$  (Bischoff and Rosenbauer, 1983), to  $x \approx 0.25$  (Bischoff and Rosenbauer, 1983;

Table 1. X-ray diffraction data for caminite

Synthetic			Hochella et al. (1983)**				Natural†		
Bischoff and Seyfried (1978)*			d(Å)	2θ	I/I <sub>0</sub>	hkl	d(Å)	2θ	I/I <sub>0</sub>
-	-	-	4.861	18.25	10	101	4.858	18.26	10
3.35	26.59	vs	3.339	26.70	100	103	3.345	26.65	100
3.219	27.69	vs	3.220	27.71	91	112	3.220	27.70	80
2.607	34.37	m	2.621	34.21	22	200	2.628	34.12	15
2.292	39.27	w	2.307	39.04	9	211	2.309	39.01	10
2.058	43.96	s	2.062	43.91	16	213	2.062	43.90	20
-	-	-	2.040	44.41	15	204	2.041	44.39	20
1.874	48.54	w	1.870	48.69	8	116	1.871	48.66	50
1.845	49.37	vw	1.853	49.16	5	220	1.854	49.14	20
1.744	52.42	w	1.741	52.27	5	215	?	?	?
1.667	55.04	s	1.670	55.00	17	206	1.671	54.93	20
-	-	-	1.620	56.81	13	303	1.620	56.84	25
-	-	-	1.610	57.22	20	224	1.609	57.26	20
1.606	57.32	s	1.606	57.36	11	312	-	-	-
1.462	63.59	m	1.455	63.97	7	217	1.455	64.00	10
1.385	67.58	w	1.381	67.88	4	208	-	-	-
1.317	71.59	m	1.316	71.69	8	316	?	?	?
-	-	-	1.311	72.08	11	400	?	?	?

\* Observed powder pattern measured with a Gandolfi camera on a single crystal.  
\*\* Calculated powder pattern from single crystal data obtained with CuKα radiation.  
† Observed powder pattern measured by diffractometer using CuKα radiation.  
? = peaks masked by anhydrite.

Janecky and Seyfried, 1983), to  $x = 0.5$  (Janecky and Seyfried, 1983).

Microprobe analysis of our natural caminite sample (Table 2) shows a composition of  $37.3 \pm 1.2$  wt% MgO and  $52.7 \pm 1.7$  wt% SO<sub>3</sub>, corresponding to a stoichiometry of MgSO<sub>4</sub>·0.4Mg(OH)<sub>2</sub>·0.2H<sub>2</sub>O. This composition is slightly more Mg-rich than the MSHS synthesized by Keefer et al. (1981; Fig. 3). Although substitution into caminite of divalent cations other than Mg<sup>2+</sup> (e.g., Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, or Zn<sup>2+</sup>) is theoretically possible (Keefer et al., 1981), the natural caminite from EPR, 21°N contains traces of Ca<sup>2+</sup> only (Table 2). This indicates that our chimney caminite precipitated from pure seawater that did not mix significantly with the metal-rich hydrothermal fluids flowing through the chimney structure and that no subsequent cation exchange between caminite and the hydrothermal fluids occurred.

#### GEOCHEMICAL ROLE OF CAMINITE IN SUBMARINE HYDROTHERMAL SYSTEMS

##### Potential importance of caminite formation

The geochemical importance of caminite is linked to where and how abundantly it precipitates in submarine hydrothermal systems. We have documented the formation of caminite at a seafloor vent, where it is produced from heating of ambient bottom seawater above 240°C by discharging hydrothermal fluids. Since each unit volume of discharging 350°C fluid can heat only a much smaller volume of 2°C seawater above the caminite saturation point, the total mass of caminite that precipitates at any time in the discharging part of a seafloor hydrothermal system is probably small. If, however, caminite forms within ocean crust from geothermal heating of downwelling seawater during hydrothermal recharge, a larger mass of caminite may be produced with profound effects on the Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> content and pH of the re-

charging waters. Sulfate incorporated into caminite and anhydrite is made unavailable for reduction to aqueous sulfide species, and pH decreases drastically as OH<sup>-</sup> ions are taken into caminite. Depending on the Mg composition of the caminite, up to  $2.8 \times 10^{-2}$  mol of H<sup>+</sup> per liter of seawater can be liberated into solution by quantitative uptake of all dissolved seawater sulfate into caminite solid solution. In seawater-heating experiments by Bischoff and Seyfried (1978), the steep decline of the pH at 250–350°C from 5.8 to 2.5 may have been caused mainly by removal of just 29% of seawater sulfate and 20% of seawater Mg<sup>2+</sup> into caminite.

The experiment cited above demonstrates the potential effects of caminite precipitation on the chemistry of downwelling seawater, but it is not clear from present data whether abundant formation of caminite actually is occurring during submarine hydrothermal recharge. Recharging seawater may become undersaturated with respect to caminite if dissolved Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> are taken up into Mg silicate + anhydrite assemblages during reaction with oceanic crust. Seawater-basalt hydrothermal experiments carried out at 300°C and 500 bars over a broad range of water:rock ratios suggest that incorporation of Mg<sup>2+</sup> into clay minerals and leaching of Ca<sup>2+</sup> from basalt lowers the Mg/Ca ratio in the fluid, thereby

Table 2. Chemical composition of caminite

Oxide (wt %)	Calc. range of compositions for theoretical caminite solid solution*		Meas. composition of natural caminite**
MgO	29.1	40.5	37.3(±1.2)
CaO	--	--	trace
SO <sub>3</sub>	57.9	53.5	52.7(±1.7)
H <sub>2</sub> O	13.0	6.0	10.0†
Total	100.0	100.0	100.0

\* Calculated from general formula: MgSO<sub>4</sub>·xMg(OH)<sub>2</sub>·(1-2x)H<sub>2</sub>O, 0 ≤ x ≤ 0.5 (Hochella et al., 1983).  
\*\* MgO, CaO, and SO<sub>3</sub> measured by electron microprobe analysis of caminite from a black smoker chimney.  
† H<sub>2</sub>O calculated by difference.

stabilizing anhydrite relative to caminite (Seyfried and Mottl, 1982; Janecky and Seyfried, 1983). When low-Ca peridotite is substituted for basalt in these experiments, caminite formation is observed (Janecky and Seyfried, 1980, 1983). The Mg/Ca ratio in the fluid evidently is the key parameter controlling whether caminite or anhydrite precipitates (McDuff and Edmond, 1982), and thus it is the relative directions and rates of  $Mg^{2+}$  and  $Ca^{2+}$  exchange between seawater and basalt that ultimately determine which sulfate mineral predominates.

Little is known about the paths, flow rates, and residence times for seawater convecting through ocean crust, nor are the kinetics of seawater-ocean crust exchange reactions well constrained by present data. Also, the relative directions and rates of exchange for  $Mg^{2+}$ , and to some extent  $Ca^{2+}$ , between seawater and oceanic crust vary spatially and temporally within hydrothermal systems. The kinetics and spatial-temporal variations in natural seafloor hydrothermal systems are not fully imitated in laboratory experiments. In most hydrothermal water-rock interaction experiments, the starting rock material is ground to a powder to facilitate reaction by increasing reactive surface area (see, for example, methods in Bischoff and Dickson, 1975; Seyfried and Mottl, 1982). This may cause much faster rates of  $Mg^{2+}$  uptake into silicates and leaching of  $Ca^{2+}$  from basalt in the experiments than in a natural system. Because reaction rates are relatively slow at temperatures less than 50°C, experimental temperatures are usually higher; also, the experiments do not reproduce the flow-through characteristics of a natural hydrothermal system. In a natural system, seawater downwelling on ridge flanks may be modified by low-temperature reaction with basalt before percolating to hotter regions. Recent studies of ocean-crust alteration at DSDP site 417 show that during extensive low-temperature alteration (less than 50°C; Böhlke et al., 1984), the formation of zeolites and calcite results in an increase in the bulk Ca content of altered basalt, and the formation of aluminous smectite and potassium feldspar is accompanied by decreases in bulk Ca and Mg contents (Alt and Honnorez, 1984). These observations are consistent with increases in the Mg/Ca ratios of downgoing seawater during the early stages of recharge from reactions with basalt at less than 50°C, a situation that would enhance the possibility of subsequent caminite formation at higher temperatures. The percentage of glass relative to crystalline basalt in a natural system may also be important, since glass alters to Mg-rich smectites and chlorites more easily than does crystalline basalt (Coish, 1977; Seyfried and Mottl, 1982). In areas where thick massive flows dominate the volcanic section, or in mature hydrothermal systems where little unaltered glass remains in the system, higher Mg/Ca ratios in circulating fluids may permit caminite formation at high temperatures.

We conclude that the present data on seafloor-alteration processes do not unambiguously rule out the formation of caminite during hydrothermal recharge, and thus the potential geochemical results of its formation

must be considered. These results include depletion of  $Mg^{2+}$  and  $SO_4^{2-}$  and drastic lowering of pH in recharging seawater heated above approximately 240°C, and reversed effects from caminite dissolution below this temperature.

#### **Possible influence of caminite and anhydrite precipitation on oxygen-isotope composition of seawater sulfate**

The  $\delta^{18}O$  value of present-day seawater sulfate is rather constant at +9.6–9.8‰ (SMOW)<sup>1</sup> (Longinelli and Craig, 1967; Rafter and Mizutani, 1967). This value is much lower than the calculated value of +38‰ (SMOW) for equilibrium at 4°C with seawater  $\delta^{18}O = 0‰$  (Lloyd, 1967, 1968). Several hypotheses have been developed to explain the observed disequilibrium between seawater sulfate and ocean-water oxygen isotopes; most recently, Chiba and Sakai (1985) proposed that the kinetics of oxygen-isotope exchange reactions between water and aqueous sulfate are so slow that a time period longer than the age of the Earth is required for equilibration. This proposal does not explain, however, how present-day seawater sulfate has acquired a  $\delta^{18}O$  value of +9.6–9.8‰ (SMOW), or what has governed variations in  $\delta^{18}O$  values of marine sulfates through geologic time (Sakai, 1972; Claypool et al., 1980).

We suggest that precipitation of caminite and anhydrite at elevated temperatures within oceanic crust, and subsequent recycling of these hydrothermal phases by dissolution at lower temperatures, may play a part in maintaining the  $\delta^{18}O$  value of dissolved seawater sulfate at distinctly lower values than the equilibrium value. At 280°C according to Lloyd (1967, 1968), or at only 200°C according to Chiba et al. (1981), the  $\delta^{18}O$  value of anhydrite precipitated in equilibrium with seawater oxygen isotopes is equal to the  $\delta^{18}O$  value of present-day seawater sulfate. Although the oxygen-isotope fractionation factors for caminite-water are unknown, the  $\delta^{18}O$  values for caminite precipitated in equilibrium with ocean water theoretically should be lower than those for anhydrite at any given temperature. Mixtures of anhydrite and caminite precipitated in isotopic equilibrium with seawater oxygen above 130°C and 240°C, respectively, therefore can create a reservoir of sulfate with a  $\delta^{18}O$  value around +9.6–9.8‰ (SMOW). This sulfate would be released into the oceans by dissolution of these phases at lower temperatures. In closing, we note that even if caminite does not precipitate during hydrothermal recharge, so that its formation is confined to discharge zones and its abundance within the hydrothermal system is low at any given moment, the cumulative, time-integrated effect of caminite formation on the oxygen-isotope composition of seawater sulfate may be significant. Seawater sulfate recycled from caminite + anhydrite dissolution will retain its  $\delta^{18}O$  value owing to sluggish equilibration at low temperatures with ocean-water oxygen and will accumulate in the oceans

<sup>1</sup> A distinctly different value of +8.6‰ (SMOW) was reported by Sakai (1976) and Holser et al. (1979).



with time from ongoing production and recycling of sulfate in oceanic hydrothermal systems.

#### ACKNOWLEDGMENTS

We wish to thank L. Rudee for assistance in determining the hardness of caminite, and R. Fujita for help with microprobe analysis. We thank M. Hochella, Jr., and an anonymous reviewer for valuable discussions and critiques of the manuscript. This work was supported by NSF Grant OCE78-21082.

#### REFERENCES

- Alt, J.C., and Honnorez, J. (1984) Alteration of the upper oceanic crust, DSDP site 417: Mineralogy and chemistry. *Contributions to Mineralogy and Petrology*, 87, 149–169.
- Arnold, M., and Sheppard, S.M.F. (1981) East Pacific Rise at latitude 21°N: Isotopic composition and origin of the hydrothermal sulfur. *Earth and Planetary Science Letters*, 56, 148–156.
- Bischoff, J.L., and Dickson, F.W. (1975) Seawater-basalt interaction at 200°C and 500 bars: Implications for origin of seafloor heavy metal deposits and regulation of seawater chemistry. *Earth and Planetary Science Letters*, 25, 385–397.
- Bischoff, J.L., and Seyfried, W.E. (1978) Hydrothermal chemistry of seawater from 25° to 350°C. *American Journal of Science*, 278, 838–860.
- Bischoff, J.L., and Rosenbauer, R.J. (1983) A note on the chemistry of supercritical seawater: 350–500°C. *Geochimica et Cosmochimica Acta*, 47, 139–144.
- Blount, C.W., and Dickson, F.W. (1969) The solubility of anhydrite (CaSO<sub>4</sub>) in NaCl-H<sub>2</sub>O from 100 to 450°C and 1 to 1000 bars. *Geochimica et Cosmochimica Acta*, 33, 227–245.
- Böhlke, J.K., Alt, J.C., and Muehlenbachs, K. (1984) Oxygen isotope-water relations in altered deep-sea basalts: Low-temperature mineralogical controls. *Canadian Journal of Earth Science*, 21, 67–77.
- Chiba, H., and Sakai, H. (1985) Oxygen isotope exchange rate between dissolved sulfate and water at hydrothermal temperatures. *Geochimica et Cosmochimica Acta*, 49, 993–1000.
- Chiba, H., Kusakabe, M., Hirano, S.I., Matsuo, S., and Somiya, S. (1981) Oxygen isotope fractionation factors between anhydrite and water from 100 to 550°C. *Earth and Planetary Science Letters*, 53, 55–62.
- Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., and Zak, I. (1980) The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretations. *Chemical Geology*, 28, 199–260.
- Coish, R.A. (1977) Ocean floor metamorphism in the Betts Cove ophiolite, Newfoundland. *Contributions to Mineralogy and Petrology*, 60, 255–270.
- Edmond, J.M., Von Damm, K.L., McDuff, R.E., and Measures, C.I. (1982) Chemistry of hot springs on the East Pacific Rise and their effluent dispersal. *Nature*, 297, 187–191.
- Glater, J., and Schwartz, J. (1976) High-temperature solubility of calcium sulfate hemihydrate and anhydrite in natural seawater concentrates. *Journal of Chemical Engineering Data*, 21, 47–52.
- Haymon, R.M. (1983) Growth history of hydrothermal black smoker chimneys. *Nature*, 301, 695–698.
- Haymon, R.M., and Kastner, M. (1981) Hot springs on the East Pacific Rise at 21°N: Preliminary description of mineralogy and genesis. *Earth and Planetary Science Letters*, 53, 363–381.
- Hochella, M.F., Jr., Keefer, K.D., and de Jong, B.H.W.S. (1983) The crystal chemistry of a naturally occurring magnesium hydroxide sulfate hydrate, a precipitate of heated seawater. *Geochimica et Cosmochimica Acta*, 47, 2053–2058.
- Holser, W.T., Kaplan, I.R., Sakai, H., and Zak, I. (1979) Isotope geochemistry of oxygen in the sedimentary sulfate cycle. *Chemical Geology*, 25, 1–17.
- Janecky, D.R., and Seyfried, W.E., Jr. (1980) Experimental peridotite-seawater interaction at 200°C and 300°C: Chemical exchange and kinetics of serpentine mineral formation. *Third International Symposium on Water-Rock Interaction, Proceedings*, Edmonton, Canada, 173.
- (1983) The solubility of magnesium hydroxide sulfate hydrate in seawater at elevated temperatures and pressures. *American Journal of Science*, 283, 831–860.
- (1984) Formation of massive sulfide deposits on oceanic ridge crests: Incremental reaction models for mixing between hydrothermal solutions and seawater. *Geochimica et Cosmochimica Acta*, 48, 2723–2738.
- Keefer, K.D., Hochella, M.F., Jr., and de Jong, B.H.W.S. (1980) Crystal structure of magnesium hydroxy-sulfate, MgSO<sub>4</sub>·½Mg(OH)·½H<sub>2</sub>O. *Third International Symposium on Water-Rock Interaction, Proceedings*, Edmonton, Canada, 50–51.
- (1981) The structure of magnesium hydroxide sulfate hydrate MgSO<sub>4</sub>·½Mg(OH)·½H<sub>2</sub>O. *Acta Crystallographica*, B37, 1003–1006.
- Kerridge, J.F., Haymon, R.M., and Kastner, M. (1983) Sulfur isotope systematics at the 21°N site, East Pacific Rise. *Earth and Planetary Science Letters*, 66, 91–100.
- Lloyd, R.M. (1967) Oxygen-18 composition of oceanic sulfate. *Science*, 156, 1228–1231.
- (1968) Oxygen isotope behavior in sulfate-water system. *Journal of Geophysical Research*, 73, 6099–6110.
- Longinelli, A., and Craig, H. (1967) Oxygen-18 variations in sulfate ions in seawater and saline lakes. *Science*, 156, 56–59.
- McDuff, R.E., and Edmond, J.M. (1982) On the fate of sulfate during hydrothermal circulation at mid-ocean ridges. *Earth and Planetary Science Letters*, 57, 117–132.
- Oudin, E. (1983) Hydrothermal sulfide deposits of the East Pacific Rise (21°N). Part I: Descriptive mineralogy. *Marine Mining*, 4, 39–72.
- Rafter, T.A., and Mizutani, Y. (1967) Oxygen isotopic composition of sulphates—Part 2: Preliminary results on oxygen isotopic variation in sulphates and the relationship to their environment and to their δ<sup>34</sup>S values. *New Zealand Journal of Science*, 10, 816–840.
- Sakai, H. (1972) Oxygen isotope ratios of some evaporites from Precambrian to recent ages. *Earth and Planetary Science Letters*, 15, 201–205.
- (1976) Sulfate-water isotope thermometry applied to geothermal systems. *Geothermics*, 5, 67–74.
- Seyfried, W.E., Jr., and Mottl, M.J. (1982) Hydrothermal alteration of basalt under seawater-dominated conditions. *Geochimica et Cosmochimica Acta*, 46, 985–1002.
- Spieß, F.N., Macdonald, K.C., Atwater, T., Ballard, R., Carranza, A., Cordoba, D., Cox, C., Diaz-Garcia, V.M., Francheteau, J., Guerrero, J., Hawkins, J., Haymon, R., Hessler, R., Juteau, T., Kastner, M., Larson, R., Luyendyk, B., Macdougall, J.D., Miller, S., Normark, W., Orcutt, J., and Rangin, C. (1980) East Pacific Rise: Hot springs and geophysical experiments. *Science*, 207, 1421–1433.
- Styr, M.M., Brackman, A.J., Holland, H.D., Clark, B.C., Pisutha-Armond, V., Eldridge, C.S., and Ohmoto, H. (1981) The mineralogy and the isotopic composition of sulfur in hydrothermal sulfide/sulfate deposits on the East Pacific Rise, 21°N latitude. *Earth and Planetary Science Letters*, 53, 382–390.
- Von Damm, K.L., Edmond, J.M., Grant, B., Measures, C.I., Walden, B., and Weiss, R.F. (1985) Chemistry of hydrothermal solutions at 21°N, East Pacific Rise. *Geochimica et Cosmochimica Acta*, 49, 2197–2220.

MANUSCRIPT RECEIVED MAY 14, 1985

MANUSCRIPT ACCEPTED JANUARY 14, 1986