

Precipitation of vaterite (CaCO_3) during oil field drilling

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Abstract

Vaterite, a CaCO_3 polymorph, is a rare mineral that is said to be metastable under all known conditions. According to the literature, vaterite precipitated from carbonate solution recrystallizes spontaneously to calcite or aragonite. Yet vaterite has been identified in hard tissues of organisms, in gallstones, in contact metamorphic aureoles, in zones of thermal metamorphism, in a meteorite, and in cone-in-cone concretions. Newly precipitated vaterite has formed at the expense of carbonate rock in drilling fluids in wells of New York, Michigan, Nevada, Texas, and New Zealand. Petrographic examination reveals a light brown core of Ca_3SiO_5 surrounded by a colourless rim of vaterite. The $\delta^{18}\text{O}_{\text{PDB}}$ of New York vaterite is -12.4‰ and that of the Michigan vaterite is -17.6‰ , which reflect the oxygen isotopic composition of meteoric freshwater used in drilling. The $\delta^{13}\text{C}_{\text{PDB}}$ value of -19.2‰ for New York vaterite and that of -17.6‰ for Michigan vaterite suggest that natural gas dissolved original carbonate in the subsurface. Drilling records from both wells indicate that natural gas was released into the drilling muds from the formations exposed at the time vaterite was encountered. Crossplots of the oxygen and carbon isotopic ratios overlap those of spurrite rocks in thermal metamorphic zones in Israel. A C-14 radiocarbon analysis of the Michigan vaterite gave an age of 953 ± 39 yr. BP. $88.8 \pm 0.6\%$ is modern carbon and 11.2% is dead carbon. Hence this carbon, and therefore the vaterite, is essentially modern. A sample of the New York vaterite yielded a modern age.

KEYWORDS: vaterite, CaCO_3 polymorph, oil-field drilling.

Introduction

THE purpose of this paper is to relate observations on newly precipitated vaterite in oil-field drilling to natural vaterite occurrences. A preliminary note on vaterite formed in drilling mud has been published (Friedman *et al.*, 1993); the current paper compares this vaterite with the nature, origin, and occurrence of naturally precipitated vaterite.

Linck (1903) named vaterite or 'Vater's third modification' after its discoverer H. Vater, even though no evidence existed at the time of its existence as a natural mineral. Gibson *et al.* (1925)

showed that a laboratory-synthesized form of CaCO_3 gave a distinct X-ray pattern that differed from calcite and aragonite and established vaterite as a third polymorph of calcium carbonate. Vaterite is very rare in sediments and rocks, but is readily precipitated in the laboratory (Meyer, 1969). It is metastable under all known conditions (Deer *et al.*, 1962); in aqueous solution at room temperature it transforms to calcite (Johnston *et al.*, 1916) or aragonite (Bischoff, 1968). At room temperature, vaterite that has precipitated from carbonate solutions recrystallizes to calcite in a period of 20–25 hours (Silk, 1970). At 50°C

vaterite transforms predominantly to aragonite within 60 min (Ogino *et al.*, 1987); it takes several hours for the transformation of vaterite to calcite (Fischer and Ferguson, 1966; Yamaguchi and Marakawa, 1981). The transformation is not a direct solid phase reaction, but a recrystallization of calcium carbonate through the dissolution of vaterite and growth of calcite or aragonite (Ogino *et al.*, 1987). Yet the lattice structure of vaterite is similar to that of calcite; hence vaterite may convert to calcite even in the solid state. Albright (1971) predicted that vaterite would be stable below 10°C at 1 atm pressure. Plummer and Busenberg (1982), following the procedures of Turnbull (1973), prepared vaterite which consisted of spherules 4–6 µm in diameter. The material, precipitated at 65°C, approached equilibrium very slowly; at 25°C vaterite reached equilibrium rapidly.

Organic matter influences which polymorph of calcium carbonate may form. An increase in the concentration of taurine, glutamate, serine, glycine, and glycoprotein decreases the rate of calcium-carbonate formation, but increases the potential for vaterite to form (Kitano and Hood, 1965). Silica gels are particularly suitable for growth of vaterite (Schwartz *et al.*, 1971). In the presence of a scale inhibitor (hydroxyethylidene 1, 1 diphosphoric acid [HEDP]) the rate of crystallization of vaterite is higher than that of calcite or aragonite. At low concentrations of HEDP, vaterite grows exclusively on vaterite seed crystals, and it may be stabilized under these conditions (Nancollas and Sawada, 1982).

In 1955 Ievins *et al.* reported that vaterite can 'be prepared artificially but is not found in nature' and McConnell (1960) notes, in reference to a vaterite occurrence in an Irish metamorphic aureole, 'to the best of the author's knowledge vaterite has not previously been recorded as a natural mineral'.

TABLE 1. Mineral composition of vaterite samples in New York well

Mineral	Depth in well (m)		
	1263/70	1263/70	1467/70
Quartz	5%	5%	3%
Calcite	10%	8%	63%
Vaterite	70%	75%	25%
Portlandite	15%	8%	2%
Dolomite	Trace	1%	7%
Pyrite	Trace	3%	
Smectite	Trace		

Although vaterite is so unstable that it is most uncommon, it occurs in unexpected places: in the tissues of gastropods, pelecypods and Ascidiacea (Hall and Taylor, 1971; Lowenstam and Abbott, 1975; Mayer and Weineck, 1932; Sommer, 1972), in gallstones (Phemister *et al.*, 1939; Rodgers, 1983), in urinary calculi (Prien and Frondel, 1947), in early carbonation of Portland cement (Cole and Kroone, 1959), in lake water (Rowlands and Webster, 1971), and as breakdown products of laboratory-grown ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) (Shaikh and Shearman, 1986). In ancient settings it has been recorded from contact-metamorphic aureoles in Ireland as a pseudomorph after larnite (McConnell, 1960), from zones of thermal metamorphism in Israel (the Mottled Zone) (Kolodny and Gross, 1974), and from the Pesyanoe meteorite (Du Fresne *et al.*, 1962). The Pesyanoe meteorite cooled from 1100°C and vaterite formed during complex cycles of subsequent heating and cooling. Vaterite has also been recorded in the Appalachians of Quebec, where it occurs in cone-in-cone calcite of carbonate concretions in Ordovician shales (Fong, 1981).

Vaterite occurrences

In this study vaterite has been identified in wells from New York, Michigan, Nevada, Texas and New Zealand. The newly discovered vaterite from New York was found in the ARCO Susi 1 well of Ulster County in the interval of Lower Ordovician dolostones of the Beekmantown Group at depths of 1263–1270 m and 1467–1470 m. The gamma-ray and bulk-density logs showed no change in response to the presence of vaterite. The samples for study were well cuttings, ¼–¾ cm in diameter, of light-grey material enclosing numerous black, chert-like rounded grains a fraction of a millimetre in diameter.

Under the petrographic microscope the vaterite resembles tephra and initially was misidentified by one author (G.M.F.) as such. Its mineralogy is given in Table 1. X-ray patterns at the 1263–1270 m interval identified vaterite 70–75%, portlandite 8–15%, and accessory inclusions of quartz, dolomite and pyrite. At the deeper 1467–1470 m interval vaterite is less common (25%) and calcite (63%) probably replaced vaterite; quartz, portlandite, and dolomite are present in minor amounts. As vaterite gives poor diffraction patterns and its major peaks overlap those of other minerals, several analytical laboratories, including those of Mineralogy, Inc. (Tulsa, Oklahoma) and ARCO Oil & Gas Company (Plano, Texas), contributed to its identification. Petrographic examination (Fig.1) reveals a light-brown core of high relief

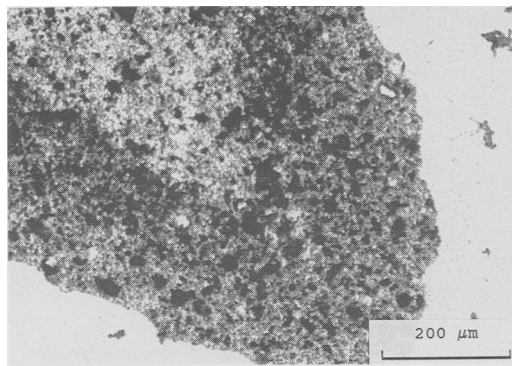


FIG. 1. Thin-section of light-brown core of amorphous calc-silicate (Ca_3SiO_5) surrounded by vaterite rim.

surrounded by a colourless rim of low relief. Samples from the 1467–1470 m intervals have a thick core and thin rim, whereas in those from the 1263–1270 m interval the core is thin, even lacking, and the rim is thick. These core-and-rim textures are evident at several scales, including that of the scanning electron microscope (Fig. 2). This distribution of core and rim confirms the X-ray pattern and microprobe analysis: the core is not a carbonate mineral at all, but an amorphous calc-silicate of composition Ca_3SiO_5 (the actual analysis is closer to $\text{Ca}_{13}\text{Si}_4\text{O}_{21}$) (Table 2, Analysis 2). Ca_3SiO_5 is known as alite and constitutes 50–70% of Portland cement (Taylor, 1990). Vaterite apparently formed at the expense of this calc-silicate, which recalls the reaction in a contact-metamorphic aureole in Ireland, where the calc-silicate mineral larnite [$\text{Ca}_2(\text{SiO}_4)$] changed to $1.5\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ (Long and McConnell, 1959), and then to vaterite and a gelatinous hydrate phase (McConnell, 1960). In vaterite-bearing

TABLE 2. Microprobe analyses of vaterite and calcium-silicate samples in New York well

	Vaterite (wt.%)	Calc-silicate (wt.%)	Transitional phase (wt.%)
CaO	45.4	72.1	20.2
MgO	0.5	1.6	6.0
FeO	0.6	0.6	1.3
MnO	0.1	0.4	0.4
SiO ₂	11.9	23.9	45.6
CO ₂	36.6		23.4
Total	95.1	98.8	96.9

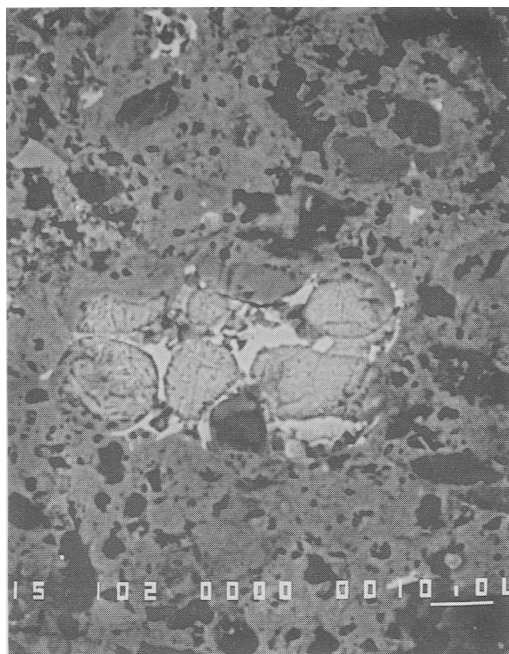


FIG. 2. Scanning electron micrograph of vaterite showing central core of amorphous calc-silicate (Ca_3SiO_5) (light) surrounded by vaterite (dark). Scale bar = 10 μm .

metamorphosed Cretaceous-Tertiary rocks of Israel (Mottled Zone) the metamorphic calc-silicate mineral is spurrite ($2\text{Ca}_2(\text{SiO}_4)\cdot\text{CaCO}_3$) and interestingly the composition of this spurrite rock is similar to that of the vaterite of this study (see Table 2, analysis 1 and Table 3, analyses 1 and 3). The origin of the calc-silicate in the studied wells is uncertain. Table 2 (analysis 3) presents another calc-silicate phase in the studied vaterite rock. The original unmetamorphosed micritic carbonate rock (Table 3, analysis 4) of the Mottled Zone of Israel is almost identical to (1) its metamorphosed analogue (spurrite rock) (Table 3, analysis 3) and (2) the vaterite of this study.

The petrography of the Michigan vaterite, discovered in Ordovician strata in the ARCO Granger well in Clare County, is comparable to that of the New York vaterite, once again showing a central core surrounded by a rim. This well was drilled in 1991, and vaterite was recovered from a depth of 3186 m. Samples recovered from the Michigan well, however, represent circulated samples recovered during an attempt to dislodge the stuck drilling pipe (Underdown, R. D.,

TABLE 3. Comparison of chemical composition of vaterite and calcium-silicate samples from New York well with that of spurrite rock and micritic limestone of Mottled Zone, Israel

	Vaterite	Calc-silicate	Spurrite rock Mottled Zone	Original micritic limestone Mottled Zone
	(wt.%)	(wt.%)	(wt.%)	(wt.%)
CaO	48.3	75.1	51.1	51.4
SiO ₂	12.7	24.9	15.1	10.2
CO ₂	39.0		33.8	38.4
Total	100.0	100.0	100.0	100.0

Vaterite samples normalized for CaO, SiO₂ and CO₂ to 100%; see Table 2

Schultz, D. J., Kullman, J. and Friedman, G. M., in prep.). Newly precipitated vaterite in wells interferes with well drilling and completion. Interestingly, shale chips have been found within the vaterite. The chips (drill cuttings) resulted from the drilling operation, hence the vaterite must have precipitated around the shale and limestone fragments indicating that the vaterite is a modern precipitate and not part of the rock record. Contrary to Sommer (1972) none of the vaterite samples showed luminescence under a cathodoluminescence microscope.

Trace amounts of vaterite have also been identified in the drill cuttings of the upper Cambrian Wilberns Formation at a depth of 2960 m in a 1947 well in Frio County, Texas. Other occurrences include vaterite cuttings from a 1985 well in the Devonian Devils Gate Limestone at a depth of 928 m in White Pine County, Nevada, and in cuttings from a 1991 well in the Oligocene Turi Formation in New Zealand.

The $\delta^{13}\text{C}_{\text{PDB}}$ of the New York vaterite is -19.2% and $\delta^{18}\text{O}_{\text{PDB}}$ is -12.4% ($\delta^{18}\text{O}_{\text{SMOW}} = 17.9\%$). The vaterite from Michigan yielded -24.4% for $\delta^{13}\text{C}_{\text{PDB}}$ and -17.6% for $\delta^{18}\text{O}_{\text{PDB}}$ ($\delta^{18}\text{O}_{\text{SMOW}} = 12.2\%$). To understand the origin of the vaterite, comparison must be made with the carbon and oxygen isotopic chemistry of carbonate sediments and rocks from various geologic settings. Figure 3 shows the isotopic patterns of different kinds of carbonates. The isotopic chemistry of the vaterite of this study differs from all other kinds of carbonate, except that it overlaps with the isotopic chemistry of the spurrite rocks from the Mottled Zone of Israel. As already pointed out, the chemical composition of the studied vaterite is similar to that of the spurrite rocks of the Mottled Zone (Tables 2 and 3). As part of this study, one author (G.M.F.) examined in the field the spurrite rocks of the Mottled Zone

in Maale Adumim, Israel. Without X-ray diffraction studies their unusual mineral composition would not be known, even though, since the days of the Bible, their red colour has drawn attention to these rocks (Avnimelech, 1964). The $\delta^{13}\text{C}_{\text{PDB}}$ of the spurrite rocks ranges from -17.2 to -20.7% ; organic matter has been invoked as a participant in the reaction. The vaterite with $\delta^{13}\text{C}_{\text{PDB}}$ of -19.2% and -24.4% likewise reflects the effect of organic matter.

Drilling records of the New York and Michigan wells indicate that natural gas was released into the drilling muds from the formations. Natural gas which has a $\delta^{13}\text{C}_{\text{PDB}}$ of approximately -40% must have dissolved the original carbonate rocks through which it was passing, and the $\delta^{13}\text{C}_{\text{PDB}}$ of the resultant vaterite reflects the involvement of gas. Rapid degassing precipitated vaterite; the presence of amorphous calc-silicate suggests a rapid precipitation. The $\delta^{18}\text{C}_{\text{PDB}}$ of vaterite (-12.4% and -17.6%) reflects oxygen isotopic composition of meteoric freshwater used in drilling. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the New York vaterite is 0.70934 and that of the Michigan vaterite is 0.70949 which may reflect either: (1) radiogenic strontium contamination from clastic units in the overlying stratigraphic section, or (2) is consistent with some of the data for Ordovician seawater (Burke *et al.*, 1982).

A radiocarbon analysis by accelerator mass spectrometry of the Michigan vaterite gave a C-14 age of 953 ± 39 yr BP (C-13 corrected). $88.8\% \pm 0.6\%$ is modern carbon and 11.2% is dead carbon with zero activity (Krueger Enterprises, analysis). Hence this carbon is essentially modern and, therefore, the vaterite is modern. A sample of the New York vaterite yielded a modern age [<100 C-14 yr BP (C-13 corrected); $(139.3 \pm 1.5\%$ of the modern (1950) C-14 activity].

As already pointed out, vaterite is unstable in the presence of water at room T and P , and dissolves readily with concomitant precipitation of calcite or aragonite. Hence, at depth, the involvement of gas as a fluid and the absence of water may explain the formation and preservation of vaterite. The initial precipitation must have involved conditions of supersaturation; this, in

fact, is the basis of the methods by which vaterite has been synthesized (McConnell, 1960). Despite literature claims of spontaneous recrystallization, modern precipitates of vaterite have been sufficiently stable to have survived 20–45 yr. The chemistry of the drilling mud must have stabilized the vaterite. In the dry state, after sampling, vaterite remained stable.

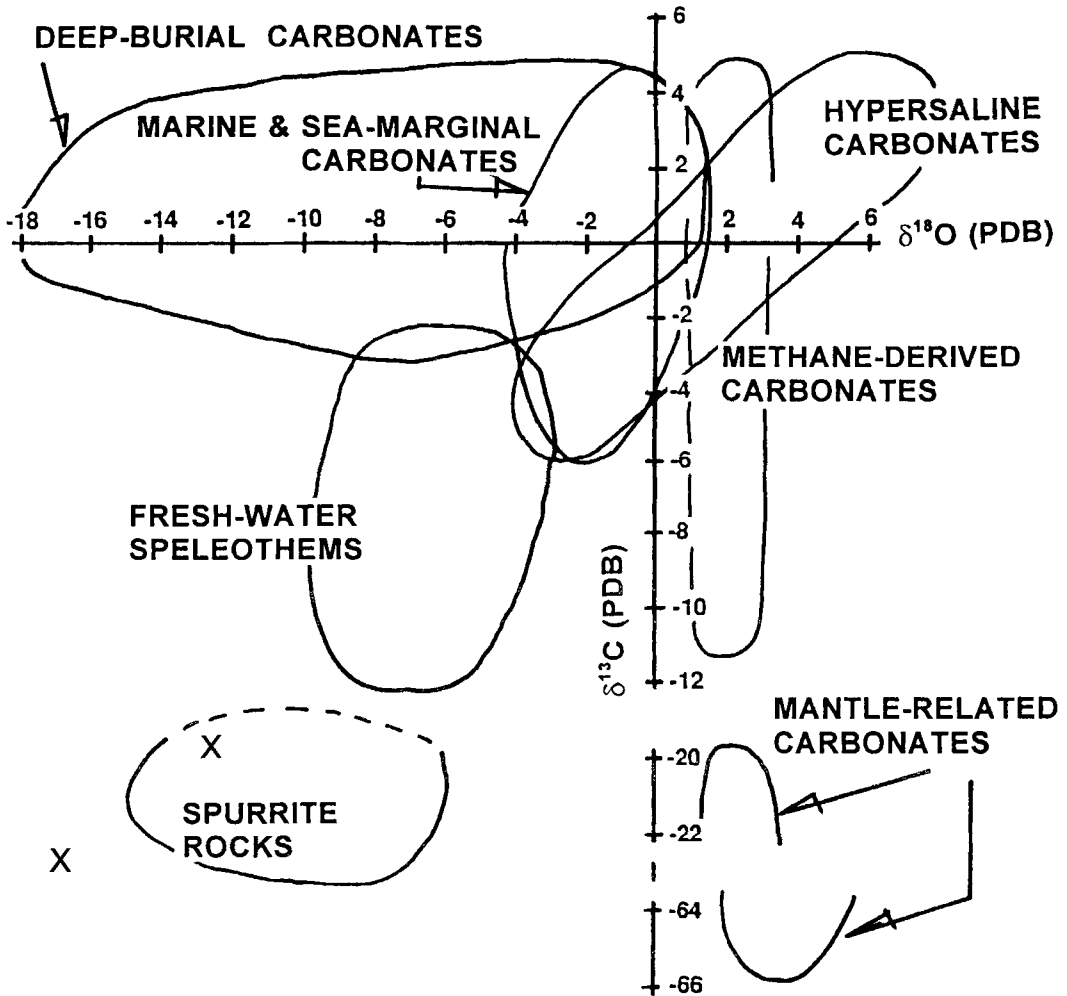


FIG. 3. Stable isotope composition of carbonates from different geologic settings, including spurrite rocks from Mottled Zone (Israel), and the studied vaterite (indicated by X). Sources: speleothems (Bar-Mathews *et al.*, 1991); mantle-related carbonates (Lawrence and Taviani, 1988); marine- and seamarginal meteoric carbonates (Friedman, 1964, 1968); hypersaline carbonates (Friedman, 1965; Friedman and Sanders, 1967); deep-burial carbonates (Friedman, 1987a,b and unpublished data); methane-derived carbonates (Allen *et al.*, 1969; Friedman, 1991a; Ritger *et al.*, 1987); spurrite rocks (Kolodny and Gross, 1974).

In a well in Hudspeth County, Texas, vaterite was discovered to have remained resistant to heating below 450°C, but then decreased in intensity on X-ray patterns, and completely disappeared at 600°C. This relative stability at such high T is at variance with the literature.

The discovery of vaterite in the New York well was in two intervals within Lower Ordovician carbonates of the Appalachian Basin. A previous report of an outcrop discovery in correlative units of the Appalachian Basin in Quebec (Fong, 1981) initially convinced Friedman (1991b) that the vaterite may likewise be Ordovician in age. However, both the radiocarbon age and the retrieval of vaterite samples containing inclusions of shale and limestone chips from the drilling operation which vaterite coats and embeds provides evidence for the modern age of the vaterite.

Conclusions

(1) Modern vaterite has formed downhole in drilling muds in wells at the expense of subsurface carbonates in New York, Michigan, Texas, Nevada and New Zealand.

(2) Observations from petrographic and scanning electron microscopes show that vaterite occurs in rims surrounding an amorphous calc-silicate of composition Ca_3SiO_5 , a compound known as alite which constitutes 50–70% of Portland cement. Vaterite replaced the calc-silicate. This reaction recalls a setting in a contact-metamorphic aureole in Ireland, where the calc-silicate mineral changed to vaterite.

(3) Drilling records indicate that natural gas was released into drilling muds from the formations. The $\delta^{13}\text{C}_{\text{PDB}}$ value suggests that natural gas released during drilling operations dissolved a part of the original carbonate in the subsurface and rapid degassing created the vaterite.

(4) Despite literature claims of spontaneous recrystallization vaterite precipitates have been sufficiently stable to have survived 20–45 yr. The chemistry of the drilling mud must have stabilized the vaterite. In the dry state, after sampling, vaterite remained stable.

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