Fracture-fill calcite as a record of microbial methanogenesis and fluid migration: a case study from the Devonian Antrim Shale, Michigan Basin

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ABSTRACT

The Devonian Antrim Shale is an organic-rich, naturally fractured black shale in the Michigan Basin that serves as both a source and reservoir for natural gas. A well-developed network of major, through-going vertical fractures controls reservoir-scale permeability in the Antrim Shale. Many fractures are open, but some are partially sealed by calcite cements that retain isotopic evidence of widespread microbial methanogenesis. Fracture filling calcite displays an unusually broad spectrum of $\delta^{13}C$ values ($+34$ to $-41‰$ PDB), suggesting that both aerobic and anaerobic bacterial processes were active in the reservoir. Calcites with high $\delta^{13}C$ values ($>+15‰$) record cementation of fractures from dissolved inorganic carbon (DIC) generated during bacterial methanogenesis. Calcites with low $\delta^{13}C$ values ($<-32‰$) are solely associated with outcrop samples and record methane oxidation during cement precipitation. Fracture-fill calcite with $\delta^{13}C$ values between -10 and $-30‰$ can be attributed to variable organic matter oxidation pathways, methane oxidation, and carbonate rock buffering. Identification of ^{13}C-rich calcite provides unambiguous evidence of biogenic methane generation and may be used to identify gas deposits in other sedimentary basins.

It is likely that repeated glacial advances and retreats exposed the Antrim Shale at the basin margin, enhanced meteoric recharge into the shallow part of the fractured reservoir, and initiated multiple episodes of bacterial methanogenesis and methanotrophic activity that were recorded in fracture-fill cements. The $\delta^{18}O$ values in both formation waters and calcite cements increase with depth in the basin (-12 to $-4‰$ SMOW, and $+21$ to $+27‰$ PDB, respectively). Most fracture-fill cements from outcrop samples have $\delta^{13}C$ values between -41 and $-15‰$ PDB. In contrast, most cement in cores have $\delta^{13}C$ values between $+15$ and $+34‰$ PDB. Radiocarbon and ^{230}Th dating of fracture-fill calcite indicates that the calcite formed between 33 and 390 ka, well within the Pleistocene Epoch.

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INTRODUCTION

The Late Devonian Antrim Shale is a self-sourced, unconventional gas reservoir in the Michigan Basin, USA. Significant amounts of variably saline water (0–4 M NaCl) are coproduced with economic quantities of natural gas from the Antrim Shale. This methane reservoir occurs within a sequence of organic-rich black shales interbedded with gray and green shales and carbonate units. The most important gas-producing region occurs in an arcuate band parallel to and within the subcropping Antrim Shale along the northern margin of the Michigan Basin (Fig. 1), commonly referred to as the Northern Producing Trend (NPT). Exploration on the western, eastern, and southern margins of the basin have shown promising results, whereas exploration in the more deeply buried Antrim Shale has proven unproductive (Walter *et al.* 1997; McIntosh *et al.* 2002). A list of well core and outcrop locations used in this study is presented in Table 1 and indicated on Fig. 1.

Gas, water, and rock samples from a variety of sites around the Michigan Basin were available for analysis during exploration of this gas play. In addition, surface samples were
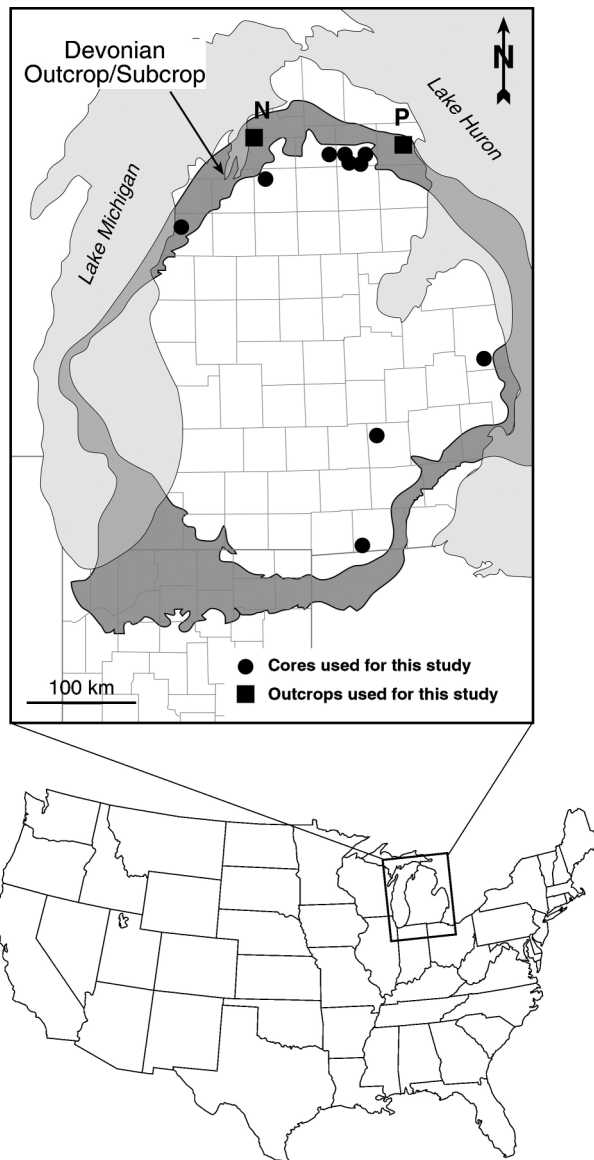
Fig. 1. Study location in Michigan, midcontinental USA. Shaded area is the subcrop/outcrop of the Devonian section in the Michigan Basin. Location of sites sampled include: well cores shown as dots; outcrops shown as solid squares. N is Norwood outcrop and P is Paxton Quarry. Figure modified from Martini *et al.* (1998).

included from a quarry and an outcrop. Although natural gas production is unpredictable using conventional basin models, it is thought to be controlled in part by the well-developed naturally fractured network within the Antrim Shale. This paper explores the geochemical record in calcite cements that occur within this important fracture network. The isotopic composition of these calcite cements is closely linked to chemical parameters of formation fluids and provides constraints on gas generation and fluid migration pathways. The importance of structural fabric in the Antrim Shale and its physical proximity to areas of freshwater recharge are supported by the chemical and isotopic results. Fracture-fill calcite and associated water and gas may provide a diagnostic tool for identifying bacterial methanogenic processes in other, less well studied basinal settings

or in ancient rocks influenced by microbial methane generation.

GEOLOGIC FRAMEWORK

The Antrim Shale subcrops below glacial sediment of variable thickness that was deposited during the waning stages of Pleistocene glaciation. Because the Michigan Basin is approximately circular, Devonian age outcrops and subcrops form an irregular ring around the basin margin (see Fig. 1). Present gas production is concentrated in the northern third of the basin, adjacent to and within the subcrop area, at relatively shallow depths (<700 m). The Antrim Shale is a highly fractured sequence dominated by two sets of orthogonal, high-angle fractures.

Table 1 Location of outcrops and cores, and members sampled. Locations are shown on Fig. 1.

	County	Sec	Twp	Rng	Member sampled
Outcrops					
Paxton Quarry	Alpena	30	31 N	7 E	Norwood through Lachine
Hycrude Core, adjacent to Paxton Quarry	Alpena	30	31 N	7 E	Upper Antrim & Norwood
Norwood Outcrop	Charlevoix	34	33 N	9 W	Norwood
Well Cores					
Shell St. S. Branch 1–19	Crawford	19	25 N	1 W	Lachine
Shell St. Kalkaska 3–11	Kalkaska	11	28 N	7 W	Lachine & Paxton
Yohe Thomas 1–28	Lenawee	28	8 S	2 E	Upper Antrim through Norwood
Oil Joseph 3–23	Manistee	23	23 N	16 W	Ellsworth through Traverse
Shell St. Loud C2-31	Montmorency	31	29 N	3 E	Norwood, Lachine, Traverse
Shell St. Loud D3-20	Montmorency	20	29 N	3 E	Upper Antrim
Shell Caruso C2–28C	Montmorency	28	29 N	3 E	Lachine
Trendwell Stevens Minerals 2–15	Montmorency	15	30 N	3 E	Norwood
Trendwell Thompson 1–8	Montmorency	8	30 N	1 E	Lachine
Caruso CH-1 & CH-2	Montmorency	28	29 N	3 E	Ellsworth through Norwood
Ward Lake Latuzcek B1-32	Otsego	32	30 N	1 W	Squaw Bay Through Lachine
Welch St. Chester #18	Otsego	13	29 N	2 W	Lachine
Dow Erda #103	Sanilac	8	9 N	15 E	Upper Antrim

Stratigraphy

In ascending order, the Upper Devonian sequence consists of the Squaw Bay Limestone (sometimes referred to as the Traverse Formation), the lower members of the Antrim Shale, the upper member of the Antrim Shale, the Ellsworth Shale, and in some locations, the Bedford Shale and Berea Sandstone (Fig. 2). The Upper Devonian section is separated from the underlying Middle Devonian Traverse Group and from the overlying Mississippian Sunbury Shale by regional unconformities (Fisher *et al.* 1988; Matthews 1993). The Antrim Shale is stratigraphically correlative with the Chattanooga and Ohio Shales of the Appalachian Basin, the New Albany Shale in the Illinois Basin, the Kettle Point Shale of western Ontario, and other upper Devonian black shales in North America and around the world. These rocks are known hydrocarbon sources or reservoirs.

In this study, we follow the nomenclature of Gutschick & Sandberg (1991) and divide the Antrim Shale into four members: the Norwood; Paxton; Lachine; and Upper Antrim (Fig. 2). The Norwood Member is exposed in the Paxton Quarry on the northeast side of the Lower Peninsula of Michigan and on the northwestern edge of Michigan near the town of Norwood (Fig. 1; Table 1). Samples were collected from both sites for this study. The Norwood Member is a laminated, pyritic black shale with calcareous and dolomitic concretions that are commonly armored with an outer layer of pyrite and other iron sulphide minerals. The Norwood attains a maximum thickness of 12 m in the basin and varies between 8 and 9 m in the NPT of the Michigan Basin. The Norwood Member has an unusually high silica content for a black shale (Table 2; Hathon *et al.* 1980; Ruotsala 1980; Matthews 1993) and has total organic carbon contents (TOC) ranging from 10 to 24 weight percent (Table 2;

Matthews 1993). The margins of the Michigan Basin have never been deeply buried and the abundant organic matter present within black shales of the Lachine and Norwood Members is still immature based on low vitrinite reflectance values (R_o approximately 0.4; Rullkötter *et al.* 1992).

The Paxton Member is an interval of light gray, argillaceous limestone interbedded with dark and light gray calcareous shale. The Paxton Member attains a maximum thickness of 22 m in the basin and varies between 6 and 16 m in the NPT. The Paxton Member has much lower TOC contents than the Norwood, but comparable silica content (Table 2). Carbonate units within the member are dolomitic limestones. Samples of the Paxton Member were collected in the Paxton Quarry in northeast Michigan (Figs 1 and 2; Table 1).

The Lachine Member is also exposed in the Paxton Quarry and the Frasnian–Famennian boundary occurs in the lowermost part of this member. The Lachine consists of laminated, pyritic black shale alternating with greenish gray to dark gray shales and contains horizons with abundant concretions like those in the Norwood Member (Fig. 3). The Lachine has a maximum thickness of 30 m in the NPT, and thins westward to 12 m along the shore of Grand Traverse Bay. Like the Norwood Member, the Lachine Member has high silica and organic matter with low thermal maturity (Table 2; $R_o = 0.4$–0.6; Matthews 1993; Rullkötter *et al.* 1992).

In the eastern half of the Michigan Basin, the Lachine Member is overlain by the Upper Antrim Member followed by the Ellsworth Shale. In the western half of the basin, the Ellsworth Shale overlies the Lachine Member. The Upper Antrim Member is late Famennian in age, consists of 7 m of black shale with rare concretions, and is capped by glacial drift at the Paxton Quarry (Fig. 3). The Upper Antrim Member has moderately high TOC, and is sometimes included in
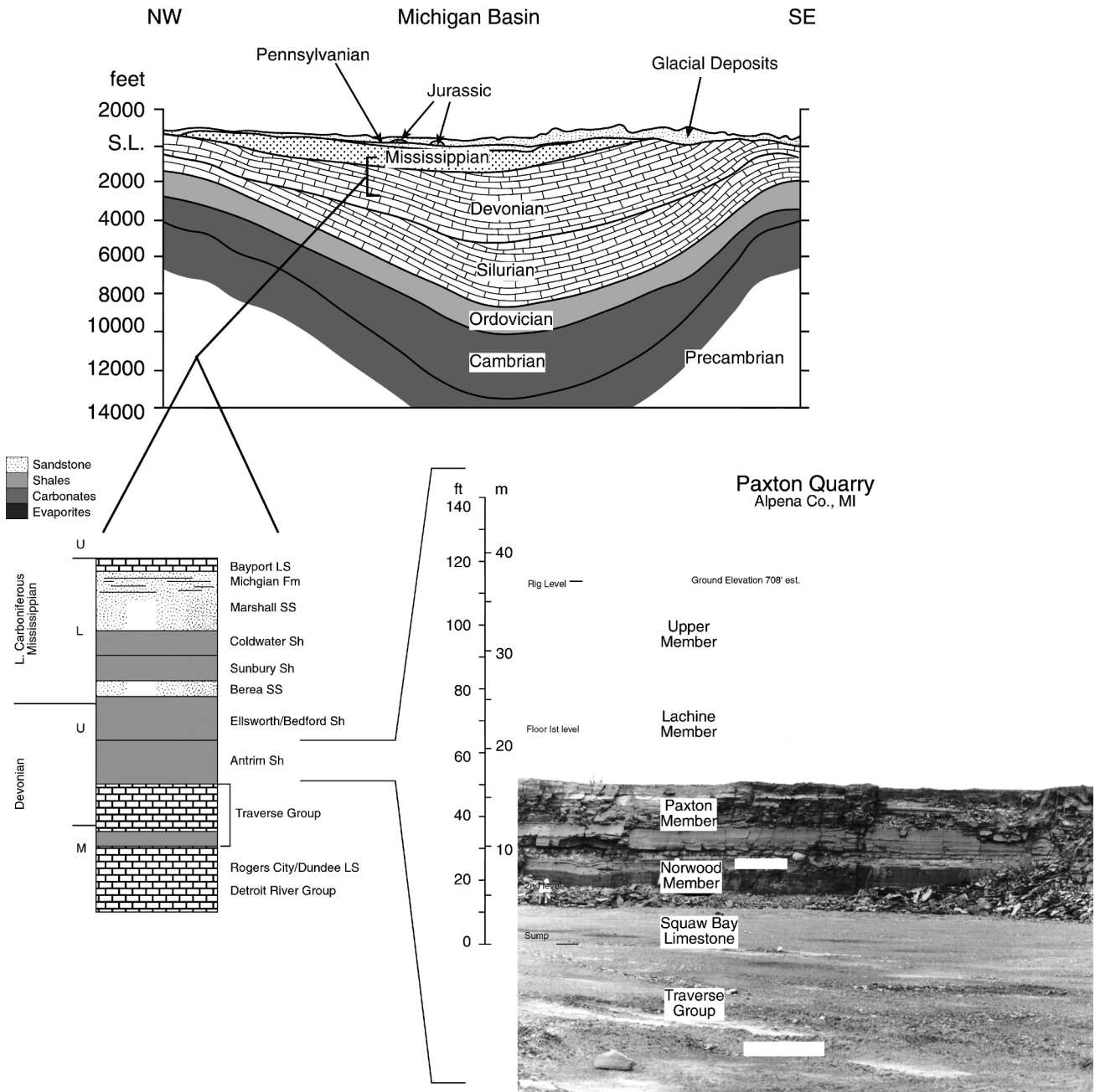
Fig. 2. The stratigraphic sequence of the Michigan Basin with expanded detail on Devono-Mississippian section and with details of the Upper Devonian Antrim Shale Section at the Paxton Quarry along with typical core log response (modified from Matthews 1993).

exploration for gas, although generally only the Lachine and Norwood Members are completed for gas production.

Fracture geometry

Fractures in the Antrim Shale have been described by many workers (Apotria *et al.* 1994; Caramanica 1994; Decker *et al.* 1992; Dellapenna 1991; Dellapenna & Harrison 1993;Holst & Foote 1981; Versical 1991; Walter *et al.* 1996). The descriptions of the dominant fracture sets are based on surface exposures of fractured Antrim Shale, as well as orientated cores and borehole-imaging logs. Most authors agree that there are two dominant sets of subvertical to vertical fractures, one orientated northwest and the other northeast, and a third set of inclined fractures that trend northeast and may be of importance to reservoir permeability. Locally important east-west fractures have also been noted (Holst & Foote 1981; Apotria *et al.* 1994).

There is less agreement on the mechanism of formation of fractures. Holst & Foote (1981) suggested that the northwest

Table 2 Quartz and organic carbon content in lower members of the Antrim Shale, Paxton Quarry and Norwood Outcrop. Quartz (wt%) determined by XRF* and TOC by coulometry.

Sample ID	Depth (m)	Lithology	Quartz (wt%)	Organic C (wt%)
Paxton Quarry				
Lachine Member				
LACH1	float	dark gray sh.	41.1	7.2
LACH 2	float	light gray sh.	24.4	0.3
LACH 3	float	black sh.	25.0	12.5
LACH 4	float	brown/gray sh.	39.2	8.7
LACH 5	float	green/gray sh.	20.6	0.4
LACH 6	float	black sh.	26.6	14.8
Paxton Member				
PAX 1	0–0.4, Top	gray sh.	29.9	1.1
PAX 2	0.4–0.56	carbonate	7.2	0.3
PAX 3	0.56–1.1	gray sh.	12.9	0.4
PAX 4	1.1–1.7	gray sh. & ls	21.9	1.2
PAX 5	1.7–1.8	dolomitic ls	5.6	0.9
PAX 6	1.8–2.2	gray sh.	22.1	3.8
PAX 7	2.2–2.4	limestone	8.8	0.4
PAX 8	2.4–2.8	gray shale	23.4	1.2
PAX 9	2.8–3.4	dark & lt. gray sh.	25.2	3.5
PAX 10	3.4–3.7	limestone	7.0	0.4
PAX 11	3.7–4.0	gray shale	27.7	5.4
PAX 12	4.0–4.1	limestone	7.4	0.5
PAX 13	4.1–4.4	dark gray sh.	25.1	7.6
PAX 14	4.4–4.7, Base	gray sh.	22.0	5.3
Norwood Member				
NOR 0	0–0.4, Top	dark gray sh.	22.5	14.8
NOR 1	0.4–1.0	black, fissile sh.	22.2	18.5
NOR 2	1.0–1.5	br/bL, massive/fissile	21.9	18.3
NOR 3	1.5–1.9	bl/br massive sh.	19.9	24.0
NOR 4	1.9–2.3	bl/br sh.	22.2	20.5
NOR 5	2.3–2.8	bl/br sh.	36.2	19.3
NOR 6	2.8–3.3, Base	br, massive sh.	41.3	14.3
Norwood Outcrop				
NOR 8	2 m above base	gray, massive	27.6	11.4
NOR 7	Base	gray, massive	32.0	11.4

*Analyses courtesy of Alden B. Carpenter, Chevron (modified from Walter *et al.* 1996).

fracture set may be tectonic fractures genetically related to northwest trending folds in the Michigan Basin, but emphasized the regional nature of fracture trends in the Devonian across the northern basin. Versical (1991) added that the northwest fractures are parallel to the principal shortening directions on deformed calcite twins in the mid-continent that are interpreted to be related to Carboniferous palaeostresses (Craddock *et al.* 1993; Craddock & van der Pluijm 1989).

In contrast, Apotria *et al.* (1994) proposed that the fractures are regional and not tectonic because they are widely distributed and independent of local structure. Based on stress history analysis and field observations, Apotria *et al.* (1994) concluded that the correlation between organic rich intervals and good fracture development commonly observed in the Antrim Shale is not fortuitous. They argued that the northwest fracture set formed as a result of natural hydraulic fracturing associated with maturation of organic matter during the maximum burial of the Antrim Shale (*c.* 250 Ma). These fractures would be orientated relative to the regional

stress field imposed by the Alleghenian Orogeny. The present-day direction of maximum compressive stress in Northeastern North America is to the ENE (Plumb & Cox 1987; Zoback & Zoback 1989; Gross & Engelder 1991). Based on this information, the northeast fracture set in the Antrim Shale is presently more likely to be open than the northwest set.

HYDROGEOCHEMISTRY OF THE ANTRIM SHALE

Water chemistry

The geochemistry of water and gas samples from Antrim Shale reservoirs is presented in detail elsewhere and provides important constraints on the work described in this study (Martini *et al.* 1996, 1998; Walter *et al.* 1996, 1997; McIntosh *et al.* 2002). In brief, spatial distributions of chemical and isotopic compositions within formation waters exhibit strong regional trends. Wells located near or within
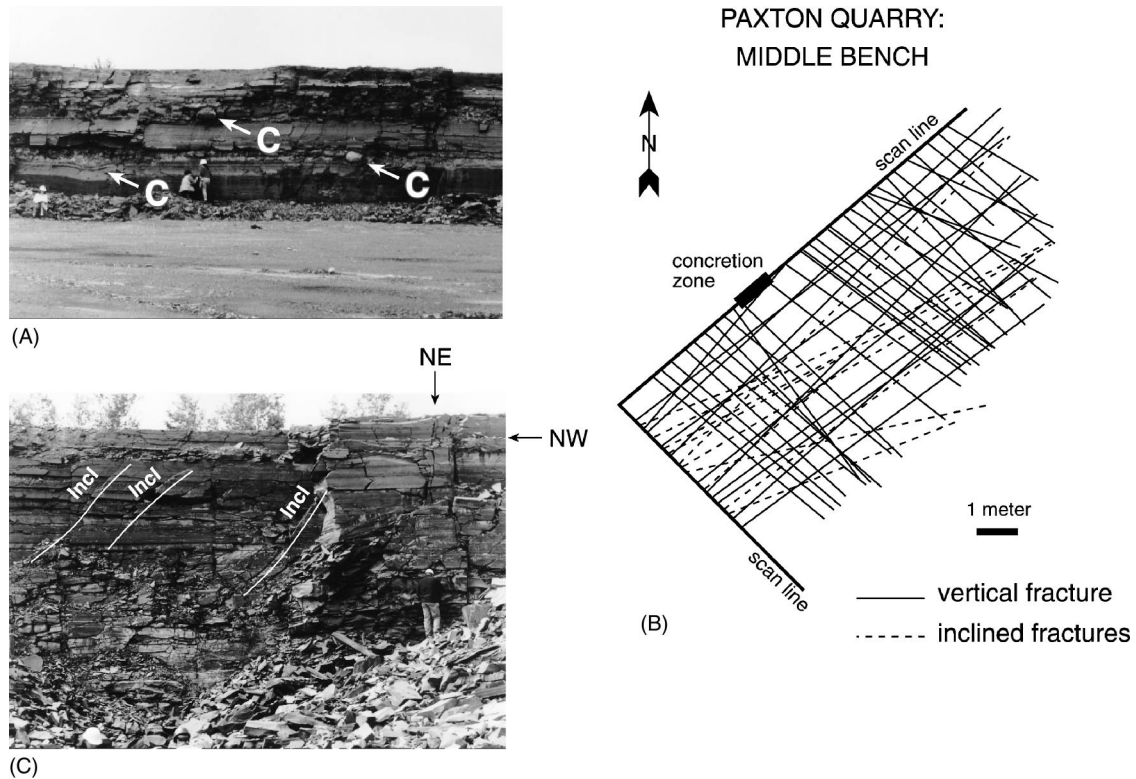
Fig. 3. (A) Paxton Quarry, upper bench, Lachine Member. Large spherical concretions in quarry wall indicated by C with arrow. The exposed face trends northwest and is cut by vertical northeast fractures and steeply dipping northeast fractures. (B) A diagram based on several scan lines of fracture measurements from the Lachine Member in the middle bench of the Paxton Quarry. Inclined fractures shown by dashed lines. Note that the large concretion in the northeast trending quarry wall exerts a shadow effect on the frequency of large, through-going fractures. Figure modified from Walter *et al.* (1996). (C) Three fracture sets are visible in this photograph from the upper bench of the Paxton Quarry. The exposed face parallel to the plane of view is a northwest trending fracture. Northeast fractures are vertical joints cutting the northwest face, and inclined fractures with northeast trends (indicated by white lines) are also visible.

the subcrop area produce water with low salinities (<0.1 M Cl^-), high concentrations of dissolved inorganic carbon (DIC; 40–60 mM), high carbon isotope values ($\delta^{13}C_{DIC}$ approximately +26 to +30‰ PDB), and low H_2O isotope values ($\delta^{18}O$ approximately $-15‰$, δD approximately $-90‰$ SMOW). Wells located in the deeper, basinward part of the reservoir produce water with high salinities (up to 5 M Cl^-), lower DIC concentrations (6–10 mM), lower carbon isotope values ($\delta^{13}C_{DIC} = +22$ to +25‰ PDB) and higher H_2O isotope values ($\delta^{18}O = -6‰$, $\delta D = -35‰$ SMOW). Complex trends in chemical and isotopic compositions of brines from the Antrim Shale appear to highlight pathways for fluid flow and mixing between the shallow and deeper part of the reservoir. These patterns suggest two sources of water: (i) a high-salinity, ^{18}O and D-enriched basinal brine component; and (ii) a dilute water with $\delta^{18}O$ and δD values that suggest recharge from a cooler climate than present surface conditions.

Distribution of dilute formation waters within the Antrim Shale implies that recharge is controlled by fracture trends in the reservoir and is focused along glacial gouge zones in the subcrop of the Antrim Shale (Walter *et al.* 1996). Radiocarbon analyses of DIC from shallow Antrim Shale formation waters yield corrected recharge times of 6000–27 000 years before present (Martini *et al.* 1996, 1998). Taken together with the δD and $\delta^{18}O$ values of formation water, these data indicate recharge of water during the Quaternary when surface temperatures were cooler than today.

Gas chemistry

The chemical and isotopic composition of gas from the Antrim Shale, like the associated water chemistry, implies a complex, mixed source history. Although carbon isotopic compositions of methane (-48 to $-58‰$) fall between thermogenic and microbial methane, the extremely high $\delta^{13}C$ values of coproduced $CO_{2(g)}$ (+22‰) and DIC in formation waters require bacterial mediation (Coleman *et al.* 1995; Martini *et al.* 1996, 1998). However, it is the positive correlation between the δD in coproduced CH_4 and formation waters reported in Martini *et al.* (1996, 1998, in review) that is the strongest evidence for methane generation via CO_2 reduction occurring within the reservoir. This relationship between the δD_{H2O} and δD_{CH4} values suggests that the timing of microbial gas generation and the emplacement of the present formation water are linked. The problem under

consideration now is the possible genetic link between calcite, which has filled fractures in this young gas reservoir, and formation fluids described previously.

METHODS

Field measurement and sample collection

Fracture attitude and spacing were measured in the Norwood and Lachine Members of the Antrim Shale at three levels within the Paxton Quarry in Alpena County and at a Lake Michigan shoreline outcrop of the Norwood Member where it is exposed about 1 km south of the town of Norwood (Fig. 1). Spacing between large, through-going fractures was tabulated along orientated transects. A summary of fracture frequency, together with dominant fracture attitudes, is presented in Table 3.

Collection of calcite from the fractures was accomplished in several ways. Most samples were thin coatings on black shale fracture walls that required a small blade to separate the cement from the wall rock. At the Norwood outcrop, most fractures were filled with a thick vein of calcite and samples were retrieved using a rock chisel and hammer to remove both vein and some wall rock samples. In core samples some specimens were highly friable, similar to cements in outcrop, and calcite was removed from these fracture faces with a knife. In many intervals, fracture cements were intact and small chips were cut for isotopic sampling and thin section preparation.

Samples from cores and outcrop were prepared for petrographic examination and isotopic subsampling by polishing cut surfaces, and, where necessary, staining with Alizarin Red S and potassium ferricyanide to distinguish calcite from dolomite and to identify ferroan cements in concretions

Table 3 Spacing of large, through-going fractures, summarized from field measurements at Paxton Quarry and the Norwood outcrop. Details tabulated in Walter et al. (1996).

Transect orientation	75–90° Dip NE fracture †frequency	75–90° Dip NW fracture †frequency	Member sampled	Comments
†**Paxton Quarry**				
Upper quarry				
10°	2.74	1.5	Lachine	2 segments of
10°	1.2	1.8	Lachine	same transect
142°	1.94		Lachine	NE inclined spacing = 1.78
231°		1.9	Lachine	
208°		1.01	Lachine	
306°	1.14		Lachine	
310°	1.98		Lachine	
311°	1.95		Lachine	
316°	2.62		Lachine	
355°	1.1	1.1	Lachine	3 interrupted
355°	0.78	0.78	Lachine	segments of
355°	1.69	1.27	Lachine	same transect
Middle bench				
140°	1.63		Lachine	
235°		1.8	Lachine	
236°		1.5	Lachine	
236°		2.25	Lachine	
Lower quarry				
65°	1.17	0.97	Norwood	
83°	0.98	1.97	Norwood	
293°	1.04		Norwood	
316°	0.58		Norwood	
340°	0.39		Norwood	
‡**Norwood Outcrop**				
336°	1.22		Norwood	
344°	1.63		Norwood	
336°	1.63		Norwood	
338°	1.63		Norwood	
338°	2.44		Norwood	
338°	1.13		Norwood	
334°	4.88		Norwood	
332°	1.53		Norwood	

*Data from quarry measured by J. A. Richards, A. M. Martini, W. Higgs and C. S. Stearns. †Scan length (in m)/number of fractures. ‡Data from outcrop measured by J. M. Budai and A. M. Martini.

(Evamy 1963). Thin sections and chips were examined in cathodoluminescence using a Nuclide Luminoscope, operating at 10–12 kV with a sample current of 100 milliamps.

A microscope mounted dental drill was used to sample carbonate components from chips and slabs of rock (Dettman & Lohmann 1995). Drilled sample sites are 0.5 mm in diameter. In some cases, fracture cements were fine, friable, pieces of calcite removed from fracture walls in the field. These were ground with a mortar and pestle and then analyzed.

Stable isotope analyses

Stable isotopes of oxygen and carbon in carbonate samples were measured in the Stable Isotope Laboratory at the University of Michigan. All samples are placed in small stainless steel boats and roasted under vacuum at 380 °C for 1 h to remove volatile components. Carbon and oxygen isotopes were determined in calcite and dolomite samples using an automated sample preparation on-line Kiel device attached to a Finnigan Mat 251 ratio mass spectrometer. Calcite and dolomite samples were reacted with anhydrous phosphoric acid at 74 °C, for 6 min and 10 min, respectively, and results compared to the internal lab standard gas, which is calibrated to the NBS 20 Salenhofen limestone standard. Measured precision is maintained at better than 0.1‰ for both $\delta^{13}C$ and $\delta^{18}O$.

The core and outcrop samples for the determination of $\delta^{13}C$ of organic matter in black shales were prepared as follows: 20–40 mg of previously acidified ground sample was mixed with cupric oxide in pyrex tubes, roasted at 480 °C for 1 h, and the evolved CO_2 gas cryogenically separated. Samples were analysed on a Finnigan MAT Delta S mass spectrometer in the Stable Isotope Laboratory at the University of Michigan. NBS 22 ($\delta^{13}C = -29.7‰$ PDB) was used as a standard.

Related geochemical analyses

The silica content of black shales was measured using an X-ray fluorescence spectrometer (XRF) at the Chevron Petroleum and Technology Company in La Habra, California. Total organic carbon was determined by combusting preacidified samples and measuring the evolved CO_2 coulometrically, in the Experimental and Analytical Geochemistry Laboratory at the University of Michigan and also at Chevron.

Radiocarbon measurements of calcite were made by accelerator mass spectrometry (AMS) at the University of Arizona. Because radiocarbon analyses required larger calcite samples than the $\delta^{13}C$ and $\delta^{18}O$ analyses, the ^{14}C was measured on larger samples from the same fracture-fill calcite. A $\delta^{13}C$ value was determined on all sample splits analyzed for ^{14}C. Uranium and thorium isotopic compositions were measured on a subset of calcite samples at the University of Minnesota Isotope Laboratory following the methods of Edwards *et al.* (1987).

RESULTS

Fracture occurrence and description

The best fracture development in the Antrim Shale at Paxton Quarry occurs in the organic-rich black shales of the Norwood and Lachine Members. The largest fractures extend through the Norwood and Lachine Members, but terminate at the contacts with the light gray shales of the intervening Paxton Member. Two sets of vertical to subvertical joints (dips >85 °), one striking northwesterly and one northeasterly, are the dominant fracture sets in the Paxton Quarry and the Norwood outcrop (Fig. 3). Where large concretions are present, fractures are more widely spaced and trends diverge away from the concretion (Fig. 3a).

A third set of large fractures strikes northeasterly with southeasterly dips, usually in the range of 55–70°. In several locations, both in the quarry and at the outcrop, mechanical interactions between individual fractures can be observed. These fractures become steeper and terminate as they approach a vertical fracture (Fig. 3c). This kind of joint interference is common in naturally forming joints (Engelder 1993; Pollard & Aydin 1988;). There are abundant smaller scale fractures as well. However, based on the link between natural gas production, fluid flow and the major throughgoing fracture network within the Antrim Shale, sample collection focused on fracture-fill calcite from the largest fractures where possible. Timing of the high angle northeast and northwest sets is probably synchronous based on mutually crosscutting relationships observed at both the quarry and outcrop exposures.

The second set of inclined, northeast-trending fractures are inferred to be younger than the vertical joints due to the change in geometry of fracture faces near vertical joints. Measurements of these three fracture sets along scan-lines in the quarry are shown in a diagram of two quarry walls (Fig. 3b). A summary of field measurements from both the outcrop and quarry is presented in Table 3.

At the outcrop south of Norwood, Michigan, along the Lake Michigan shoreline, only the Norwood Member of the Antrim Shale is preserved (Kesling *et al.* 1976). Fracture attitude and length are similar to those measured in the Paxton Quarry (Table 3). Fractures are well exposed in 3-dimensions due to wave cut benches immediately beneath a northwest trending vertical cliff of the Norwood Shale. Due to the orientation of the exposed wall, the northeast trending set of fractures is well represented, but the northwest set is only exposed on the basal surface of the submerged bench.

The largest fractures in cores are high angle and generally have straight margins. Smaller scale, low angle and bedding parallel fractures are also present. Studies based on fracture imaging logs indicate that the buried Antrim section hosts a network of high angle fractures similar to those exposed at the surface (Caramanica 1994; Walter *et al.* 1996). Completion

practices used in the Antrim Shale include artificial fracturing to open existing natural fractures (Zuber 1995), making the dominant orientations of fractures an important component of exploration strategies.

Fracture-fill calcite

Cements within fractures range from coarse-grained calcite mosaics that completely seal fractures, to microcrystalline calcite coatings that partially seal fractures. At the Paxton Quarry, cements are thin, microcrystalline to fine-grained calcite coating on fracture walls (Fig. 4A). There was no petrographic evidence of multiple cementation events within this sparsely cemented group of fractures. A small diameter core taken adjacent to the Paxton Quarry recovered most of the section and also the upper part of the underlying Traverse Group. Unfortunately, the fractures intersected were largely low angle, smaller scale fractures rather than the large, through-going fractures from which calcite cement was sampled in the quarry. Very minor calcite cement partly coats some of the core fractures. The surface texture of the cements is fine, granular and indistinguishable from cements observed and sampled in the quarry. This similarity in cementation between the core and the exposed quarry walls suggest that: (i) evidence of modern surface weathering is not greater in samples from exposed quarry walls than in subsurface samples; and (ii) calcite cements in a broad range of fracture scales and attitudes may be genetically related.

In contrast to exposures in the quarry, northeast and northwest fractures at the Norwood outcrop host thick calcite cement fillings (up to 7 mm in thickness) that are easily seen under and at lake level, but are poorly preserved in the outcrop a meter above lake level (Fig. 4b). In the outcrop above lake level, cements are thinner and some are encrusted with a coating of secondary weathering products. In fractures that can be traced out into the sublake bench, well preserved, coarse calcite cements may include fine iron-sulphide crystals along the fracture margins and commonly contain thin slivers of wall rock, suggesting that fracturing and cementation were intermittent. Figure 4C illustrates diagrammatically the various fracture fill orientations and stable isotope values. The calcite cements within fractures from the two outcrop sites have patchy variations in luminescence that range from dull to bright orange, but are not systematically zoned when examined in cathodoluminescence. The most ferran cements are nonluminescent. Luminescent variations do not appear to be related to either fracture orientation or location of sample.

Cementation is not common in core fractures. Thin layers of calcite occur irregularly on one or both walls of vertical fractures. Small inclined fractures and bedding-parallel fractures are more completely cemented than vertical fractures. Fracture-fill cements from a number of well cores were examined and appeared petrographically similar to cements
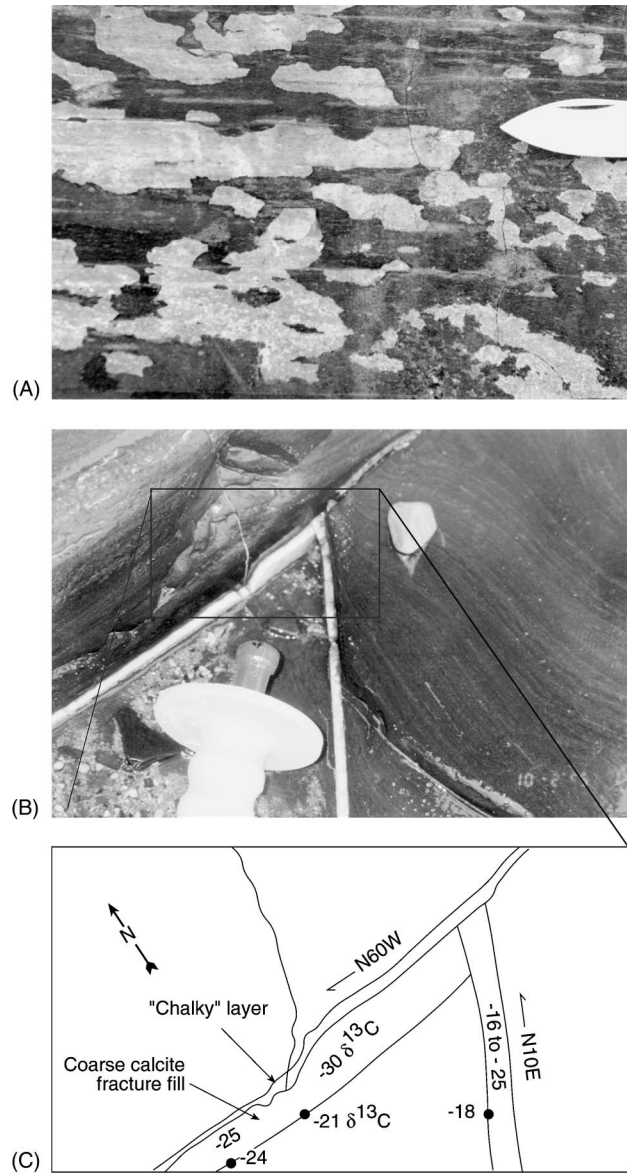
(A)

(B)

(C)

Fig. 4. (A) Thin, irregular patches of calcite cement on a fracture face at the Norwood outcrop. Tip of a small pocket knife blade for scale. (B) Northeast and northwest fractures filled with thick calcite veins at the Norwood outcrop. This site is in the shallow wave zone, just below cliffs of the Norwood Member of the Antrim Shale. The handle of a rock chisel, about 10 cm long, is shown for scale. (C) Diagrammatic view of crosscutting calcite fractures having different stable isotope compositions. Carbon isotope values in ‰ PDB.

studied from outcrop samples. Calcite appeared homogenous under microscopic examination. Fractures with the thickest calcite fill were coarser-grained than the fine to microcrystalline cement in thin fracture fill. Commonly, a small amount of pyrite had intergrown with calcite in core fractures, either as part of the vein or as discrete nodules. Fine pieces of wall rock are entrained within fracture cement (Fig. 5A,B). In thin section, calcite has patchy dull to bright orange luminescence,
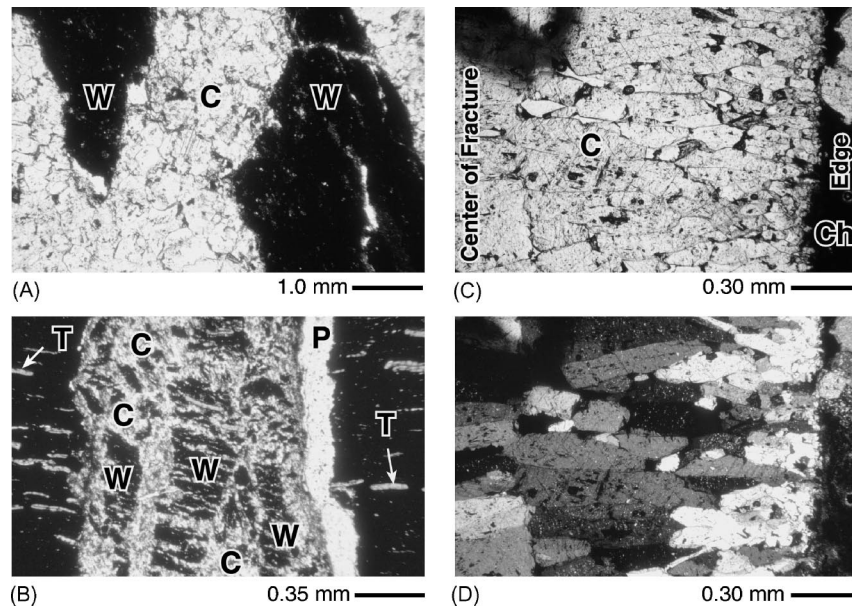
Fig. 5. Photomicrographs of fractures with calcite fillings. (A) Coarse calcite cement within a fracture trending N76°E from the Norwood outcrop, Norwood Member of the Antrim Shale. Complete fracture fill is 6 mm in width. Dark areas are slivers of black shale wall rock entrained in the vein. Long dimension of field of view is 3 mm. (B) Fine-grained calcite (c) and fragments of wall rock (w) within a fracture in a core sample (approximately 480 m depth (1437 ft)). Bright platelets are tasmanites (t) orientated parallel to shale bedding. Clear strip (p) parallel to fracture is pore space caused by thin section preparation. This fracture is high angle, N45E, and 1 mm wide. Field of view is 3 mm wide. (C) Plane light photomicrograph of fracture margin and coarse, bladed calcite (c) fill from an outcrop sample. Fracture trend is N63°E and calcite fill is 5 mm wide. Between the coarse calcite and wall rock margin, a thin layer of chalky calcite (ch) looks dark in the photo. Field of view is 2.5 mm wide. (D) Same view as in 5C, under cross-polarized light. Partial extinction illustrates calcite crystal orientation, which is normal to fracture wall.

with rare later stage nonluminescent calcite crosscutting veins. As with outcrop samples, cathodoluminescent variations are not clearly related to stratigraphic position, geographical location, or isotopic composition (as discussed below).

A coarse zoning of crystal fabric and color is present in the thickest veins. On one or both margins of vein fill there is commonly a thin layer of chalky, microcrystalline calcite (Fig. 5C,D). In thin section and polished chips an irregular, corroded contact is visible between the chalky layer and the coarse calcite that fills most of the fracture. This suggests that the chalky coating formed subsequent to the main, coarse-grained calcite fill in the fracture and has etched and replaced the fracture wall margins of coarser crystals. The coarse calcite that comprises most of the fracture fill ranges from prismatic and scalenohedral to equant in crystal fabric. Where cements are prismatic to scalenohedral, the long axes of the calcite crystals are normal to the fracture wall (Fig. 5D).

The highly weathered appearance of thin cement layers on the Norwood outcrop walls, especially when compared to calcite cement in the same fracture at lake level, strongly suggests that these fracture fills have not preserved an accurate record of original cement chemistry. The chalky coating that occurs only on fracture fills presently under lake water may record periodic exposure and surficial weathering of the shale outcrop during times of lowered lake levels, a common event throughout the Pleistocene and Holocene. The coarse-grained calcite fills in fractures at lake level, when chalky margins are excluded, are the best record of geochemical conditions during original fracture cementation.

Isotopic record in the Antrim Shale

Due to the very low matrix porosity of the Antrim Shale, it can be inferred that formation fluids and gases moved preferentially through the fracture network that crosscut the shale. Calcite cementation provides a record of that fluid's composition. Petrographic study and stable isotopic analyses of 13 well cores and two outcrop locations (Table 1) reveal a history of fracture-fill calcite that varies widely in $\delta^{13}C$ values, suggesting a link to microbial processes during cementation.

The average composition of limestone units within the Paxton Member and in the underlying Squaw Bay Limestone were used to estimate the potential contribution of wall rock carbonate to fracture-fill calcite. The $\delta^{13}C$ of organic carbon, measured in several black shale samples from the reservoir, is -29 to -30‰ PDB (Appendix), typical of Late Devonian organic matter globally (Galimov *et al.* 1975; Galimov 1980). Carbonate cements within large concretions and calcite cements lining through-going fractures and smaller scale fractures in both surface exposures and cores were sampled for this study. Coarsely crystalline calcite and dolomite cements are common within large concretions and both are
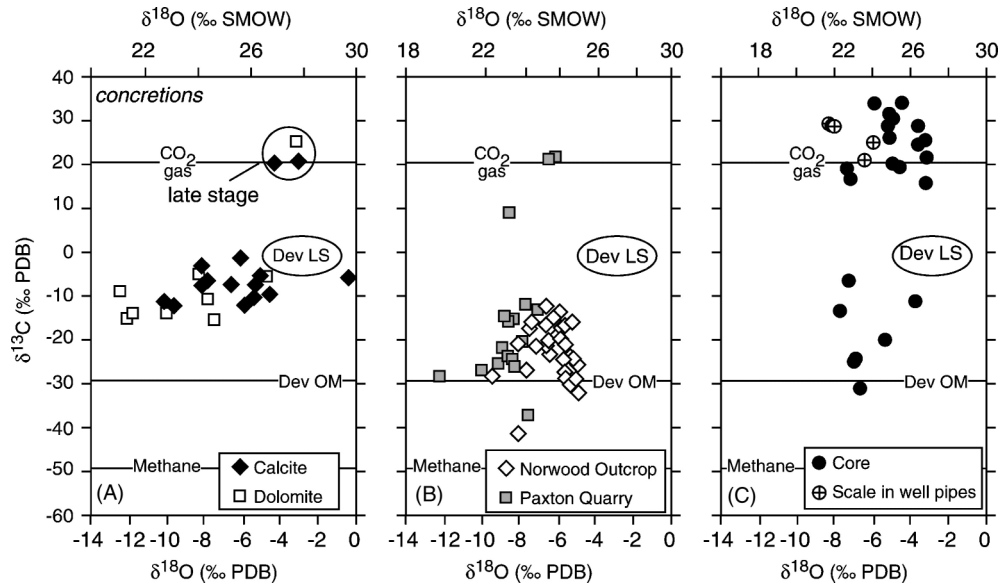
Fig. 6. Stable isotopes ($\delta^{18}O‰$ PDB and SMOW, $\delta^{13}C‰$ PDB) in (A) concretions, (B) outcrop and quarry samples, and (C) well core and scale samples. Horizontal lines indicate the $\delta^{13}C$ of methane and CO_2 produced from the Antrim Shale and the $\delta^{13}C$ of organic matter (Dev OM) from black shales of the Lachine and Norwood Members. The field indicated as Dev Ls was determined by analyses of Devonian limestones, within the Antrim Shale and from the underlying middle Devonian Traverse Group. (A) Cements within large concretions from the Lachine Member of the Antrim Shale. The first cements are generally calcite, followed by several generations of coarse dolomite cements. Rare, final stage carbonate cements ('late stage') have high $\delta^{13}C$ values, similar to those in fractures. (B) Calcite in fractures from outcrop and quarry locations. (C) Calcite in core fractures and calcite scale samples taken from well pipes of producing gas wells in the Antrim Shale.

ferroan, based on staining with potassium ferricyanide (Evamy 1963). Isotopic study of cements from several concretions indicates that the first generations of calcite and dolomite cements have moderately low isotopic values (calcite −1 to −12 $\delta^{13}C$ ‰, −5 to −10 $\delta^{18}O$ ‰ PDB; dolomite −12 to −15 $\delta^{13}C$ ‰, −7.5 to −12.5 $\delta^{18}O$ ‰ PDB; Fig. 6A; Appendix). Rare, late-stage calcite and dolomite cements in concretions have high carbon and oxygen values ($\delta^{13}C = +22‰$, $\delta^{18}O = -4‰$ PDB; Fig. 6A).

These values are similar to one population of fracture cements described below, which may indicate that some concretion fractures were open to fluid flow during later diagenetic stages in the Antrim Shale or that similar biogeochemical reactions have occurred within individual concretions. A previous petrologic study of concretions in the Antrim Shale concluded that they formed very early in the diagenetic history of the unit (Wardlaw 1981). However, in a study of similar concretions from the Middle Devonian Marcellus Shale in central New York, Siegel *et al.* (1987) inferred that the complicated cementation sequence recorded early to late stage mineralization in that unit, including isotopic evidence of methane fermentation during carbonate precipitation.

Carbon isotopes in fracture-fill cements

There is an unusually broad range of carbon isotopic compositions in fracture-fill cements from the NPT of the Antrim

Shale (Appendix). There is nearly a continuum of $\delta^{13}C$ values, from extremely low (−42‰) to markedly high (+34‰). Figure 6 shows the range in carbon and oxygen isotopic values for carbonate concretions and from fracture-fill calcite cements. The isotopic compositions obtained from concretion samples (Fig. 6A) tend to be the least extreme. Many concretions have isotopic values close to that of Devonian-age limestone. This is consistent with an origin relatively early in diagenesis.

Fracture-fill calcites with the highest and lowest values are the two groups that require special consideration (see Figs 6B,C). The first population has high carbon isotope values ($\delta^{13}C = +15$ to $+31‰$), whereas the second group has unusually low carbon values ($\delta^{13}C = -10$ to $-42‰$ PDB). The oxygen isotope values are similar in both groups ($\delta^{18}O = -3.0$ to $-9.0‰$ PDB). Calcite in the first population has carbon isotope values comparable to those in modern calcite scale forming within well pipes carrying brines and gas from the Antrim Shale to the surface ($\delta^{13}C = +21$ to $+29‰$; Fig. 6C). The $\delta^{13}C$ values of DIC in brines from the NPT reported in Martini *et al.* (1998) were between +19 and +32‰. Because there is a approximately 2‰ fractionation during precipitation (at 10 °C, Deines *et al.* 1974), the modern calcite scale is in isotopic equilibrium with the produced fluids. Fracture cements with high $\delta^{13}C$ values occur primarily in samples from well cores, but several cements collected from the Paxton Quarry have values in this

range. Calcite fracture fill in the second population with very low $\delta^{13}C$ values occurs predominantly in surface samples, but also in several well cores (Fig. 6B,C). All fracture-fill calcites at the Norwood outcrop are in the second, lower $\delta^{13}C$ group.

In spite of the broad range in $\delta^{13}C$ values reported for all fracture fills, on an individual fracture scale the isotopic compositions were nearly homogeneous, with the exception of coarse calcite veins in the Norwood outcrop. Multiple analyses from the same calcite fill in an individual fracture yielded nearly identical results in most fracture fills (Appendix). In contrast, samples from the Norwood outcrop, which contained some of the lowest $\delta^{13}C$ values, exhibited a marked heterogeneity within individual fracture fills, suggesting multiple episodes of cementation.

Several core samples of fractured Antrim Shale from the western, eastern and southern margin of the Michigan Basin were included in this study (Fig. 1, Appendix). On the western and eastern edge of the basin, calcite cements in fractures have high $\delta^{13}C$ values, comparable to the first group in the NPT. There is active gas exploration and production in the area southwest of the NPT. However, exploration wells on the eastern side of the Michigan Basin have very low gas production rates. The high $\delta^{13}C$ values in calcite cements from a core on the eastern margin of the Michigan Basin may indicate a former microbial gas deposit that has since been degraded or eroded. On the southern edge of the Basin, the Antrim Shale is well fractured and has organic carbon contents as high as black shales in the NPT, but cementation within fractures was extremely sparse and there were no cements with high $\delta^{13}C$ values. These fracture-fill cements have moderately low carbon isotope values (-11 to -18 $\delta^{13}C$ ‰; Appendix).

Oxygen isotopic composition of fracture-fill cements

In contrast to the broad range of $\delta^{13}C$ values in fracture-fill cements, there is a narrow range in $\delta^{18}O$ values. There is a predictable geographical distribution of $\delta^{18}O$ values in brines from the Antrim Shale (Walter *et al.* 1996) that is also observed in the $\delta^{18}O$ composition of fracture-fill calcite (Fig. 7a). In shallow, northern parts of the reservoir, the $\delta^{18}O$ of calcite cements is lowest, whereas farther south, deeper in the Antrim reservoir, fracture-fill calcite has higher $\delta^{18}O$ values. The $\delta^{18}O$ values of formation brines from presently producing gas wells increase with depth in the reservoir due to mixing with freshwater (Fig. 7A). This increase (from -12 to -4.0 $\delta^{18}O$ ‰ SMOW) occurs within a geographically narrow area ($\sim$20 km, 12 miles; Martini *et al.* 1998). Calcite cements from Antrim fractures within the western, eastern, and southern margins of the Michigan Basin have $\delta^{18}O$ values comparable to fracture cements in the NPT, although present gas production in most of these areas is quite low compared to that in the NPT (Fig. 7B, Appendix).

In an effort to evaluate a possible connection between calcite cements in fractures and present-day formation fluids, the $\delta^{18}O$ (SMOW) values of cements were compared to those in brines from nearby producing gas wells (Fig. 8; Appendix) using data presented in Walter *et al.* (1997) and Martini *et al.* (1998). When these calcite-water data are compared to experimentally determined fractionation curves for calcite and water between 0 °C and 25 °C (Fig. 8; O'Neil *et al.* 1969), it is apparent that most fracture-fill calcite from the shallowest part of the reservoir is not in isotopic equilibrium with present day formation fluids. These calcite cements all have high $\delta^{13}C$ values and may have formed at temperatures lower than in the present day reservoir (about 15 °C) or precipitated from waters with lower $\delta^{18}O$ values than are present in the modern reservoir. Calcite from fractures in deeper sections of the Antrim Shale, also with high $\delta^{13}C$ values, have $\delta^{18}O$ values that could be derived from present day formation waters. However, it is more likely that the cements from the deeper sections of the Antrim Shale formed at some time in the past from waters with comparable isotope values to those presently in the reservoir.

The modern calcite scale samples, plotted in Fig. 8, reflect formation at higher temperatures than were measured in formation fluids, or precipitation so rapid during degassing within well tubing that the oxygen values are not in equilibrium with reservoir conditions. The higher temperatures implied by the $\delta^{18}O$ values are related to summer surface temperatures, not reservoir temperatures. Fluid temperatures in the range of 12–17 °C reported for many wells in the NPT (Martini *et al.* 1998) are probably not accurate formation temperatures because they were measured at the well head and not at depth in the reservoir. Given the shallow depth in most of the NPT of the Antrim Shale, maximum fluid temperatures should not be greater than 25 °C (Speece *et al.* 1985; Cercone & Pollack 1991) and are probably actually cooler than measured at the surface today.

Whereas local methanogenic processes may control the $\delta^{13}C$ values in brines within the reservoir, the $\delta^{18}O$ values are a reflection of mixing between dilute surface recharge water and formation brines at some time in the past. Based on the geographical distribution of $\delta^{18}O$ in present-day formation water and in calcite cements, it is likely that this reservoir has hosted fluids with similar compositional gradients for a long time. Martini *et al.* (1998) reported ^{14}C dates of DIC from Antrim Shale brines in the NPT that range from 6 to 27 ka BP. They have interpreted them as residual glacial melt water, which is consistent with their low $\delta^{18}O$ values (Desaulniers *et al.* 1981 and references therein). Calcite samples with the lowest oxygen isotopic values are from locations that are within the northern edge of the producing trend where the reservoir is closest to the surface (Figs 7 and 8). It is unlikely that these fractures were filled by calcite at temperatures below 0 °C, but it is certainly plausible that lower values in
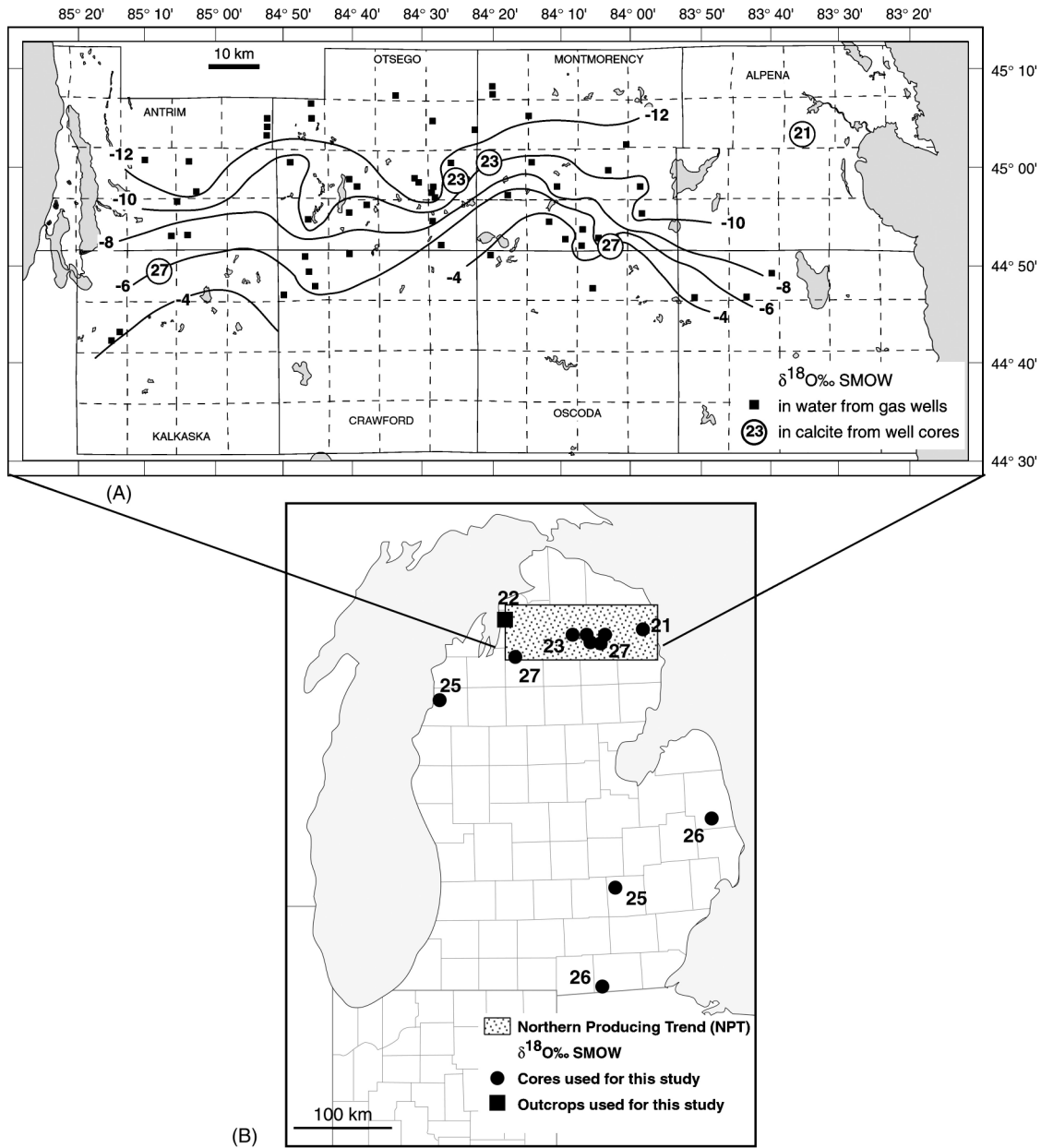
Fig. 7. (A) Detailed map of the Northern Producing Trend of the Antrim Shale showing the $\delta^{18}O$ (SMOW) of formation brines as contours (ranging from −4 to −12‰). The stable isotope compositions of calcite cement in core fractures are given as values in circles. (B) Larger state-wide map of $\delta^{18}O$ (SMOW) values of calcite from Antrim Shale fractures shown as whole numbers. Most samples are from wells (dots) and outcrop sample location is marked by a solid square.

the cements reflect precipitation from fluids with lower $\delta^{18}O$ values, such as those expected from glacial melt water.

^{14}C and ^{230}Th dating of fracture-fill cements

Radiocarbon analyses of calcite cement from four well cores and one sample from the Norwood outcrop are listed in Table 4. The amount of ^{14}C in the well core cements was below the AMS detection limits of 0.0022–0.00152 Fm

(fraction modern), thus these cements formed earlier than 33–49.1 ka BP. The calcite cement sample from the Norwood outcrop had ^{14}C contents of 0.61 ± 0.2 Fm, which yields an uncorrected ^{14}C age of 40.9 ka BP This sample had a $\delta^{13}C$ of −17.2‰.

Three calcite cement samples from the Norwood outcrop sample were analysed for U and Th isotopic compositions to provide another age estimate. The ^{230}Th ages from the Norwood outcrop cements were between 273 and 390 ka.

Table 4 Age determinations of fracture-fill calcite.

Sample ID	δ¹⁸O (‰ PDB)	δ¹³C (‰ PDB)	¹⁴C (Fm) ± 1 σ	¹⁴C age (ka BP)	δ¹³C (‰ PDB)*	²³⁰Th age (ka) ± 2σ†
Outcrop samples						
NOR94-2.1	−7.2	−21.6	0.61 (±0.2)‡	41 (+2.5/−1.9)‡	−17.2	390 (+62/−41)
NOR94-2.2	−6.7	−12.4				338 (+63/−41)
N95–1B.1	−4.9	−31.5				273 (+33/−23)
Well cores						
WLL 1588.1	−7.5	17.3	$F < 0.0022$	>49	17.6	
SSK 1639	−3.2	25.6	$F < 0.0022$	>49	24.1	
TT 1437–1 A	−7.0	−24.0	$F < 0.0152$	>33	−29.4	
SC 1179.4	−3.6	24.3	$F < 0.0050$	>42	12.7	

*Values from samples analysed for radiocarbon. †Assumes $(^{230}Th/^{232}Th)_i = 50 \pm 50$ ppm. Uranium and thorium concentrations and isotopic compositions are available from the Correspondence. ‡Analyses from calcite vein NOR94.2, but not same splits as δ¹⁸O and δ¹³C.

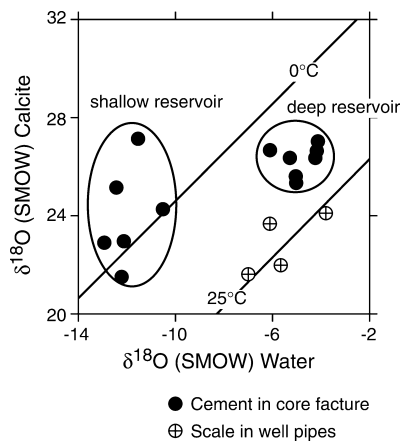**Fig. 8.** δ¹⁸O (SMOW) values of water samples from producing gas wells paired with fracture-fill calcite samples from nearby well cores (dots). Also shown are δ¹⁸O (SMOW) values of water samples paired with calcite scale samples that precipitated as scale in gas well pipes (circles with crosses). Lines marked with 0 and 25 °C indicate equilibrium relations between calcite and water, from O'Neil *et al.* (1969).

DISCUSSION

The Antrim Shale is an economic natural gas reservoir for a number of reasons, but two factors can be considered within the framework of this study. The first is related to the glacial history of the Great Lakes area. The second factor is the relatively immature condition of the abundant organic matter available within the reservoir itself (Rullkötter *et al.* 1992). On the margins of the Michigan Basin, the Devonian section was never deeply buried, precluding thermal maturation of the organic rich black shales of the Antrim Shale. The calcite cement lining fractures within the Antrim Shale provides evidence of water sources through its oxygen isotope content, carbon sources through its unusual δ¹³C values, and a temporal framework during which these biogeochemical reactions proceeded.

The role of continental glaciation

Erosional and depositional processes associated with continental glaciation are critical in the development of surface geology and hydrology in the Great Lakes region (Farrand 1982; Farrand & Drexler 1985; Farrand & Eschman 1974; Hoagland 1996). Of special note is the glacial history of northern Michigan, where repeated glacial advances and retreats during the Pleistocene eroded the margins of the basin, alternately exposing Palaeozoic rocks to surficial weathering and then covering subcrops with thick deposits of sand and gravel derived from erosion of the Canadian Shield. The final glacial retreat occurred between 12 and 10 ka BP, leaving behind large moraines composed of gravel, sand, and fine sediment. In the northern part of the Southern Peninsula of Michigan the significant relief of glacial moraines (up to 500 m) has provided a thick reservoir for groundwater. Furthermore, rapid glacial rebound of northern Michigan following unloading of the Laurentide ice sheet may have served to open pre-existing fracture networks (Clark 1982), enhancing the infiltration of glacial melt waters. Morainal topography developed as the ice sheet waned and supplied enough hydraulic head to drive surficial recharge into underlying Palaeozoic units that subcrop around the northern margin of the basin.

The northern gas producing trend of the highly fractured Antrim Shale is located immediately basinward of Devonian age subcrops, adjacent to the highest glacial moraines in Michigan. As the Laurentide ice sheet receded, large volumes of meltwater with stable isotopic values distinct from modern meteoric water filled lakes of Late Pleistocene age over much of northern Michigan (Desaulniers *et al.* 1981; Farrand 1988). In a study closely related to this one, the importance of meteoric recharge in developing microbial methanogenesis within the Antrim Shale has been suggested by evidence from isotopic relations among methane, water and CO_2 presently being produced from the NPT and from other Michigan Basin margins (Martini *et al.* 1996, 1998; Walter

et al. 1997). Recharge of glacial melt water into a number of other mid-continent basins has been suggested by hydrological and isotopic studies (Coleman *et al.* 1988; Siegel 1991; Stueber & Walter 1994; McIntosh *et al.* 2002).

The timing of fresh water recharge with associated methane production is constrained by the ages of fracture-fill calcite, which record $\delta^{13}C$ values indicating both methane generating and methane oxidizing processes. The ^{230}Th ages of the fracture fill from the Norwood outcrop range between 273 and 390 ka (Table 4). These results appear to be in conflict with the ^{14}C age of 41 ka BP (Table 4). However, there are several ways to account for this discrepancy. Fracture-fill calcite was taken at the present lake water level at the Norwood outcrop. Over the past 10 ka it is likely there have been recurrent fluctuations in lake level and mean annual temperatures, both of which can cause changes in calcite solubility. Modern Lake Michigan is saturated with respect to calcite, so some amount of modern ^{14}C may have been incorporated into these cements during intermittent dissolution and precipitation events within the calcite lined fractures. There is evidence of multiple cementation events at this location, based on carbon isotope results and petrographic observations, described earlier (Figs 4B,C). The addition of any modern ^{14}C would yield an anomalously young age relative to the primary calcite precipitation phase. Alternatively, U loss would cause the ^{230}Th ages to be too old. Uranium is a soluble, mobile element, and U loss could have occurred as lake levels fluctuated, causing variable weathering and precipitation cycles. Calcite cement from fractures in well core samples have ^{14}C concentrations below detection limits and therefore have ages greater than 33–49 ka BP; further U–Th measurements should constrain the formation time of these cements. Despite the uncertainties of calcite cement ages, the measured $\delta^{234}U$ values of cements (130–152) indicate that the U system is not in secular equilibrium, therefore the cements must have formation ages less than ~750 ka. The U–Th isotopic compositions, in conjunction with the ^{14}C results place the formation of the Norwood calcite samples within the Pleistocene Epoch (1.6 ma to 10 ka), with the ^{230}Th ages taken to be a maximum and the ^{14}C ages a minimum age (e.g. Ivanovitch & Harmon 1982; Edwards *et al.* 1987).

Microbial methanogenesis

Thermal immaturity of organic matter in the highly organic Antrim Shale provided an environment favorable to microbial methanogenesis. Due to the recharge of surface water via glacial melting, the salinity of basinal brines was diluted and made hospitable for methanogens to flourish in an irregularly shaped mixing interface within the reservoir (Martini *et al.* 1998). The well-developed fracture network enhanced fluid flow into the black shale, carrying in surface bacterial communities necessary to initiate a complex sequence of microbial

reactions leading to methane generation (Martini *et al.* 1996, 1998).

Given the radioactive age determinations, it is likely that calcite cements in fractures are older than the formation waters presently being produced from the Antrim Shale, and were formed sometime during the Pleistocene. Furthermore, the range of isotopic values within these fracture cements and their geographical distribution strongly suggest that those cements with high $\delta^{13}C$ values (> 8‰ $\delta^{13}C$) formed as a by-product during active methanogenesis within the reservoir (Irwin *et al.* 1977; Siegel *et al.* 1987). During biogenically mediated methanogenesis, ^{12}C is preferentially concentrated in methane while ^{13}C is enriched in the surrounding water as DIC. Brines from the Antrim Shale are Ca-rich, which allows calcite precipitation when DIC concentration is high (Martini *et al.* 1998). Calcite cements precipitating from reservoir fluids during this process should have unusually positive $\delta^{13}C$ values, like those found in these fracture cements. Only microbial processes, via fermentation or CO_2 reduction pathways, are capable of producing the extremely high $\delta^{13}C$ values measured in these cements. All other accessible sources of carbon in rock within this system have $\delta^{13}C$ values that are much lower. Devonian carbonate units within and adjacent to black shales of the Antrim have a $\delta^{13}C$ of about 0‰; organic carbon in the section has a $\delta^{13}C$ of −29‰, and early diagenetic calcite and dolomite cements in concretions have negative carbon values (−5 to −12‰). However, present-day formation brines have high DIC contents with correspondingly high $\delta^{13}C$ values (+30‰), as do coproduced CO_2 gas ($\delta^{13}C = +19$ to +22‰; Fig. 6). As described in Martini *et al.* (1996, 1998), the deuterium isotope values of coproduced methane and formation water indicate methanogenesis via a CO_2 reduction pathway. Taken together, the isotopic relationships between carbon and hydrogen within water, CO_2 and CH_4 form compelling evidence of active microbial methanogenesis via CO_2 reduction in the reservoir (Martini *et al.* 1996).

The highly negative $\delta^{13}C$ values (−15 to −42‰ PDB) contained in the second fracture cement group suggest that these record oxidation of methane or other local organic carbon sources. Both abiotic and biogenically mediated methanotrophic activity could contribute a source of low $\delta^{13}C$ values to DIC within formation water (Raiswell 1988). Several lines of evidence point to bacterial oxidation within the shallowest parts of the Antrim Shale reservoir (Martini *et al.* 1998). The isotopic relationships and gas chemistry of methane and ethane reported in Martini *et al.* (1998) imply that ethane has been preferentially removed, producing a higher $C_1/(C_2 + C_3)$ in the residual methane resource around the northern margin of the Antrim Shale gas producing zone. The $\delta^{13}C$ values of organic carbon and methane from the Antrim Shale are −29‰ and −50‰ (PDB), respectively. Fracture-fill cement formed from CO_2 released via oxidation mixing with calcium-rich formation waters would

yield calcite with low $\delta^{13}C$ values, like those in the second group of fracture-lining calcite. The lowest $\delta^{13}C$ values ($-42‰$ $\delta^{13}C$) occur in an outcrop exposure of the Norwood Member on the northwest coast of Antrim and Charlevoix Counties, near Norwood, Michigan (Fig. 1, Appendix). These values are much lower than values of DIC in Lake Michigan water ($-7.0‰$ $\delta^{13}C$), or of carbonate minerals within concretions (Fig. 6).

Microbial sulphate reduction can also lead to precipitation of calcite by increasing the saturation state of carbonate minerals through addition of DIC (e.g. Irwin *et al.* 1977; Morse & MacKenzie 1990). Pyrite and other iron sulphide minerals are abundant throughout the Antrim Shale section. However, sulphate reducing bacteria are presently not an important factor in the Antrim reservoir because the concentration of dissolved SO_4 is very low (<1 mM) in nearly all Antrim formation waters from the NPT (Walter *et al.* 1996). Periodic recharge of fresh water at the basin margin could initiate minor sulphate reduction that would yield associated calcite with a $\delta^{13}C$ of approximately -10 to $-15‰$ (Irwin *et al.* 1977) and there are many samples that are within that range (Fig. 6A,B; Appendix). Alternatively, carbonate rock buffering during organic matter oxidation would yield similar intermediate values (Fig. 6A). However, the only way to explain $\delta^{13}C$ values lower than $-30‰$ (PDB) is through oxidation of methane, providing an unequivocal record of microbial degradation of former hydrocarbons within the Antrim reservoir. Figure 9 provides a summary of the range of isotopic values of carbonate in the Antrim Shale and relates them to various pathways of organic matter oxidation.
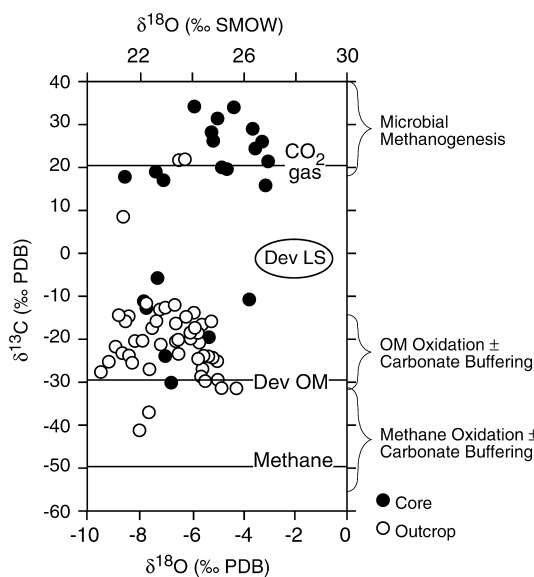
Calcite fracture-fill cement is not common within shallow up-dip areas of the Antrim Shale, either in well cores or exposed in the Paxton Quarry. We infer that fracture cement preservation at the Norwood locality on the northwest edge of the Antrim Shale subcrop was made possible by contact with Lake Michigan water, which is saturated with respect to calcite. Cements are poorly developed within fractures in core samples in all locations examined. The biogeochemical processes that give rise to economic levels of methane may not be favorable for significant carbonate precipitation. The inorganic precipitation of calcite would compete for dissolved carbon with a dynamic microbial community that metabolizes CO_2 as part of the methanogenic process (Martini *et al.* 1996, 1998).

Evidence is retained by unusual calcite fracture fill of a past dynamic microbial community that produced natural gas in a shallow, unconventional reservoir around the margins of the Michigan Basin. There are other, large intracratonic basins with Pleistocene glacial histories and organic black shale sections like that of the Michigan Basin. The conditions that led to the development of an economic gas deposit in the Antrim Shale are not unique and present the possibility of finding shallow, inexpensive natural gas reserves in other North American basins. Gas exploration around the margins of the Michigan Basin, and also within the New Albany Shale of the Illinois Basin, presently continues and studies there suggest that microbial methanogenesis plays an important role in moderating brine chemistry (McIntosh *et al.* 2002).

CONCLUSIONS

(1) Calcite with very high $\delta^{13}C$ values filled fractures in the Antrim Shale and records bacterial methanogenic processes.

(2) Calcite with very low $\delta^{13}C$ values that also fill fractures in the Antrim Shale formed during bacterial or abiotic methane oxidation.

(3) Methane producing and oxidizing processes were initiated by the recharge of surface waters into the black shale around the shallow margins of the Michigan Basin.

(4) Isotopic evidence supports the interpretation that the cause of this recharge was Pleistocene glacial loading, erosion, deposition and ablation that provided a unique and abundant source of water and the physical drive to infiltrate freshly eroded subcrops of the Antrim Shale.

(5) Identification of unusually high and low $\delta^{13}C$ values in calcite can be used as evidence of microbial methane generation and oxidation, respectively, and may be helpful in recognizing gas deposits in other sedimentary basins.

Fig. 9. Stable isotopes ($\delta^{18}O‰$ PDB and SMOW, $\delta^{13}C‰$ PDB) of calcite in core fractures (dots) and outcrop fractures (circles) with fields indicating the dominant source (s) of carbon and processes operating within the reservoir to drive calcite precipitation.

ACKNOWLEDGEMENTS

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APPENDIX: STABLE ISOTOPE DATA FROM OUTCROP AND CORE SAMPLES. ALL DATA COLLECTED IN THE STABLE ISOTOPE LABORATORY AT THE UNIVERSITY OF MICHIGAN.

LOCATION	MEMBER SAMPLED	MIN	δ^{18}O (‰ PDB)	δ^{18}O (‰ SMOW)	δ^{13}C (‰ PDB)	[1]COMMENTS
			OUTCROPS			
ALPENA COUNTY						
Paxton Quarry, SEC30 T31N-R7E						
PQ3	FLOAT	CAL	−5.9	24.3	−11.8	Prismatic cement in concretion
PQ4	FLOAT	CAL	−12.2	17.8	0.8	1st side of vein
PQ4	FLOAT	CAL	−11.6	18.4	3.4	2nd side of vein
PQ94-3.1	FLOAT	CAL	−7.0	23.1	−11.0	Vein
PQ94-3.2	FLOAT	CAL	−7.8	22.4	−10.3	Vein
PQ94-5B.1	LACHINE	CAL	−7.2	23.0	−13.2	horizontal vein
PQ94-5B.2	LACHINE	CAL	−7.1	23.1	−13.1	horizontal
PQ94-5A.1	LACHINE	CAL	−8.5	21.6	−24.3	vertical
PQ94-5A.2	LACHINE	CAL	−8.0	22.2	−20.6	vertical
PQ94 CONC. 1	FLOAT	CAL	−6.1	24.1	−0.9	cement in concretion, brown, coarse
PQ94 CONC. 2	FLOAT	DOL	−7.5	22.7	−15.2	cement in concretion, pink, course
PQ94-6.1	LACHINE	CAL	−7.6	22.6	−37.3	vertical vein, 1st face
PQ94-6.2	LACHINE	CAL	−8.4	21.8	−25.9	vertical vein, 2nd face
PAX 2.1	PAXTON	CAL	−4.9	25.4	−1.6	wall rock
PAX 2.2	PAXTON	CAL	−5.3	24.9	−1.0	wall rock

APPENDIX: Continued

LOCATION	MEMBER SAMPLED	MIN	$\delta^{18}O$ (‰ PDB)	$\delta^{18}O$ (‰ SMOW)	$\delta^{13}C$ (‰ PDB)	[1]COMMENTS
PAX 5.1	PAXTON	CAL	−5.2	25.0	−2.3	wall rock
PAX 5.2	PAXTON	CAL	−5.1	25.2	−2.3	wall rock
PAX 7.1	PAXTON	C+D	−6.1	24.1	−6.9	wall rock
PAX 10.1	PAXTON	C+D	−5.0	25.3	−0.8	wall rock
PAX 12.1	PAXTON	C+D	−7.3	22.9	−4.8	wall rock
PAX 7.2	PAXTON	DOL	−5.4	24.8	−4.7	Dol crust/vein?
PAX 10.2	PAXTON	DOL	−4.9	25.3	−0.5	dol crust/vein?
PAX 12.2	PAXTON	DOL	−5.1	25.1	−2.2	dol crust/vein
PQ94L-1.1	LACHINE	CAL	−8.6	21.6	−15.7	bedding plane vein
PQ94L-1.2	LACHINE	CAL	−8.5	21.7	−15.2	bedding plane vein
PQ94L-2.1	LACHINE	CAL	−9.0	21.1	−22.2	vertical vein, N64E, brown stain
PQ94L-3.1	LACHINE	CAL	−8.7	21.4	8.6	vertical vein, N49E
PQ94L-4.1	LACHINE	CAL	−6.5	23.7	21.4	vertical vein, N46E
PQ94L-4.2	LACHINE	CAL	−6.3	23.8	21.7	vertical vein, N46E
PQ94L-5.1	LACHINE	CAL	−7.7	22.4	−12.1	vertical vein, N53W
PQ94L-5.2	LACHINE	CAL	−7.8	23.3	−12.1	vertical vein, N53W
PQ94L-6.1	LACHINE	CAL	−9.3	20.8	−25.5	vertical vein, N61W
PQ94L-62	LACHINE	CAL	−8.7	21.4	−23.9	vertical vein, N61W
PQVH 1.1	PAXTON	CAL	−9.7	20.4	−0.3	hi angle vein
PQVH-2.1	PAXTON	CAL	−9.3	20.8	7.5	hi anlge vein
P95-1	LACHINE	CAL	−7.4	22.8	−6.4	bp vein
P95-2	LACHINE	CAL	−8.8	21.3	−14.9	vertical N55W vein (315)
Hycrude Core-Paxton Quarry						
HC18.1	UP-ANTR	CAL	−9.5	20.6	−24.1	low angle frac coating
HC18.2	UP-ANTR	CAL	−10.0	20.0	−27.2	low angle frac coating
HC19.1	UP-ANTR	DOL	−6.9	23.2	−9.9	brn dol-1, concretion
HC19.2	UP-ANTR	DOL	−8.2	22.0	−16.2	white dol-2, concretion
HC19.3	UP-ANTR	DOL	−7.0	23.2	−12.2	clear dol-3, concretion
HC19.4	UP-ANTR	DOL	−7.8	22.4	−14.4	yellow dol-4
HC28.1	LACHINE	CAL	−8.9	21.2	−16.4	mad angle frac coating
HC28.2	LACHINE	CAL	−12.3	17.7	−28.7	med angle frac coating
HC57.9	LACHINE				−30.0	organic carbon in black shale
HC101.1	NORWOOD/TRAV	CAL	−9.8	20.3	−3.2	cal-1, concretion
HC101.2	NORWOOD/TRAV	DOL	−10.6	19.5	−15.6	pink dol, concretion
HC101.3	NORWOOD/TRAV	CAL	−2.1	28.2	−9.7	cal-2, brown, concretion
HC107.9	NORWOOD				−28.0	organic carbon in black shale
ANTRIM COUNTY						
Norwood Outcrop, SEC3-T32N-R9W						
NOR94-1	NORWOOD	CAL	−8.0	22.1	−41.7	vein, N60E
NOR94-2.1	NORWOOD	CAL	−7.2	22.9	−21.6	edge of vein, N34W
NOR94-2.2	NORWOOD	CAL	−6.7	23.5	−12.4	center of vein N34W
N95-1A.1	NORWOOD	CAL	−5.2	25.0	−24.3	N76E, center of vein, piece 1
N95-1A.2	NORWOOD	CAL	−5.9	24.3	−17.5	N76E, near edge of vein, piece 1
N95-1A.3	NORWOOD	CAL	−5.4	24.9	−24.3	N76E, wall edge of vein, piece 1
N95-1A.4	NORWOOD	CAL	−6.6	23.6	−20.7	N76E, stained, center, piece 2
N95-1A.5	NORWOOD	CAL	−7.4	22.8	−16.1	N76E, stained, edge, piece 2
N95-1A.6	NORWOOD	CAL	−6.0	24.2	−19.9	N76E, center, piece 3
N95-1A.7	NORWOOD	CAL	−4.2	26.0	−31.7	N76E, edge, piece 3
N95-1B.1	NORWOOD	CAL	−4.9	25.3	−31.5	N76E, center of vein, piece 1
N95-1B.2	NORWOOD	CAL	−5.4	24.8	−24.1	N76E, edge of vein, pc 1
N95-1B.3	NORWOOD	CAL	−5.7	24.5	−27.0	N76E, stained, center, pc 2
N95-1B.4	NORWOOD	CAL	−6.7	23.5	−16.7	N76E, stained, edge, pc 2
N95-3A.1	NORWOOD	CAL	−5.5	24.7	−29.7	N60W, center coarse vein pc 1
N95-3A.2	NORWOOD	CAL	−8.2	21.9	−20.9	N60W, wall edge of vein, pc 1
N95-3A.3	NORWOOD	CAL	−5.7	24.5	−24.6	N60W, center coarse vein, pc 2
N95-3A.4	NORWOOD	CAL	−6.5	23.6	−23.5	N60W, wall edge of vein, pc 2
N95-3B.1	NORWOOD	CAL	−5.7	24.5	−28.7	N10E, thinner than A, vein center, pc 1
N95-3B.2	NORWOOD	CAL	−5.6	24.6	−16.9	N10E, wall edge of vein, pc 1
N95-3B.3	NORWOOD	CAL	−5.3	24.9	−15.9	N10E, center of vein, pc 2, coarse>pc1

APPENDIX: Continued

LOCATION	MEMBER SAMPLED	MIN	δ^{18}O (‰ PDB)	δ^{18}O (‰ SMOW)	δ^{13}C (‰ PDB)	[1]COMMENTS
N95-3B.4	NORWOOD	CAL	−5.8	24.4	−20.8	N10E, wall edge, vein, pc 2
N95-3B.5	NORWOOD	CAL	−5.0	25.2	−25.4	N10E, between center and edge, pc 2
N95-4A.1	NORWOOD	CAL	−5.9	24.2	−13.9	N63E, vertical, center, white, pc 1
N95-4A.2	NORWOOD	CAL	−9.5	20.6	−28.3	N63E, vertical, wall edge of vein, gray, pc 1
N95-4A.3	NORWOOD	CAL	−6.2	24.0	−14.9	N63E, stained, wall edge, needle xls, pc 2
N95-4A.4	NORWOOD	CAL	−7.6	22.6	−17.2	N63E, center of vein, pc 2
N95-4B.1	NORWOOD	CAL	−5.0	25.2	−29.7	N30W, center of vein, pc 1
N95-7.1	NORWOOD	CAL	−6.1	24.1	−19.3	N30W, stained, vein center, pc 1
N95-7.2	NORWOOD	CAL	−7.7	22.5	−27.2	N30W, stained, wall edge vein, pc 1
N95-7.3	NORWOOD	CAL	−5.9	24.3	−18.4	N30W, unstained, vein center, pc 2
N95-7.4	NORWOOD	CAL	−6.5	23.6	−20.3	N30W, frac wall edge, pc 2

WELL CORE SAMPLES (depth in feet)

CRAWFORD COUNTY

SWEPI St. S. Branch 1–19, SEC 19-T25N-R1W

2098.3	LACHINE				−20.3	organic carbon in black shale

KALKASKA COUNTY

Shell St. Kalkaska 3–11. SEC 11-T28N-R7W

1604.4		CAL	−3.6	26.7	24.3	hi angle vein
1639		CAL	−3.2	27.1	25.6	hi angle vein
1641		CAL	−3.1	27.2	21.3	hi angle vein
1621.2A		CAL	−4.4	25.9	20.7	last cement in concretion, dedolomite
1621.2B		DOL	−7.8	22.3	−10.4	hi angle vein in concretion, 1st cement

LENAWEE COUNTY

Yohe Thomas 1–28, SEC 28-T8S-R2E

LIVINGSTON COUNTY

Mercury Dey A1–15, SEC 15-T3, R3E

MD 1693.5A	NORWOOD	CAL	−4.8	25.4	20.0	hi angle vein
MD 1693.5B	NORWOOD	CAL	−4.6	25.6	19.6	hi angle vein w/br stuff
MD 1537	LACHINE	Blk Shale			−30.1	organic carbon
MD 1674.7	NORWOOD	Blk Shale			−30.5	organic carbon

MANISTEE COUNTY

Oil Joseph 3–22, SEC 22-T23N-R16N

OJ 1026-1	LACHINE	CAL	−15.7	14.2	8.4	cement on low angle fracture
OJ 1047-1	LACHINE	CAL	−5.0	25.2	31.3	bp vein w/pyrite nuggets
OJ 1047-1 SPLIT			−5.0	25.3	30.9	split of same
OJ 1047-2	LACHINE	CAL	−5.9	24.3	34.0	same, different spot
OJ 1063-2	LACHINE	CAL	−5.2	25.0	28.5	bp vein
OJ 1064.5-1	LACHINE	CAL	−5.1	25.1	25.6	bp vein w/pyrite
OJ 1064.5-2	LACHINE	CAL	−5.1	25.1	26.2	same, different spot
OJ 1064.5-2 SPLIT			−5.2	25.0	26.1	split of above
OJ 1114-2	NORWOOD	CAL	−5.4	24.8	−19.6	low angle fracture, thin cement
OJ 1078.5-1	PAXTON	CAL	−5.8	24.4	−9.7	limestone (stained)
OJ 1078.5-2	PAXTON	CAL	−8.0	22.2	−6.1	1st cement in concretion (stained)
OJ 1078.5-3	PAXTON	DOL	−4.7	25.5	−5.1	2nd cement in concretion (stained)
OJ 1078.5-4	PAXTON	CAL	−0.4	30.0	−5.3	3rd cement in concretion (stained)
OJ 1078.5-5	PAXTON	CAL	−5.6	24.6	−7.2	limestone wall rock (unstained)
OJ 1078.5-6	PAXTON	CAL	−6.6	23.5	−7.1	1st cement in concretion (unstained)
OJ 1078.5-7	PAXTON	DOL	−8.4	21.8	−4.7	2nd cement in concretion (unstained)

MONTMORENCY COUNTY

Shell St. Loud C2–31, SEC 31-T29N-R3E

1579.9A	TRAVERSE	CAL	−7.3	22.8	−4.0	wall rock
1579.9B	TRAVERSE	DOL	−7.5	22.7	−3.2	wall rock
1584.9A	TRAVERSE	CAL	−7.3	22.9	−4.1	wall rock
1584.9B	TRAVERSE	DOL	−7.0	23.2	−2.9	wall rock
1564.9	NORWOOD	CAL	−7.8	22.3	−4.5	conforted veinlet w/pyrite
1470	LACHINE				−29.5	organic carbon in black shale
1559.5	NORWOOD				−30.2	organic carbon in black shale

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963.8	UP ANTR				−29.4	organic carbon in black shale

APPENDIX: Continued

LOCATION	MEMBER SAMPLED	MIN	$\delta^{18}O$ (‰ PDB)	$\delta^{18}O$ (‰ SMOW)	$\delta^{13}C$ (‰ PDB)	[1]COMMENTS
Shell Caruso C2–28C SEC 28-T29N-R3E						
1179.4	LACHINE	CAL	−3.6	26.7	24.3	vertical vein w/pyrite
1226.2A	NORWOOD	DOL	−3.2	27.1	25.6	gash vein (in concretion?)
1226.2B	NORWOOD	CAL	−3.1	27.2	21.3	gash vein (in concretion?)
1226.2C	NORWOOD	CAL	−5.5	24.8	−10.0	gash vein (in concretion?)
Trend Stevens Mins 2–15, SEC 15-T30N-R3E						
747A	NORWOOD	DOL	−11.8	18.2	−13.7	Concretion, vein center
747B	NORWOOD	CAL	−5.4	24.8	−7.2	Concretion, vein edge
747C	NORWOOD	CAL	−8.2	21.9	−2.8	Concretion, vein center
747D	NORWOOD	CAL	−5.0	25.2	−4.9	Concretion
757.5	NORWOOD	CAL	−8.1	22.0	−6.8	concretion? breccia zone w/prite
758	NORWOOD	CAL	−3.1	27.2	15.9	hi angle fracture coating, sparse
Trendwell Thompson 1–8, SEC 8-T30N-R1E						
1437-1A	LACHINE	CAL	−7.0	23.1	−24.0	hi anlge vein, N45E
1437-1B	LACHINE	CAL	−7.1	23.1	−24.6	hi angle vein w/pyrite, N45E
1437-2	LACHINE	CAL	−6.8	23.4	−30.3	hi anlge vein, N45E
1518.7A	SQB/TRAV	CAL	−7.8	22.4	−13.2	lo anlge vein
1518.7B	SQB/TRAV	CAL	−3.6	26.7	−6.1	wall rock
Caruso CH-2, SEC 28-T29N-R3E						
CCH2-1189-1	LACHINE	CAL	−3.4	26.8	29.1	hi anlge fracture, N60E
CCH2-1189-2	LACHINE	CAL	−3.8	26.5	24.2	dif site, same fracture, N60E
OTSEGO COUNTY						
Ward Latuscek B1–32, SEC 32-T30N-R1W						
1602.3A	LACHINE	DOL	−9.7	20.4	−9.6	Concretion wall rock
1602.3B	LACHINE	DOL	−9.5	20.6	−11.5	Concretion wall rock
1602.3C	LACHINE	CAL	−9.6	20.4	−11.9	Concretion
1602.3D	LACHINE	DOL	−12.1	17.9	−15.1	Concretion
1717A	SQ BAY	DOL	−12.5	17.5	−8.5	Concretion
1717B	SQ BAY	CAL	−4.2	26.0	−1.7	Concretion
1716.6	SQ BAY	CAL	−4.6	25.6	−9.1	Concretion
1588.1	LACHINE	CAL	−7.5	23.1	17.3	vein
1589A	LACHINE	CAL	−8.6	21.5	17.6	Thin vertical vein
1589B	LACHINE	CAL	−7.1	23.0	16.9	vertical vein, N70E
1589C	LACHINE	CAL	−7.4	22.7	16.7	vertical vein, N56E
1613.7	LACHINE	CAL	−7.4	22.7	18.8	bedding plane vein, prismatic
1646.7A	PAXTON	CAL	−7.3	22.8	−6.3	lo angle vein, clear
1646.7B	PAXTON	CAL	−5.2	25.0	−0.8	wall rock
1705A	NOR/SQB	CAL	−10.2	19.9	−10.9	Concretion
1705B	NOR/SWB	CAL	−3.9	26.4	−11.4	wall rock
Welch St. Chester #18, SEC 13, T29N, RZW						
1519A	LACHINE	DOL	−10.0	20.1	−13.6	Concretion
1519B	LACHINE	DOL	−9.2	20.8	−10.1	wall rock
SANILAC COUNTY						
DOW ERDA #103, SEC 8-9N-15E						
1335	Upper Antrim	CAL	−4.4	25.8	34.0	vertical fracture, N24E
SCALE						
scale from a Crawford Cty well						
inner edge, oldest scale		CAL	−8.1	22.0	29.0	
next		CAL	−8.1	22.0	28.9	
next		CAL	−8.4	21.8	29.2	
next		CAL	−8.2	22.0	29.1	
next		CAL	−8.4	21.7	29.3	
next		CAL	−8.3	21.8	29.4	
outer edge, youngest scale		CAL	−8.2	21.9	29.2	
scale from a Montmorency Cty well						
scale A		CAL	−6.0	24.2	25.0	
scale B		CAL	−6.5	23.7	21.3	

[1]''Stained'' or ''unstained'' in comments refers to Alizarin Red S stain for calcite.