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The Origin of Quartz
in the Antrim Shale

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THE ORIGIN OF THE QUARTZ
IN THE
ANTRIM SHALE

By

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ABSTRACT

Study of the macroscopic and microscopic properties of the Antrim Shale indicated an important anomoly, the quartz. The Antrim Shale (Devonian, Michigan Basin) contains a large, but quantitatively undeterminable volume of authigenic quartz. The shale contains approximately 50% quartz by weight of which, in the >500 mesh size fraction, 56% is polycrystalline. This is approximately 2X the amount of quartz in most shales and 10X the amount of polycrystalline quartz in the silt-size fraction of sandstones and shales. Scanning electron microscopy reveals an authigenic surface composed of hexagonal tabular plates which coalesce to form smooth grain surfaces. These plates have not been previously reported on quartz grains. Oxygen isotopes of quartz and carbonate phases are interpreted to indicate a gradual isotopic lightening of the pore fluids, from approximately -4 ‰ to -8 or -10 ‰. Most of the authigenic quartz has a $\delta^{18}O$ = 22 ‰ (SMOW).

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INTRODUCTION

Anomalous characteristics of the quartz in the Antrim Shale (Devonian, Michigan Basin) led to an investigation of the origin and evolution of that quartz.

Antrim contains approximately 50% quartz compared to ~ 30% in the average shale (Shaw and Weaver, 1965) and > 50% of the silt sized quartz in polycrystalline, whereas < 5% of the quartz is polycrystalline in the average mudrock (Blatt and Schultz, 1976). These data led to the hypothesis that a large portion of the quartz in the Antrim could be authigenic.

Because of the small grain size, thin section analysis of Devonian black shales has not revealed any unusual characteristics of the quartz (Harvey and others, 1977). We examined quartz separates to determine the nature of the quartz and the monocrystalline to polycrystalline quartz ratios for the >500 mesh size fractions. As a working hypothesis, it was assumed that a large fraction of polycrystalline quartz probably indicates a large authigenic component because there is no apparent source of predominantly polycrystalline quartz. Scanning electron microscopy (SEM) was used to identify surface features which have been interpreted to be authigenic. The most common surface feature observed is a hexagonal plate. This represents a new growth morphology for quartz. Oxygen isotopic analysis of both the quartz and authigenic carbonates indicates that the pore fluids in which the diagenetic reactions occurred had $\delta^{18}O$ values between approximately -4 to -10 ‰. These data are surprising because the Antrim is generally believed to be a marine shale and the diagenetic pore fluids were expected to have nearly normal marine values ($\delta^{18}O \simeq 0$ ‰).

Much of the quartz in the Antrim is authigenic, but there is no accurate determination of how much. The source of the silica is unknown and the possible role of organics (≃ 20% by weight of the shale) can only be speculated. The purpose of this paper is to demonstrate the presence of the authigenic quartz and its unsuspected isotope composition.

ANTRIM SHALE

The Antrim Shale is the Michigan Basin correlate of the Upper Devonian, Lower Mississippian black shale deposit which covers most of the mid-continent. Equivalent formations are variously named Chattanooga, New Albany, Ohio, etc.

The Antrim Shale is stratigraphically underlain by the Traverse Limestone which is characterized by shallow reef carbonates. Between the Traverse Limestone and Antrim Shale lies the Traverse Formation which contains interlayered carbonates and gray to black shales. The Antrim Shale, which overlies both the Traverse Limestone and Traverse Formation, reaches a maximum thickness of 200 meters (Fisher, 1953). The overlying formations are geographically split within the Michigan Basin. The Ellsworth Shale is found in the western portion, and in the eastern portion (slightly higher in the section) are the Bedford-Berea Formations. The Sunbury overlies the Bedford-Berea and is lithologically indistinguishable from the Antrim (Fisher, 1953). In some areas of the basin the Sunbury Shale can be found lying directly on the Antrim Shale.

The Antrim is a black shale with an average organic content of $\simeq$ 20% by weight. The shale has a much stronger tendency to break conchoidally than along laminations when unweathered. The shale is thinly laminated and very uniform; the laminations are defined by organic material, quartz and pyrite. There are also layers of green shale within the Antrim which contain bioturbation structures and less organics. Carbonate concretions are a common occurrence within the Antrim; size ranges from .5 to 3 meters in diameter. Pyrite can be found as nodules, .5 to 20 cm, thin laminations and encasing smaller concretions.

The components of interest within the shale are the organics (≈20%), clays (≈30%), carbonate (<5%) and quartz (≈50%). The origin of the organic material is predominantly marine (Levanthal, 1978; Maynard, 1978). Visually identifiable organic material are the marine spores, Tasmanites, and preserved remains (coal, vitrain bands) of the terrestrial plant Callixyon. The clay fraction is composed of illite with minor kaolinite and chlorite (Nowak, 1978). Carbonate material is almost exculsively ankerite with the exception of dolomite in the Ellsworth Shale. With no preserved fossils or carbonate mud, the entire carbonate phase is authigenic in origin.

SAMPLING

The majority of the samples were obtained from the Michigan Basin (Figure 1). Vertical and horizontal homogeneity with respect to the amount of quartz in the shale was determined at the Paxton Quarry, Alpena County. Samples were taken at one foot intervals vertically and at one hundred foot intervals horizontally. A basinal distribution of the Antrim was approximated by an additional three sites: Kettle Point, Ontario, Canada; Dow Chemical core #101, Sanilac County, Michigan; and the Antrim type locality at Norwood, Michigan. The Ohio Shale, USGS Devonian Black Shale standard (SDO-1) and the Blocher Shale (lower member of the New Albany Shale) were also analyzed. This was done to determine if the quartz typical of the Antrim was also common to other stratigraphically equivalent black shales.

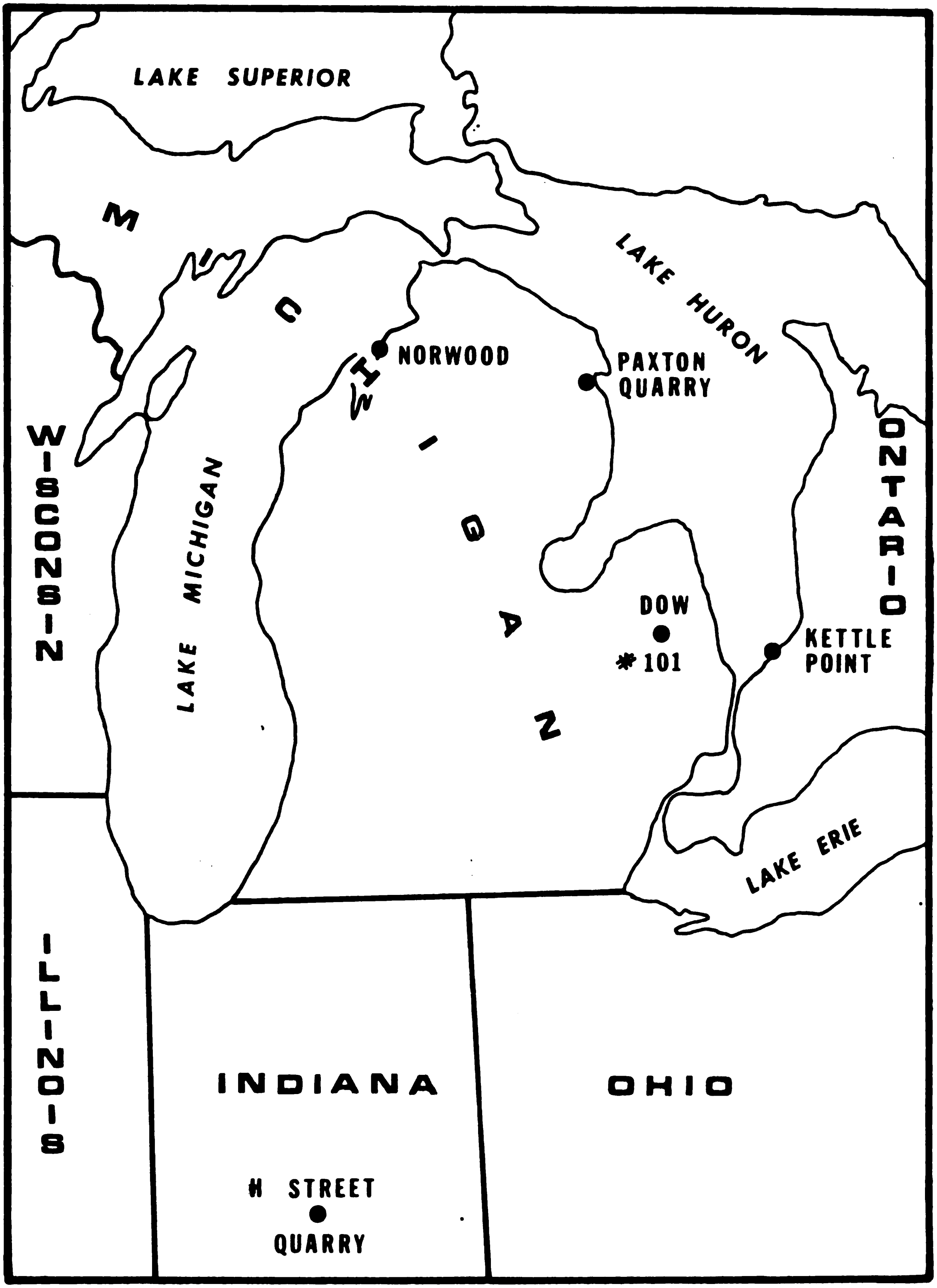

Figure 1. Sample Location.

ANALYTICAL TECHNIQUE

Sample Preparation

The quartz and feldspar were isolated from the shale by potassium pyrosulfate fusion (Syers, et al., 1968). Prior to fusion the organic material, pyrite and carbonate were removed from the shale. Initially, an approximation of the organic content was determined by ashing the shale. Afterward the sample was boiled twice in concentrated nitric acid (30 min.) to remove the pyrite, carbonate and any remaining organics. After the fusion, each sample was sieved into six size fractions: 125, 200, 325, 400, 500 and <500 mesh. Feldspar was removed from some samples by etching with H_2SiF_6. Some quartz samples were also progressively etched with HF. Splits from each size fraction were used for petrographic, SEM and oxygen isotope analysis.

The two cherts and the silicified evaporite nodule were boiled in hydrochloric acid to remove carbonate material. The coal samples underwent the same quartz extraction process as the shale samples.

Isotope Determination, Quartz

Oxygen was liberated from the quartz by using the bromine pentafluoride process (Clayton and Mayeda, 1963). Reactions were run at approximately 500^{o}C for 12 hours. The carbon dioxide conversion reactions were completed in a 10-minute period using a heated carbon disc. The carbon dioxide was isotopically analyzed by a double collector mass spectrometer.

Isotope Determination, Carbonate

Isotopic analysis of the carbonate material was performed by Geochron Laboratories. Both oxygen and carbon isotopes were obtained on all carbonate material.

Petrographic and SEM

For petrographic work, grains were mounted in Lakeside 70. Polycrystalline to monocrystalline ratios were determined by 200-300 grain point counts. To determine the surface textures of monocrystalline and polycrystalline grains, individual grains were selected and mounted for SEM observation. Afterward, the grains were individually mounted for petrographic analysis. This allowed correlation of petrographic and SEM characteristics.

NOTATION

The $^{18}O/^{16}O$ values are reported as $\delta^{18}O$, defined by the equation:

$$\delta^{18}O = \frac{(^{18}O/^{16}O)\ \text{sample} - (^{18}O/^{16}O)\ \text{standard}}{(^{18}O/^{16}O)\ \text{standard}} \times 1000.$$

The values are related to standard mean ocean water (SMOW) as defined by Craig (1961). For this analysis, SMOW has been defined by:

$$\delta^{18}O_{SMOW} = 1.0100\delta^{18}O_{NBS28} + 10.00.$$

The fractionation factor for the mineral-water system is based on the equation:

$$\alpha\text{mineral-water} = \frac{^{18}O/^{16}O\ \text{mineral}}{^{18}O/^{16}O\ \text{water}}$$

The value of α is determined by the equation:

$$1000\ln\alpha = A(10^6T^{-2}) + B,$$

with A and B specific constants for individual minerals and temperature ranges.

SIZE DISTRIBUTION

The weight percent quartz for 20 samples was determined by weighing the samples before fusion and by weighing the quartz fractions remaining after fusion. The results of this analysis show that the Antrim contains 49 ± 6% quartz, whereas X-ray analyses by Ruotsala (1979) indicate that the quartz content is 53 ± 16%. This is almost 2X the amount of quartz in the average shale (Shaw and Weaver, 1965). The size distribution of quartz was determined by weighing the sized quartz separates. The results are that >90% of the quartz is in the <500 mesh (25μm) size fraction (see Table 1). In contrast, the majority of quartz in most shales is in the silt-size fraction (Blatt, Middleton and Murray, 1972). The distribution in the Antrim may be real, or polycrystalline quartz in the larger size fractions may have been broken down during the fusion technique. If it is an artifact of the fusion technique, it indicates that the polycrystalline quartz has impurities which are removed during the fusion, and this removal then allows the quartz to disaggregate. This situation could occur if, as we have concluded, most of the quartz is authigenic. The authigenic quartz might have included clay particles which would dissolve during the fusion and thereby allow the quartz to disaggregate. Alternatively, the size distribution may be real and due to a large authigenic component in the <500 mesh size fraction. Yeh and Savin (1977) studied authigenic quartz in Tertiary shales from the Gulf Coast and found that most of the authigenic quartz is in the <1μm size fraction.

PETROGRAPHY

Petrographic Analysis

Petrographic analysis of the quartz in thin section and quartz separates was undertaken to determine the nature of the quartz (monocrystalline, polycrystalline, inclusions) and its relationship to other components of the rock.

The greatest amount of polycrystalline quartz (67%) is in the 325 mesh size fraction (see Table 2). In the 500 mesh size fraction, 49% of the quartz is polycrystalline. No attempt was made to point count finer size fractions although qualatative estimates indicate that there is less polycrystalline quartz in the <500 mesh size fraction. The amount of polycrystalline quartz we observed is much greater than the amount found in other shales in the >10μm size fraction (1.9 to 9.6%, Blatt and Schultz, 1976). It is extremely unusual to find such a large ratio of polycrystalline quartz in any sediment.

In thin section (Figure 2) the quartz occurs as laminations, lenses and discrete grains. However, because most of the quartz is smaller than the thin section thickness, most useful information comes from quartz separates. These separates show a high percentage of polycrystalline quartz in the >500 mesh size fractions. The polycrystalline quartz is probably authigenic because there is no apparent source for such a large amount of detrital polycrystalline quartz.

The polycrystalline quartz exhibits various stages of subgrain development (Figure 3), which is probably related to coalescence of authigenic tabular plates of quartz which may be observed with the SEM. Most grains are microcrystalline with diffuse intragranular boundaries (subgrains) defined by strongly undulose extinction (right-hand grain, Figure 3). Also common in the shale are grains (left-hand grain, Figure 3) with a few large crystals surrounded by much smaller crystals. These subgrains (crystals) are defined by diffuse undulose extinction and are characterized by the SEM as areas of plate coalescence which produce a smooth, coherent surface. The central grain (Figure 3) has a segmented birefringence with the boundaries of the subgrains defined by strongly undulost lines which disperse through the grain upon rotation. This type of grain has a surface morphology which exhibits extensive coalescence of

Size Fraction	Total Quartz Percent Per Size Fraction	Total Weight Percent Quartz
Antrim Shale*		
200 mesh	0.6 ± 0.6	49.5 ± 6.3
325 mesh	1.8 ± 1.5	52.6 ± 15.7**
400 mesh	1.6 ± 1.1	
500 mesh	2.0 ± 1.3	
<500 mesh	94.0 ± 2.0	
Radiolaria, 78H30		
125 mesh	12.2	47.1
200 mesh	10.6	
325 mesh	7.7	
400 mesh	2.6	
500 mesh	1.1	
<500 mesh	65.8	
Ohio Shale		
200 mesh	0.1	45.1
325 mesh	3.2	
400 mesh	3.2	
500 mesh	2.8	
<500 mesh	90.7	

* 20 Samples

** 234 Samples (Routsala, 1979)

Table 1. Quartz percentages of the Antrim, USGS Devonian Black Shale standard (SDO-1), and Antrim sample 78H30 (unusual because it contains radiolarian fossils).

Size Fraction	Percent Monocrystalline	Percent Polycrystalline
Antrim Shale*		
325 mesh	33 (±13)	67
400 mesh	48 (±16)	52
500 mesh	51 (±10)	49
Ohio Shale**		
325 mesh	41	59
400 mesh	49	51
500 mesh	61	39

Feldspar content 6.5% ± 3.7, average for all samples and size fractions except <500 mesh.

* 14 Samples

** 1 Sample

Table 2. Monocrystalline and polycrystalline percentages of the total quartz based on 200-300 grain point counts.

Figure 2. Thin section photomicrograph of typical Antrim Shale. Quartz (light areas) appears as laminations, lenses and discrete grains. Scale bar = 2 mm.

plates. Presumably, plates with a similar crystallographic orientation are more likely to coalesce than grains with different orientations. The undulose extinction is probably due to the slightly different crystallographic orientation of the coalesced plates. This type of undulose extinction is distinctly different than that observed in strained quartz which is due to a strained lattice and occurs as a band sweeping across the grain upon rotation.

The polycrystalline quartz contains abundant inclusions of pyrite. Pyrite is a common authigenic mineral in the Antrim and, as in Recent organic rich sediments, may have formed early in the diagenesis of the Antrim.

Small lenses of coal within the Antrim are the remains of the terrestrial plant Callixyon. Samples of coal contain approximately 20% quartz by weight. The quartz is unique and differs from any other observed forms of quartz in the Antrim. The quartz is polycrystalline with smooth boundaries and the grains are inclusion free; a dramatic contrast to the other polycrystalline quartz. Tasmanites (marine algal spores) are common in the Antrim, and they too have been silicified with polycrystalline quartz.

Chert nodules, 2-35 mm, were found in a sample from the Blocher Shale in Indiana which is equivalent to the Antrim. Microprobe analysis of the inclusions within the nodules indicate that quartz replaced calcium sulfate. The chert nodules are composed of fibrous quartz radiating inward from the outer edge of the nodule with the megaquartz development towards the center. Inclusions of calcium sulfate are limited to the megaquartz. Pseudocubic quartz development is common within the nodules.

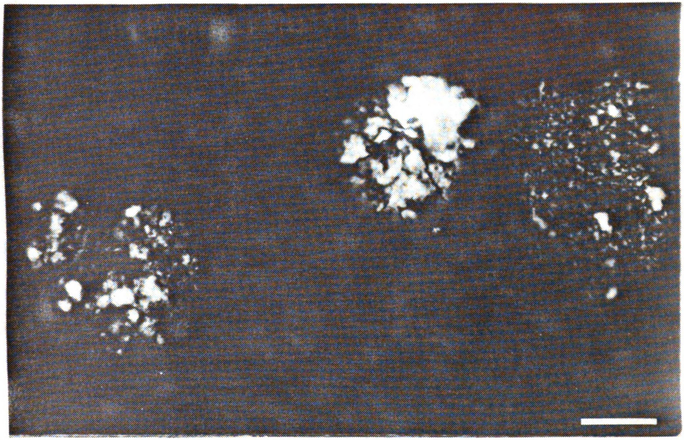

Figure 3. Polycrystalline quartz types in the Antrim. The grain to the right is the most common type, characterized by pin point birefringence. The center grain has large areas of diffuse extinction. The grain to the left has characteristics which are intermediate between the other two. Scale bar = 40 μm.

Recrystallized radiolaria are abundant in one sample. The interior structures are often not preserved. The centers of the radiolaria are normally filled with fibrous quartz.

Scanning Electron Microscope

Scanning electron microscopy was used to observe surface features on the quartz grains. Solution and abrasion features are expected on detrital grains and smooth crystal faces are expected on authigenic surfaces. The surface features on radiolaria, monocrystalline and polycrystalline quartz were observed. On all grains, the most common feature is a prism with a basal pinacoid. The prisms grow laterally (a_1 - a_3 plane) and not along the c-axis. Growth perpendicular to the a_1 - a_3 plane is by irregular stacking of plates. This form of quartz (tabular plates) has not been described previously and is interpreted to be authigenic.

Radiolaria are uncommon, but their surface features were studied because they are undoubtedly authigenic. Radiolaria have recrystallized into two quartz morphologies, the common prismatic form and hexagonal plates. Figures 4 and 5 show the plate morphology. The plates form a very irregular surface but at high power the surface of the individual plates is seen to be smooth and free of solution or abrasion features. Also, the plates merge or coalesce to form smooth surfaces which are larger than the individual plates (Figure 5).

Polycrystalline quartz surfaces are mostly coalescing hexagonal plates .25-5 μm in diameter. Figure 6 is a typical polycrystalline grain. The various smooth versus rough areas represent different degrees of plate coalescence. Figures 7 and 8 are high magnification photographs of polycrystalline grains, and these clearly show the predominant plate-like

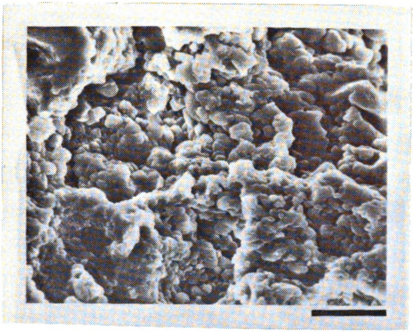

Figure 4. Radiolaria surface showing hexagonal plates. Scale bar = 10 μm.

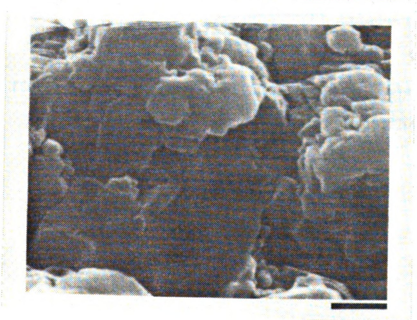

Figure 5. Radiolaria surface at higher magnification. Individual plates coalesce to form a smooth surface. Scale bar = 1 μm.

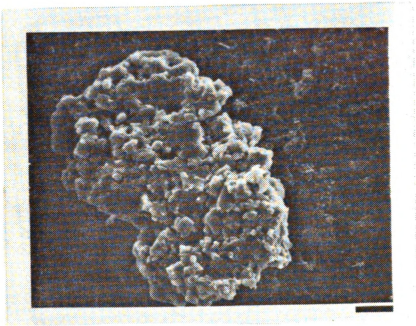

Figure 6. Polycrystalline quartz similar to grain on the left in Figure 1. The large smooth areas have an undulose extinction. The smaller plates give a pin point extinction. Scale bar = 10 μm.

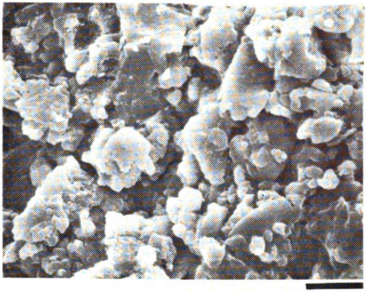

Figure 7. Irregular surface of a polycrystalline grain. The individual plates are difficult to discern even at 3000X. Scale bar = 5 μm.

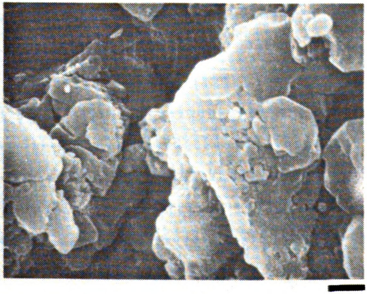

Figure 8. Higher magnification (10,000X) of the center portion of the surface shown in Figure 7. Hexagonal plate morphology is apparent. Scale bar = 1 μm.

morphology of the polycrystalline quartz surface. This morphology is the same hexagonal plate morphology observed on the radiolaria.

Monocrystalline quartz grains also have a hexagonal plate surface morphology. Figures 9 and 10 show several stages in the development of monocrystalline quartz surface textures. On the right side of the grain, there are discrete plates which coalesce toward the lower left (Figure 10). The left side of the grain has a ridge and swale topography (Figure 9) which has been interpreted by Krimsley and Doornkamp (1973, Figure 5) to be a solution-precipitation feature.

The most common surface feature observed is the tabular plates. This is interpreted to be authigenic, but has not been previously reported. The smooth surface and hexagonal outline is consistent with their being authigenic. It is difficult to explain why growth along the c-axis has been stunted; perhaps the crystals were poisoned.

The alternative interpretation for the formation of the tabular plate surface texture is that it represents grain solution. Direct solution of quartz crystals may accentuate crystal faces and one could argue that the hexagonal plates are a dissolution feature. However, conspicuously absent are scales, irregular shaped pits, solution crevasses, upturned cleavage plates, and V-shaped etch pits. These features have been attributed to a solution origin by Krinsley and Doornkamp (1973, Figures 89-106). Therefore, the smooth surfaces of the hexagonal plates and the lack of known solution features favors the interpretation of the tabular plates as being a precipitation feature.

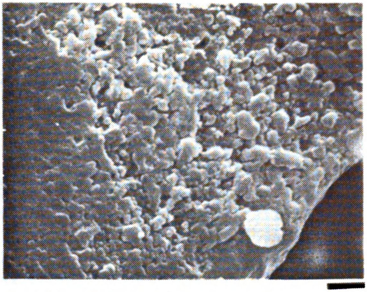

Figure 9. Monocrystalline quartz with hexagonal plates which appear to merge into a smooth surface on the left side of the grain. Scale bar = 1 μm.

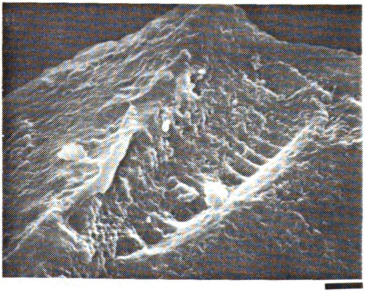

Figure 10. Monocrystalline quartz with coalescing plates on the right surface and ridge and swale topography (also authigenic) on the left. Note the obvious surface coating in the lower left which produces the ridge and swale topography (arrow). Scale bar = 2 μm.

ISOTOPE ANALYSIS

Oxygen isotope data show that authigenic and detrital quartz in the Antrim have similar $\delta^{18}O$ values. SEM and petrographic analysis support the observation that much of the quartz is authigenic in origin. Polycrystalline to monocrystalline ratios indicate a mixing of authigenic and detrital quartz within the >500 mesh size fractions. Isotopic data from the quartz samples as well as the carbonate samples are interpreted to indicate a diagenetic evolution of the authigenic phases and an isotopic lightening of the pore fluids.

Oxygen isotope analysis of both the quartz and carbonate material were used to determine the $\delta^{18}O$ value of the pore fluid. The equation for low temperature quartz-water fractionation was developed by Knauth and Epstein (1976):

$$1000 1\alpha = 3.09 \times 10^{6} T^{-2} - 3.29.$$

The carbonate material was microprobed and X-rayed; all samples except the Ellsworth Shale were ankerite. The equation used for ankerite-water fractionation was the one developed for dolomite by Matthews and Katz (1977):

$$1000 1\alpha = 3.06 \times 10^{6} T^{-2} - 3.24.$$

Oxygen isotopes were determined for five quartz samples, each containing five size fractions; 200, 325, 400, 500 and <500 mesh. There was no correlation between monocrystalline to polycrystalline ratios and isotopic values so the 200-500 mesh values were combined. Hydrofluoric acid etchings were performed on two samples. The silicification history was also defined by analyzing two cherts from underlying formations, quartz from the coal, and a silicified evaporite nodule from the Blocher Shale.

The carbonate within the shale is diagenetic and was used to further define and support the lightening of the pore fluids suggested by the isotopically light quartz values. The carbonate samples were analyzed for both $\delta^{18}O_{SMOW}$ and $\delta^{13}C_{PDB}$. Carbonate concretions, bioturbated green shale, Blocher Shale (surrounding the chert nodule) and the Ellsworth Shale were analyzed. To avoid contamination from the high organics, the green shale of the Antrim was used instead of the black shale. With the Blocher sample, organics were not a problem due to a higher amount of carbonate material.

The isotopic data for the quartz and carbonate material are listed in Table 3.

Quartz Material

The >500 mesh size fraction of the quartz has a $\delta^{18}O$ of 18.4 ‰ ± 1.7; based on 21 analyses. The <500 mesh size fraction has a $\delta^{18}O$ of 20.6 ‰ ± 1.5; based on seven analyses. The difference between the two groups is not statistically significant at the 90% confidence level. In the Ohio Shale, the >500 mesh has a $\delta^{18}O$ of 18.6 ‰ and the <500 mesh a $\delta^{18}O$ of 19.9 ‰.

The Antrim sample, 78H30, which contained abundant recrystallized radiolaria has the highest $\delta^{18}O$ value, 26.4 ‰. The 325 and 400 mesh, which contained radiolaria fragments, yielded values of 25.5 ‰ and 21.1 ‰, respectively.

Hydrofluoric acid etchings were done in an attempt to identify any isotopic layering of the quartz. This procedure has been used to identify the isotopic value of quartz overgrowths (Yeh and Savin, 1977). The isotopic values of the etchings are seen in Table 3 as the value of the quartz remaining and the quartz removed. The isotopic value of the quartz

Sample	$\delta^{18}O_{SMOW}$* Quartz	$\delta^{18}O_{SMOW}$ Removed	$\delta^{18}O_{SMOW}$** Carbonate	$\delta^{13}C_{PDB}$
Whiskey Creek Chert	30.1 ‰			
Charlevoix Limestone Chert	27.1			
>500 Mesh Antrim Shale	18.4 ± 1.7			
<500 Mesh Antrim Shale	20.6 ± 1.5			
>500 Mesh Ohio Shale	18.6			
<500 Mesh Ohio Shale	19.9			
<500 Mesh Blocher Shale	24.4			
Radiolaria 200 Mesh	26.4			
Blocher Chert Nodule	23.0			
Quartz in Coal	21.9			
HF Etching				
Radiolaria 200 Mesh	26.4			
25% removed	26.4	26.4 ‰		
50% removed	26.2	26.7		
75% removed	26.2	26.5		
93% removed	22.4	26.8		
77H8 325 Mesh	18.6			
50% removed	18.1	19.1		
70% removed	17.9	18.9		
90% removed	17.8	18.8		
77H8 <500 Mesh	20.6			
76% removed	15.9	22.1		
96% removed	16.9	20.7		
77H30 <500 Mesh	21.4			
70% removed	20.4	21.8		
93% removed	19.1	21.6		
Carbonate				
Ellsworth Shale			26.7 ‰	-2.0 ‰
Blocher Shale			26.3	-9.4
Antrim Green Shale			23.7	-7.2
Concretion, Inner			23.9	-11.3
Concretion, Middle			23.3	-12.2
Concretion, Outer			22.6	-10.1

* Value ± .3

** Value ± .1

1 and 2 are cherts from Devonian limestones below the Antrim.

Table 3. Oxygen and Carbon Isotopic Data.

removed is calculated using mass balance considerations. The isotopic values of the quartz removed are very uniform throughout all the etching intervals.

Two samples with two size fractions each were etched. A radiolaria sample (200 mesh) was etched to determine the isotopic ratio of the fibrous quartz infilling, the intervals were 25%, 50%, 75% and 93% weight material removed. There was little isotopic variation from the original value of 25.4 ‰ until the final etching (93%), which has an isotopic ratio of 22.4 ‰. The quartz removed has an average isotopic composition of 26.6 ‰. The <500 mesh fraction of the radiolaria sample was etched in two stages, 70% and 93%. The isotopic values of the quartz removed were 21.8 ‰ (70%) and 21.6 ‰ (93%).

The results of the other etching indicate that the $\delta^{18}O$ of most of the authigenic and detrital quartz are similar (see Table 3). Sample 77H8 has 70% polycrystalline quartz in the 325 mesh size fraction and petrographic examination of the etched material showed that the polycrystalline quartz was preferentially removed. However, even with 93% removed, there was still some polycrystalline quartz present. Whereas the exact $\delta^{18}O$ of the polycrystalline and monocrystalline quartz cannot be determined, the polycrystalline must be approximately 19 ‰. The <500 mesh size fraction contains more than 95% of the quartz in the shale. In this size fraction there is a clear distinction between the $\delta^{18}O$ of the quartz removed and that which remains. The data are interpreted to indicate the presence of authigenic quartz in the <500 mesh fraction, with a $\delta^{18}O$ in the range of 20 to 22 ‰.

The authigenic quartz within the coal fragments has $\delta^{18}O$ value of 21.9 ‰. The silicified evaporite nodule from the Blocher Shale has a

$\delta^{18}O$ value of 23.0 ‰ which is not significantly different from the quartz in the <500 mesh size fraction of the Blocher ($\delta^{18}O$ = 24.0%). The Blocher Shale sample and the Blocher chert samples were collected at different localities in northern Indiana.

Two chert samples from underlying formations were also analyzed. The chert nodule from the Charlevoix Limestone has an isotopic value of 27.1 ‰. A layered chert from the Whiskey Creek Formation, which directly underlies the Antrim, has a $\delta^{18}O$ of 30.1 ‰.

Carbonate Material

For all carbonates, both oxygen and carbon isotopes were analyzed. The Ellsworth Shale dolomite has a $\delta^{18}O$ of 26.7 ‰ and a $\delta^{13}C_{PDB}$ of 2.0 ‰. The ankerite surrounding the chert nodule in the Blocher has a $\delta^{18}O$ of 26.3 ‰ and a $\delta^{13}C_{PDB}$ of -9.4 ‰. The ankerite of the bioturbated green shale has a $\delta^{18}O$ of 23.7 ‰ and a $\delta^{13}C_{PDB}$ of -7.2 ‰.

The concretions occur in both black and green layers of the Antrim Shale. The concretions have undergone three stages of carbonate diagenesis. The center of the concretions is still recognizable shale, but has an increase in ankerite content. The ankerite has a $\delta^{18}O$ value of 23.9 ‰ and a $\delta^{13}C_{PDB}$ of -11.3 ‰. The next stage is the development of bladed ankerite, which can extend over a meter in length. This ankerite has a $\delta^{18}O$ of 23.3 ‰ and a $\delta^{13}C_{PDB}$ of -12.2 ‰. Following the blade development there was a period of carbonate dissolution. This is shown by cavity development in both the center and bladed portions of the concretions. These cavities are filled with small crystals of ankerite, which is considered the final stage of carbonate diagenesis. This ankerite has a $\delta^{18}O$ value of 22.6 ‰ and a $\delta^{13}C_{PDB}$ value of -10.1 ‰. The light carbon of the carbonate material indicates that the $CO_3^{=}$ was derived from organic decomposition (Curtis, 1978).

DIAGENETIC MODEL BASED ON OXYGEN ISOTOPES

In order to interpret the $\delta^{18}O$ values of the authigenic quartz and ankerite, it is necessary to know either the temperature or $\delta^{18}O$ of the water from which the minerals precipitated. There is no independent check on the $\delta^{18}O$ of the water, but the temperature can be reasonably estimated. One way to estimate the maximum temperature is from estimated maximum burial depths and reasonable geothermal gradients.

The thickness of the preserved sediments within the Michigan Basin indicate that the Antrim was buried to a depth of approximately 1400 meters (Stratigraphic Column, Michigan Geological Survey; Strutz, 1978; Chung, 1973). This is considered a maximum depth of burial as most samples were collected from the flanks of the basin. Assuming a geothermal gradient of $2^{o}C/100$ m and a surface temperature of $30\text{-}35^{o}C$, maximum burial temperature would be $60^{o}C$. A second method of estimating the maximum temperature is from vitrinite reflectance. The reflectance of two samples was measured and both have mean-random reflectance values of 0.46% with a standard deviation of 0.02. The data indicate a level of organic maturity (LOM) of approximately 7.3. LOM is dependent on time and temperature, however, given the relatively shallow depth of burial, a maximum temperature of $50^{o}C$ is reasonable (Hood and others, 1975). Using $50^{o}C$ as a maximum and assuming the diagenesis occurred from temperatures as low as $30^{o}C$ up to $50^{o}C$, an ordering of diagenetic events can be constructed. There is some independent data which supports the ordering of the events. For instance, the chert is the Blocher Shale replaces ankerite and $CaSO_4$, therefore the carbonate diagenesis occurred prior to silicification.

The isotope values for the quartz and carbonate (Table 4) can be interpreted to indicate a gradual isotopic lightening of the pore fluids in the Antrim throughout its diagenetic history. It is assumed that the earliest diagenetic events are those with the isotopically heaviest waters. The carbonate concretions follow this evolution; the outer portion is 0.7 ‰ lighter than the inner portion of the concretion. Most of the quartz diagenesis occurred after (lighter water) the carbonate diagenesis. The quartz infilling of the radiolaria did, however, preceed the carbonate concretion. The radiolaria infilling and radiolaria outer shells show a change in $\delta^{18}O$ of 4 ‰ of the quartz which corresponds to a lightening of the pore fluids of almost 2 ‰.

The Blocher samples have $\delta^{18}O$ values of 23-24 ‰ and are interpreted to indicate formation from pore fluid with a $\delta^{18}O$ in the range of -5.5. Our data are inadequate to allow us to relate this directly to the diagenesis in the Antrim. The quartz in the coal is undoubtedly authigenic, and it has a $\delta^{18}O$ = 21.9 ‰. Assuming that the quartz formed after deposition, it is interpreted to have formed from a water with a $\delta^{18}O \approx -6.5$ ‰.

The last portion of the diagenetic history is defined by authigenic quartz. The outer radiolaria shells, discussed earlier, have an isotopic value of 22.4 ‰. Recrystallization probably occurred in a water with a $\delta^{18}O$ of -6.0 ‰ at 40°C.

The final diagenetic quartz phases are inferred from the etching experiments. The authigenic portion of the <500 mesh quartz has an average isotopic composition of approximately 21.5 ‰. Corresponding pore fluids have an isotopic value of -6.8 ‰, again at 40°C. The authigenic (polycrystalline) quartz of the >500 mesh fraction has an

Diagenetic Stages	$\delta^{18}O_{SMOW}$ Quartz	$\delta^{18}O_{SMOW}$ Carbonate	$\delta^{18}O_{SMOW}$* Water	Temp. ^{o}C
Ellsworth Shale		26.7 $^{o}/oo$	-3.7 $^{o}/oo$	$30^{o}C$
Blocher Shale		26.3	-4.2	30
Radiolaria, Quartz Infilling	26.4 $^{o}/oo$		-4.2	30
Concretion, Inner		23.9	-4.3	40
Antrim Green Shale		23.7	-4.5	40
Concretion, Middle		23.3	-4.9	40
Blocher Chert and Shale	23.0		-5.5	40
Concretion, Outer		22.6	-5.6	40
Radiolaria, Outer Shells	22.4		-6.0	40
Coal	21.9		-6.5	40
Etched <500 Mesh	21.5		-6.8	40
Polycrystalline >500 Mesh	18.5		-9.7 -7.7	40 50

* Carbonate ± .1
Quartz ± .3

Table 4. Diagenetic History and Pore Fluid Evolution.

isotopic value of approximately 18.5 ‰. This final quartz precipitated from a water which had a $\delta^{18}O$ of -9.7 ‰ assuming 40°C, or -7.7 ‰ at 50°C. This indicates a total change of at least 3.5 ‰ and possibly 5.5 ‰ in the waters from which various types of authigenic quartz precipitated.

DISCUSSION

The preceeding data and observations were presented in order to demonstrate the presence of authigenic quartz in the Antrim. Alternative interpretations should be considered. Silicification of Tasmanites is evidence of in situ quartz authigensis, but most of the presumed authigenic quartz occurs as individual polycrystalline or monocrystalline grains. Could it be detrital? A detrital origin suggests a very unusual source region, but then this is a very unusual shale. Petrographically, the polycrystalline quartz is chert-like as opposed to igneous or metamorphic quartz. Therefore, one major source would have to be a chert. The Devonian novaculites of Arkansas, Oklahoma and Texas come to mind but, like most other cherts, their $\delta^{18}O$ values are much higher ($\delta^{18}O_{SMOW} \approx$ 28-32 ‰, Knauth and Epstein, 1976) than that of the polycrystalline quartz in the Antrim. There are no possible sources of the polycrystalline quartz. The unusually high concentration of quartz also makes a detrital origin unlikely.

The <500 mesh fraction contains most of the quartz in the Antrim. The quartz in this size fraction is too fine grained for accurate petrographic analysis, but most of it appears to be monocrystalline. SEM analysis shows features interpreted to be authigenic, but they might be interpreted otherwise. The $\delta^{18}O$ value of the <500 mesh quartz falls in the range of 19-21 ‰ which is the same as the quartz in most Paleozoic shales (Churchman and others, 1976). Churchman and others (1976) interpret that quartz as being detrital so one might argue that most of the quartz in the Antrim is detrital. However, the authigenic quartz in the >500 mesh size fraction has $\delta^{18}O$ values ~ 19 ‰ and this means that the authigenic and detrital quartz in the Antrim may be isotopically indistinguishable. This further complicates the question of the origin of quartz in mudrocks. Perhaps much of the quartz is formed in the mudrocks as opposed to igneous or metamorphic rocks.

The isotopic data are interpreted to indicate diagenesis in pore fluids which are isotopically lighter than sea water and which become isotopically lighter by approximately 3.5-5.5 ‰ throughout the diagenetic history. This isotopically light water is difficult to rationalize with the presumed marine origin of the shale. The only explanation seems to be the Antrim remained a hydrologically open system during diagenesis, allowing isotopically lighter and lighter pore fluids to migrate through.

The hexagonal plate morphology observed with the SEM is also interpreted as authigenic, but this feature has not been previously reported. Nondispersive energy analysis of the plates shows they are quartz, but the unique morphology remains unexplained.

The origin of the quartz is also an enigma. The smectite-illite transformation may generate large volumes of Si^{4+} and there may have been a biogenic silica source, but these hypotheses are extremely difficult to test.

CONCLUSIONS

The Antrim Shale contains abundant authigenic quartz with an isotopic composition within the range of quartz in most Paleozoic shales. Evidence for the authigenic origin of the quartz is: 1) the Antrim has approximately 2X the quartz content of most shales, 2) most of the quartz in the Antrim is in the <500 mesh size fraction, 3) there are chert nodules, silicified coal and silicified Tasmanites, 4) most of the >500 mesh size quartz is polycrystalline and contains pyrite inclusions, and 5) the quartz grains in all size fractions commonly have hexagonal plates on the surface and these plates are interpreted to be authigenic.

The $\delta^{18}O$ values for the authigenic quartz range from +26.4 to 18.5 ‰ SMOW. Because the Antrim was never deeply buried, the range in oxygen isotopes is interpreted to indicate a gradual isotopic lightening of the pore fluids. The $\delta^{18}O$ of the quartz and ankerite are interpreted to indicate a change in pore fluid composition from -3.7 ‰ to -7.7 to -9.7 ‰.

The authigenic quartz in the Antrim has a $\delta^{18}O$ in the range of detrital quartz in shales. Perhaps much of the detrital quartz is derived from authigenic quartz that has been cycled from previous shales.

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