# Isotopic and fluid inclusion evidence for hydrothermal alteration: Mississippian Rival Subinterval, Indian Hill Reservoir, North Dakota.

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The Indian Hill Reservoir of northwestern North Dakota lies just west of the structural centre of the Williston basin (Figure 1) and produces primarily from the Mississippian Rival Subinterval of the Mission Canyon Formation. The Rival subinterval within the reservoir is composed of pisoidal and algal subtidal shoals which lie just to the west of evaporite deposits of the same age. Porosity within the reservoir is attributed to a combination of syndepositional and diagenetic fabrics.
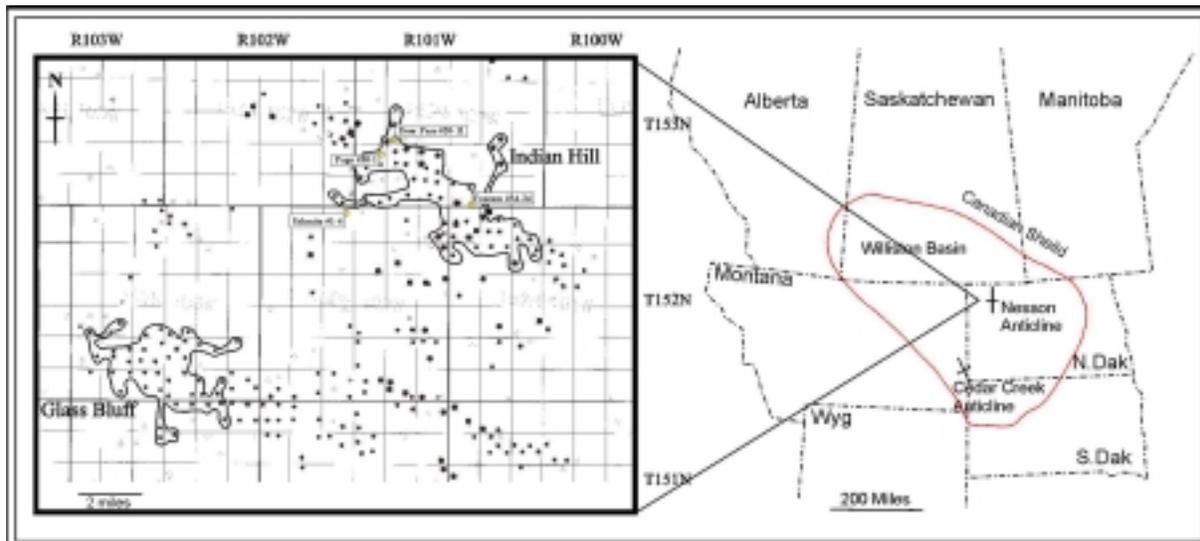
Figure 1. Location map of the Williston Basin and Indian Hill Reservoir.

Cores of the Mississippian Rival Subinterval from four different wells were analysed from the Indian Hill Reservoir. Both thin and thick (100-200µ thick) sections were produced from Rival Subinterval core. Thick sections were cut into ~1cm^2 slices and fluid inclusions were analysed through a microscope on a heating stage. Forty-three carbonate samples of pisoids, algal grains, skeletal fragments, hardgrounds, micrite matrix, and calcite spar were carefully separated from the cut blocks using a dental drill. Approximately 10mg of powdered

carbonate samples were accurately removed. Powdered samples were then prepared for the liberation of CO_2 gas, for C and O isotope analyses in the mass spectrometer (masses 44,45, and 46).

Petrographic analysis of the Rival Subinterval reveals distinct primary grains and several generations of cement. Materials with a syndepositional origin (pisoids, algal grains, skeletal fragments, hardgrounds, and micrite matrix) and those with a burial origin (cavity lining and filling cements) were analysed separately. Stable isotopes and fluid inclusion data are used in conjunction with petrographic criteria to determine a paragenetic sequence. The hydrological state of the system through time can be determined using the O-isotopic signature and homogenisation temperature of each cement generation. The O-isotopic signature of carbonate cement is a direct reflection of the O-isotopic composition of the water it formed from at a particular temperature. Therefore, fluid sources and migration mechanisms may be inferred from changes or consistency in isotopic and homogenisation signatures of the carbonate cements.

The $\delta^{18}O$ values from Rival Subinterval syndepositional material, pisoids, algal grains, skeletal fragments, hardgrounds, and micrite matrix, are –3.3 to –0.37‰; $\delta^{13}C$ values are +2.41 to +4.83‰. The $\delta^{18}O$ values of diagenetic calcite spar from the Rival Subinterval are –4.75 to –1.3‰; $\delta^{13}C$ values are +2.88 to +5.31‰. These values are displayed on figure 2.

Fluid inclusion results from equant calcite show temperatures that range from 95 to 160°C. Homogenisation temperature determination of syndepositional carbonate grains; pisoids, skeletal fragments, hardgrounds and micritic matrix are not possible due to their small grain sizes and lack of visible fluid inclusions.
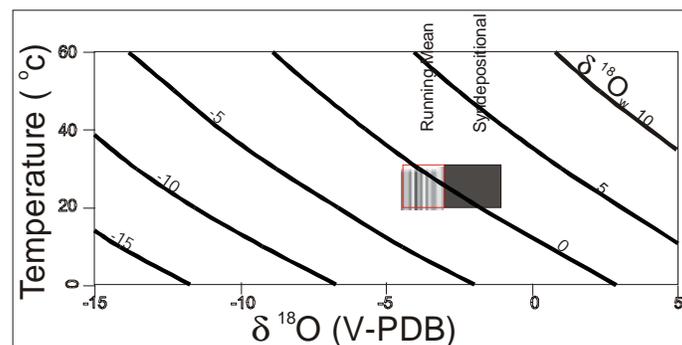
ISOTOPIC SIGNATURE AND PALEOTEMPERATURE OF SYNDEPOSITIONAL COMPONENTS

Rival Subinterval syndepositional components have a relatively narrow range of $\delta^{18}O$ and $\delta^{13}C$ values (figure 2). Their isotopic signature should therefore reflect the isotopic composition of the marine water from which they precipitated. Assuming a depositional temperature of 20 to 30°C, the $\delta^{18}O$ of the water in isotopic equilibrium with the calcite can be calculated using the relationship of O'neil (1969). This equation is for the partitioning relationship of isotopes between a solid and water as a function of temperature. As shown in figure 3 this relationship indicates that these syndepositional components formed from waters with $\delta^{18}O$ from –2 to +4‰ (SMOW). Viezer (1999) determined mean $\delta^{18}O$ values for syndepositional Mississippian shell secreting organisms from –4.3 to –3.2‰. Assuming the same temperature range of deposition (20 to 30°C) and using the relationship of O'neil (1969) this indicates Mississippian seawater to have global $\delta^{18}O$ values from –3 to +2‰ (SMOW).

δ ¹⁸O vs δ ¹³C for Mississippian Rival Subinterval Carbonates
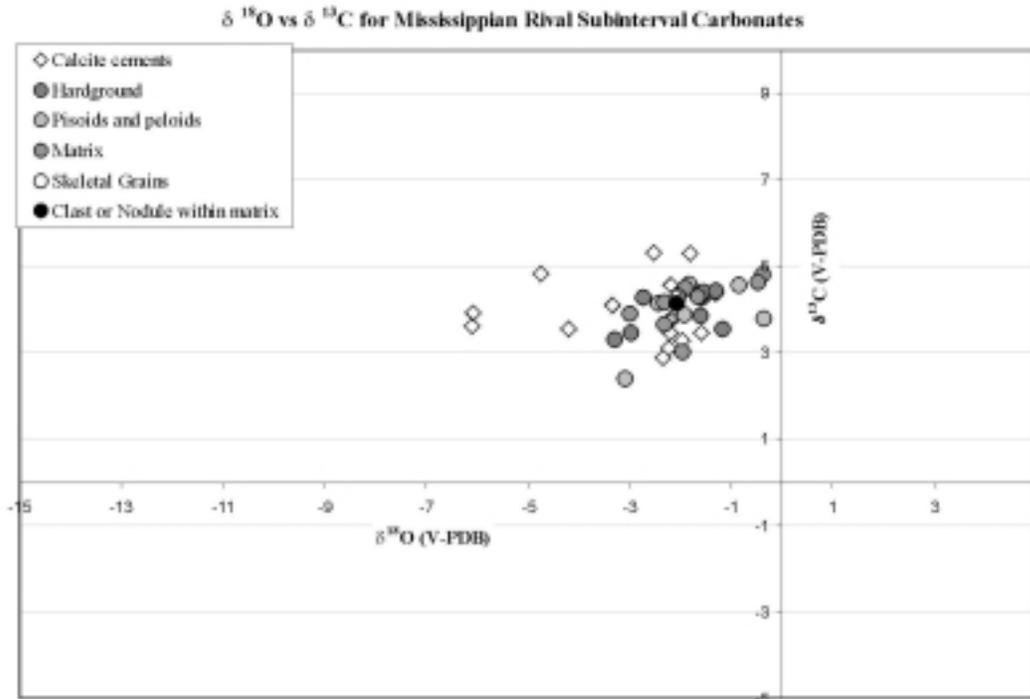
Figure 2. Isotopic Composition of Mississippian Rival Subinterval Carbonates. Samples from Indian Hill Reservoir in northwestern North Dakota.

The $\delta^{18}O_w$ value of local Mississippian seawater from which Rival Subinterval carbonates precipitated was enriched relative to the $\delta^{18}O_w$ value for global Mississippian seawater (Viezer, 1999), as shown on figure 3. A likely explanation for this enrichment is that evaporation of Mississippian seawater on the shallow shelf under semi-arid conditions results in higher salinities and ^{18}O enrichment in the remaining water. Evaporation of marine water could increase the $\delta^{18}O$ of the water by up to 6‰ (Knauth and Beeunas, 1986). The water from which Rival Subinterval syndepositional carbonates precipitated appears to be evaporated Mississippian seawater with an original $\delta^{18}O$ value between –3 to +2‰, which increased locally to –2 to +4‰ during evaporation.   This evaporated seawater is also responsible for the precipitation of the evaporites just to the east.

Figure 3. The oxygen isotope composition of Rival Subinterval evaporated seawater at 30°C. The aqueous fluid curves were determined using the equation of O'neil (1969).

C-ISOTOPIC SIGNATURE AND TEMPERATURE OF EQUANT CALCITES

The $\delta^{13}C$ values analysed for equant calcites (+2.88 to +5.31‰) closely resemble those determined for syndepositional carbonates (+2.41 to +4.83‰). Such a resemblance may be attributed to the dissolution and re-precipitation of syndepositional components during diagenesis. Petrographically, pisoids, algal grains, and skeletal fragments can be seen partially dissolved along their grain margins or totally recrystallized. Upon re-precipitation of dissolved syndepositional components the $\delta^{13}C$ is preserved in equant calcites, because of the relatively low concentration of HCO_3^- in diagenetic fluids.

O-ISOTOPIC SIGNATURE AND TEMPERATURE OF FORMATION OF EQUANT CALCITE CEMENTS

Values of $\delta^{18}O$ and temperature from syndepositional carbonate and equant calcite samples are shown on figure 4. The $\delta^{18}O$ values of equant calcite cements are consistent with or deviate only slightly from the $\delta^{18}O$ of the syndepositional carbonates. However, homogenisation temperatures determined for equant calcite (95-160°C) exceed reasonable temperature estimates for syndepositional carbonates (20 to 30°C). The similarity of $\delta^{18}O$ values between equant calcite and syndepositional cements can be explained by the persistent increase in temperature of the system and by the continuous introduction of isotopically heavier aqueous fluids as illustrated by the arrows on figure 4.

Figure 4, shows that maintaining the syndepositional O-isotopic signature of precipitating equant calcite whilst increasing temperature to between 95°C and 120°C requires a 10 to 15‰ increase in the $\delta^{18}O_w$ of aqueous fluids within the system. The consistency in $\delta^{18}O_c$ between syndepositional carbonates and equant calcite appears to be caused by both an increase in ^{18}O and a higher temperature of formation water. Not only do the average temperatures determined for the formation of equant calcites exceed syndepositional temperatures they are also higher than maximum temperatures expected for this formation given its depth of burial and assuming a geothermal gradient of 30°C/km. To effectively raise the temperature within the system heat must have come from an alternative source. Equant calcite cements appear to have formed from waters with very different oxygen isotope composition than Mississippian seawater at elevated temperature.
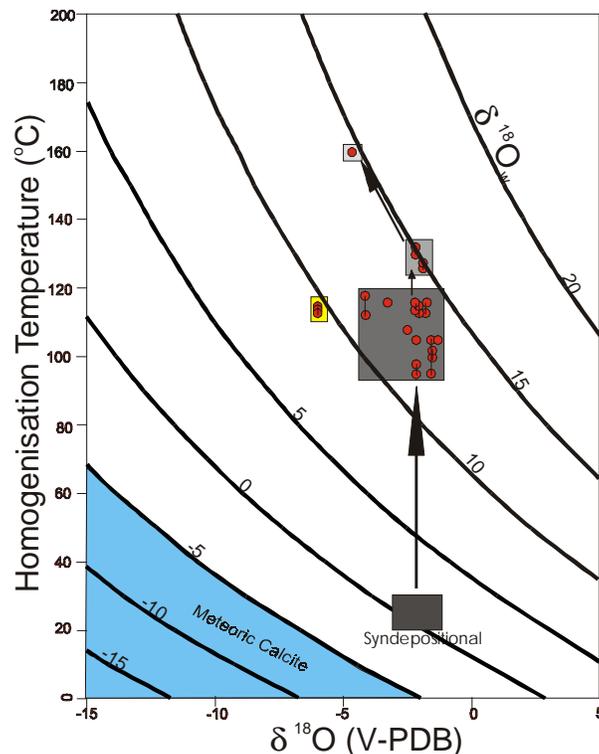
Figure 4. Diagram showing the relationship between temperature (°C) and the isotopic composition of Calcite and Water. Curves were calculated using the equation of O'Neil etal. (1969). Mississippian meteoric calcite are shown to have precipitated from waters with $\delta^{18}O_w$ values between –5 and -20‰ (Smith and Dorobek, 1993).

O-isotope composition of Fluids

Water occurring in the pore spaces and fractures of rocks in the subsurface may originate from several different sources such as: meteoric water; connate seawater; dehydration water; residual evaporite brine or hydrothermal brine.

Meteoric water, derived from precipitation and crustal weathering, has relatively low $\delta^{18}O_w$ values due to the kinetic and/or equilibrium isotope effects involved with the processes of evaporation and precipitation. Meteoric water diagenesis has been invoked to explain certain calcite cements in related Mississippian carbonates from Montana. Smith and Dorobek (1993), interpret meteoric waters to have formed equant calcite cements in these nearby Mississippian carbonates. Temperatures, at which these calcites were believed to have formed, range between 0°C and 60°C. Oxygen isotopes values for these cements range from –13.8 to –2.6‰. These cements are distinctly different from those reported here for the Rival Subinterval equant calcites as shown on figure 4. Oxygen isotopes from meteoric water have very negative $\delta^{18}O_w$ (-5 to –20‰).

Connate water is trapped with marine sediments upon deposition and remains out of contact with the atmosphere since the time of deposition. Therefore the oxygen isotope values of the connate seawater trapped within pore space is
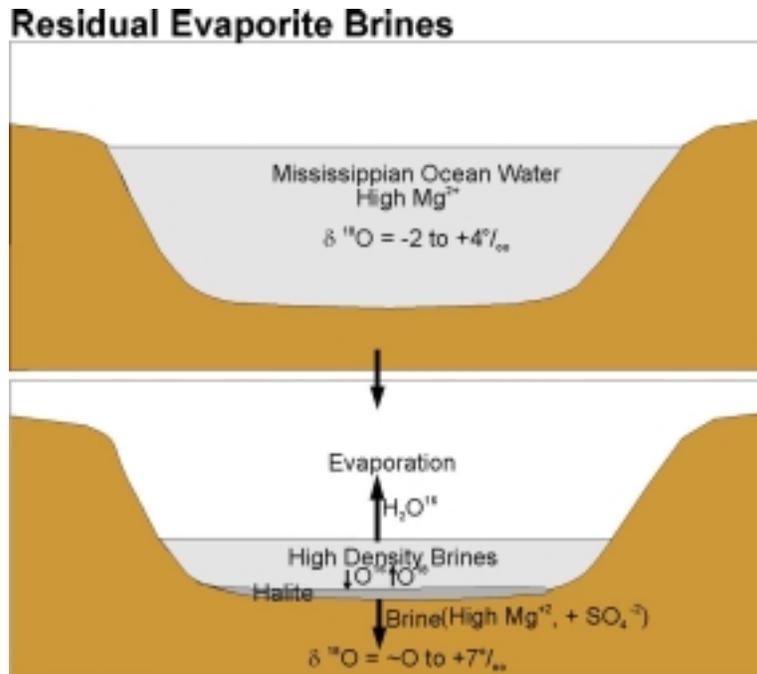
representative of the $\delta^1 O_w$ of the ancient seawater from which the rock formed. Local Mississipian connate water should have a $\delta^1 O_w$ between −2 to +4‰.

Dehydration water, derived from the dehydration of hydrous solid phases (typically gypsum) during diagenesis (Kharaka and Carothers, 1986), has higher $\delta^1 O_w$ values. The ^{18}O enrichment is a result of the accumulation of ^{18}O in the liquid as evaporates, as shown schematically in figure 5. This water becomes the hydration water of the precipitated evaporite. When gypsum is buried and the temperature rises above 60°C it is transformed to anhydrite, it's dehydrated counterpart. Fluids released by this process are saturated with respect to $CaSO_4$ (Melvin 1991). Evaporated local Mississippian waters appear to have $\delta^{18}O$ of about 4‰.
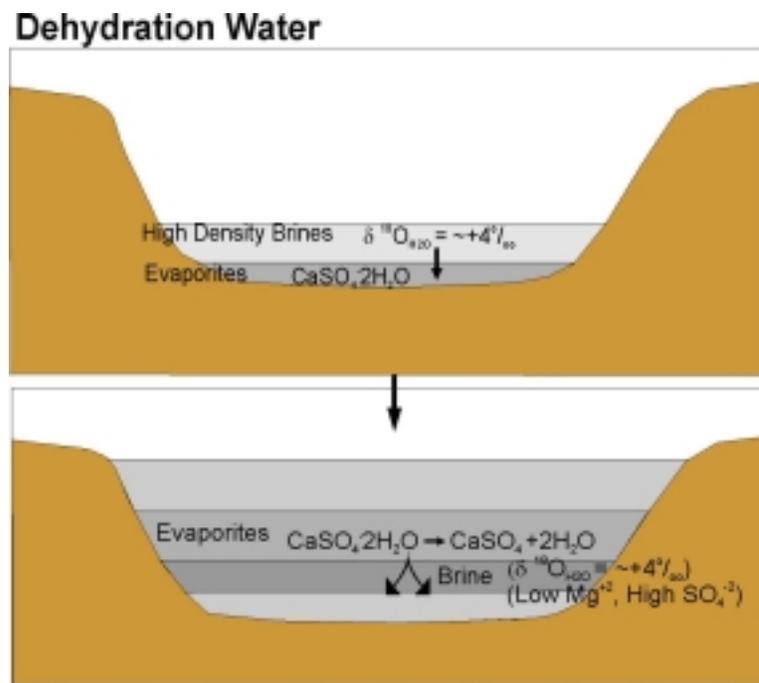
Figure 5. Diagrammatic sketch showing the process by which isotopically enriched brines are derived from the dehydration of evaporites in the stratigraphic column.

Residual evaporite brines form when hypersaline brines eventually become dense enough, by perpetual evaporation, to displace connate waters and seep downwards through permeable carbonates on the seafloor (Melvin, 1991). When $CaCO_3$ and gypsum precipitate in hypersaline environment, the solution density can become as high as 1.2 gm/cc (at Halite saturation). The Mg/Ca ratios of the remaining brines rises, and the dense Mg-enriched solutions can sink through underlying platform sediments (figure 6). Knauth and Beeunas (1986), indicate $\delta^{18}O$ enrichment of these types of residual evaporites of up to 6‰.

Residual Evaporite Brines

Figure 6. Diagramatic sketch showing the process by which isotopically enriched brines are derived from residual evaporite brines.

Hydrothermal brines, form from the alteration of meteoric, diagenetic, or residual evaporite fluids in systems that have low water/rock ratios and elevated temperatures (Faure, 1991). In hydrothermal systems the oxygen isotope composition of the water can increase significantly. Isotope fractionation factors decrease with increasing temperature, thus $\delta^1 O_w$ moves closer to the isotope composition of the rocks as equilibrium temperature rises (Faure, 1991). Waters in modern hydrothermal systems are enriched by up to 12‰ relative to the source waters (Truesdell et al., 1980). Therefore hydrothermally altered waters may obtain $\delta^1 O$ values in the range of +10 to +20‰, depending on the source.

Origin of Equant Calcite

Several periods of high evaporation occurred throughout the Paleozoic within the Williston basin. Main evaporitic formations include the Devonian Prairie, Mississippian Charles, and the Triassic Opeche, and Pine Salt (Gerhard, 1982). All of these formations reflect hypersalinity events in the centre of the basin at the time of their deposition.

The high densities of these types of brines would allow them to sink into the lowest parts of the basin, and possibly into the crystalline basement along deep-seated faults (Fritz and Frape, 1982). The Precambrian basement beneath the Williston Basin is a mosaic of tectonic blocks which were subsequently reactivated throughout the Phanerozoic (Shurr, 1995). In the southern and western Williston Basin, horizontal and vertical displacements have produced zones of fracture, permeability and porosity along the block margins (figure 7).

Consequently block margins influence vertical fluid migration (Shurr 1995), and may act as a pathway for the migration of these heated dense brines.
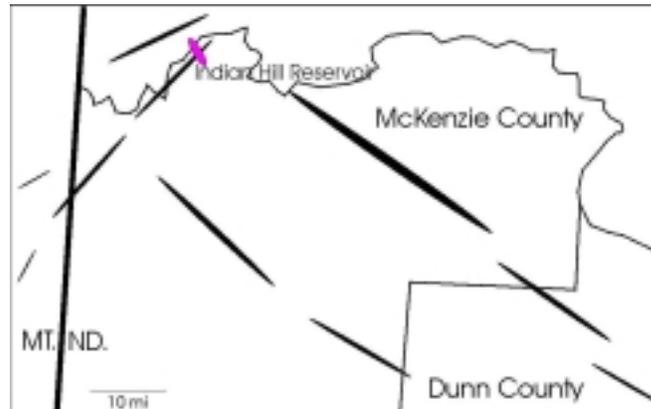
Figure 7. Regional lithosphere blocks, outlined by thick lines, near the Indian Hill Reservoir. Modified from Shurr (1995).

Modification of diagenetic and residual evaporite brines, under elevated temperatures caused by water/rock interaction with basement silicates would produce hydrothermal brines enriched in ^{18}O up to +12‰. Because of the strong density difference, brines would effectively flush out any pre-existing formation waters and mixing would not occur (Domenico and Robbins, 1985). Hydrothermal fluids would begin to ascend. Raising the temperature of the brines effectively reduces their density allowing them to ascend the stratigraphic column, along block margins, and precipitate cements in overlying formations.

CONCLUSIONS

Petrographic relations, isotopic data and homogenisation temperatures indicate that equant calcites of the Rival Subinterval precipitated during diagenetic events post dating syndepositional components. The $\delta^{13}C$ values of equant calcites are derived from re-precipitation of dissolved syndepositional, Rival Subinterval components. High $\delta^{18}O$ values in fluids that precipitated equant calcite evolved from heating highly saline waters derived from the dehydration of evaporites and evaporated seawater.

The following processes are proposed to be responsible for creating the high $\delta^{18}O$ of fluids from which equant calcite precipitated.
1) An original seawater source was evaporated,
2) precipitation of evaporites led to reflux of highly concentrated brines to depth
3) these residual evaporite brines may have mixed with dehydration waters produced from the dewatering of evaporites,
4) geothermal heating of brines occurred at depth
5) Isotopic enrichment of brines resulted from water/rock interactions at elevated temperatures,
6) movement of brines occurred upward along fault systems,
7) cements formed from dissolution, re-precipitation.

Continuous increase in the homogenisation temperatures of the equant calcite represents the evolution of circulating fluids caused by the increasing burial of system.

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