Contemporaneous Alteration of Lower Watrous Clastics and the Sub-Unconformity Alteration Zone in Southeastern Saskatchewan: Petrographic and Geochemical Evidence

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Bates, G.S., Kendall, A.C., and Millar, I.L. (2007): Contemporaneous alteration of Lower Watrous clastics and the sub-unconformity alteration zone in southeastern Saskatchewan: petrographic and geochemical evidence: *in* Summary of Investigations 2007, Volume 1, Saskatchewan Geological Survey, Sask. Industry Resources, Misc. Rep. 2007-4.1, CD-ROM, Paper A-7, 10p.

Abstract

Debate regarding the origin and timing of formation of a diagenetically altered zone underlying the sub-Mesozoic unconformity in southeastern Saskatchewan has been ongoing since its discovery in the mid-1950s. This alteration zone forms a regionally extensive caprock to numerous hydrocarbon pools within the area, as porosity and permeability have been occluded by pervasive dolomitization and void-filling anhydrite. Unconformably overlying this alteration zone are redbeds of the Watrous Formation, consisting of red-brown argillaceous siltstones and anhydritic mudstones, generally with a dolomitic cement. Locally, the Watrous redbeds are bound by primary calcite cement and the subjacent alteration zone is absent. The lack of this caprock seal often allows hydrocarbon migration into the overlying basal Watrous, resulting in the reduction of the redbeds to green strata. We use the genetic link between the absence of the alteration zone and dolomitic cement of the Watrous, alongside the relationship between the thickness and extent of the Watrous Formation and alteration zone, to propose a genetic link between the regional presence of the dolomitized zone beneath the unconformity and the dolomitic cement of the immediately overlying redbeds. Strontium isotope ratios are used to suggest a mixing event between more radiogenic waters from the overlying redbeds with less radiogenic upward-migrating fluids, with dolomitization and anhydritization resulting from the amalgamation of these two waters as they meet at the sub-Mesozoic unconformity.

Keywords: *Watrous Formation, redbeds, alteration zone, strontium isotopes, Williston Basin, anhydrite, dolomite, calcite, Mississippian.*

1. Introduction

In the Williston Basin of southeastern Saskatchewan and Manitoba, tilted and eroded Mississippian carbonates and evaporites are unconformably overlain by redbeds of the Lower Watrous Formation (the Amaranth Formation in Manitoba) (Figure 1). Immediately beneath the sub-Mesozoic unconformity is, typically, a 1 to 10 m thick, diagenetically altered zone consisting of pervasively dolomitized carbonates with secondary anhydrite present as void-fillings, partial replacement of dolomite, and near-horizontal veins after gypsum 'satin-spar' (Kendall, 1975). The origin and timing of the diagenetic changes that generated this regional alteration zone are disputed. Fuller (1956) believed the alteration resulted from "weathering" or the action of pre-Watrous brines, therefore occurring before the Watrous redbeds were deposited. Fuzesy (1960), Martin (1966), and Miller (1972) concurred that the alteration zone developed during formation of the unconformity surface. McCamis (1958), however, suggested that the alteration zone formed when brines generated during deposition of Upper Watrous anhydrites (Figure 1) descended through the underlying Watrous redbeds, basing his proposal on the inversely proportional relationship between the thickness of the Watrous redbeds and that of the immediately underlying alteration zone, and on the absence of the alteration zone beyond the geographic limits of the Lower Watrous.

The reciprocal thickness variations of the redbed unit and alteration zone were confirmed by Kendall (1975), who offered an alternative explanation: that alteration occurred during the flow of basinal brines expelled from more central parts of the Williston Basin, after the Watrous redbeds had been deposited. The original pre-Watrous interpretation has been re-introduced by Rott and Qing (2005), who suggested that, prior to the onset of redbed deposition, brines generated in a sabkha or hypersaline lagoonal environment percolated down through the underlying Mississippian strata. Qing *et al*. (2005) used differences between the isotopic composition of primary anhydrites in the Lower Watrous Formation and of primary and secondary anhydrites in Mississippian carbonate

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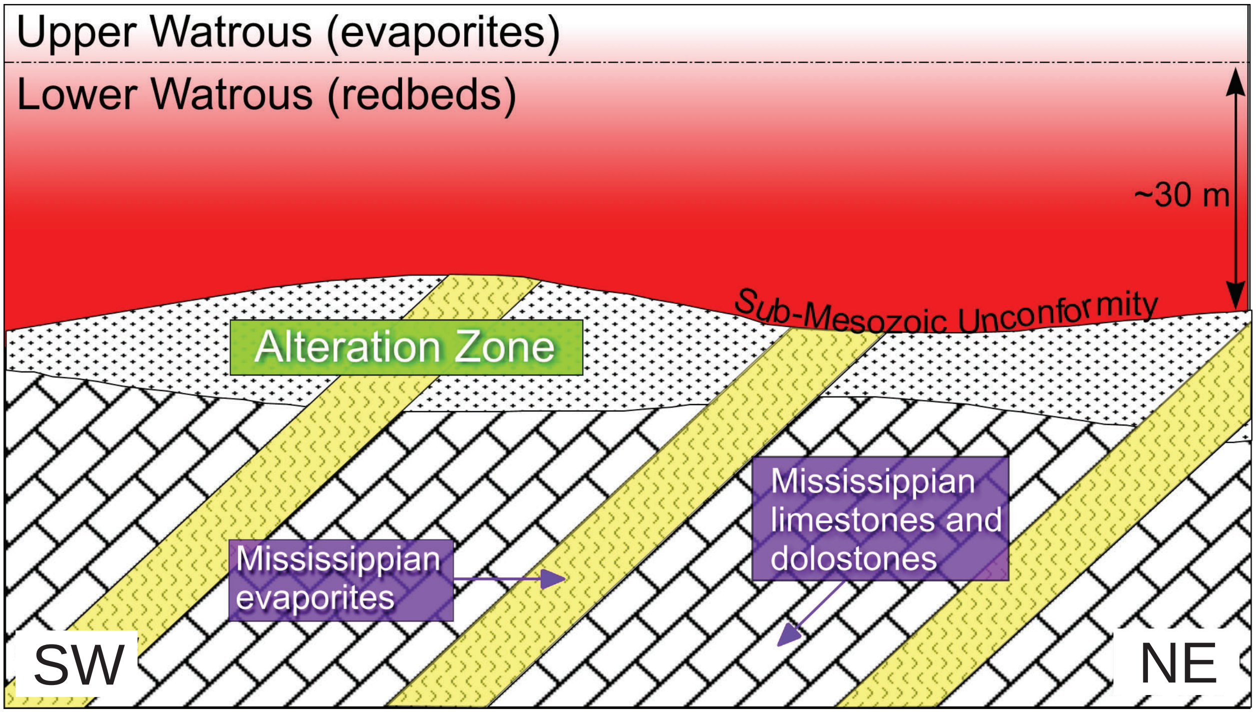

***Figure 1** - Diagrammatic cross section showing relationships of Mississippian and Watrous strata to the regional sub-Mesozoic unconformity.*

units to suggest: 1) a lack of fluid communication between Mississippian reservoirs and the Watrous sediments (*i.e.*, the Watrous has been an effective long-term seal for Mississippian reservoirs) and, as a result of this, 2) the alteration zone was not formed from descending Watrous brines. Our study disputes these conclusions.

Locally, the alteration zone is absent, with green, rather than red, Watrous sediments resting upon non-dolomitized and possibly porous Mississippian limestones. If, at these locations, nodular anhydrites were present in the Mississippian carbonates, these anhydrites may have been calcitized. Kendall (2001) suggested a genetic link between these anomalous features with 1) calcitization of anhydrite occurring at the same time as the alteration formed regionally elsewhere, and 2) hydrogen sulphide liberated from the calcitization reactions migrating upwards causing a reduction of iron pigments in the basal Watrous clastics.

We have re-examined the Fillmore area cores originally studied by Kendall (2001) and have identified cores from other locations where the regional alteration zone is anomalously absent. On the basis of this new information, we now suggest 1) dolomitization of the basal Watrous redbeds and formation of the alteration zone in the underlying Mississippian carbonates was coeval, possibly resulting from a mixing event of waters from above and from beneath the unconformity, and 2) the localized green basal Watrous clastics formed when hydrocarbons were able to gain access to the redbeds, commonly because the alteration zone was absent – reduction of Watrous pigments is thus not the direct result of anhydrite calcitization as was previously thought. One implication of these reassessments is that the basal redbeds and the regional alteration zone have not always acted as an efficient aquitard as Qing *et al*. (2005) have inferred.

2. A Genetic Link between Redbed and Alteration Zone Dolomite

Local and sporadic absence of the alteration zone has been identified (Kaldi and Hartling, 1982; Kendall, 2001; this paper) where either dolomitization or anhydritization of Mississippian limestone has not taken place, or where subsequent dissolution of porosity-occluding anhydrite has resulted in an ineffective caprock seal. The locations of three cores with this common link, but each with differing diagenetic histories, are shown in Figure 2.

In the Cal-Stan Fillmore Province (101/16-16-11-10W2) well, late-diagenetic calcitization of Mississippian anhydrites occurred instead of (but concurrently with) the formation of the alteration zone (Kendall, 2001). In the Maryfield (141/15-18-10-30W1) well, neither an alteration zone nor evidence for late-diagenetic calcitization of Mississippian anhydrites is present. In the 101/12-16-9-33W1 well (Parkman Pool), however, a ‘typical’ alteration zone has been affected by later dissolution of the porosity-occluding anhydrite.

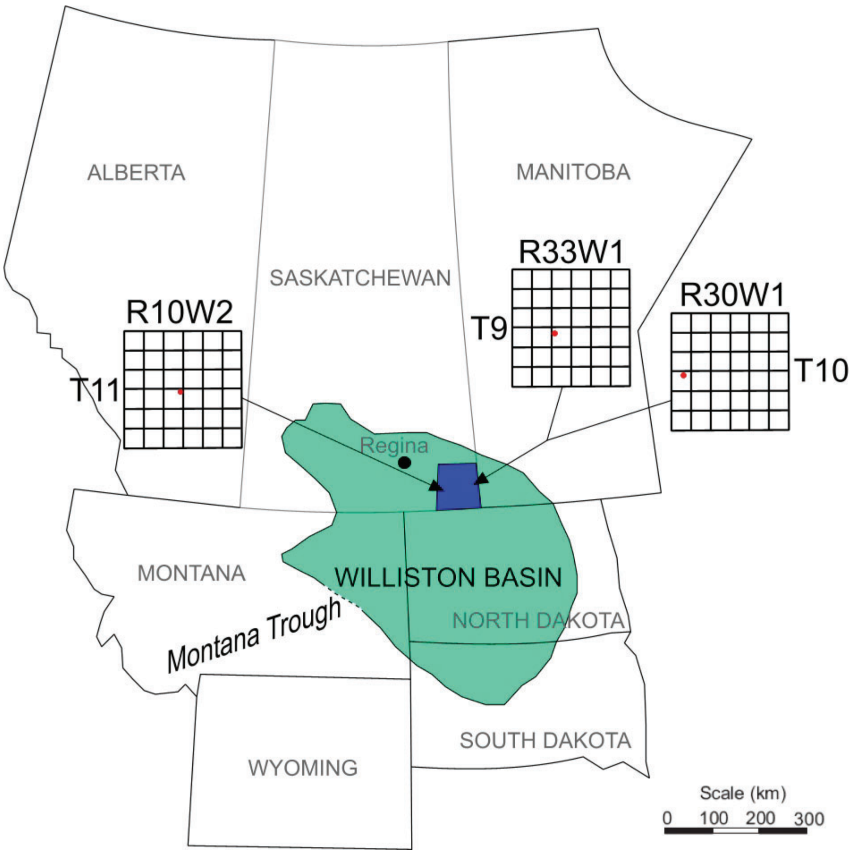

Figure 2 - Geological setting and locations of referenced samples (red dots).

Late-diagenetic calcitization is present in the area defined by Rge. 7W2 to 10W2, and Tp. 10 and 11 (Kaldi and Hartling, 1982; Kendall, 2001). The alteration zone is absent, with calcite and celestite replacing stratigraphic anhydrites. Timing of these diagenetic changes was proposed by Kendall (2001) to be *after* burial of the unconformity, but coeval with the timing of formation of the alteration zone elsewhere. Instead of the usual dolomite-cemented redbeds (Figure 3a), calcareous Watrous sediments are present immediately above the unconformity (Figure 3b). The thickness of calcitic basal Watrous Formation ranges from 1.2 m in the Maryfield 141/15-18-10-30W1 well to over 8.92 m at the Williamson Fillmore 101/1-31-11-10W2 well. In some places, these calcareous sediments are overlain by the more usual dolomitic sediments.

In the Maryfield 141/15-18-10-30W1 well, no alteration zone formed, nor was there any late-diagenetic alteration of Mississippian anhydrites. Immediately beneath the unconformity lies Mississippian limestone with only minor anhydrite cement filling porosity (Figure 4); evidence of horizontal anhydrite veins typical of the alteration zone elsewhere is absent. The basal unit of the Lower Watrous contains a chert and limestone breccia encased within a matrix of reddish brown coarse silt to medium sandstone with a primary calcite cement. The calcite cement did not form by calcitization of dolomite (dedolomitization) because the associated clasts of Mississippian limestones retain their original fabrics and clearly were never dolomitized, and partially calcitized dolomite rhombs or other indications of dedolomitization are completely absent (Figure 3d). This, together with the presence of calcareous Watrous strata overlying Mississippian carbonates (lacking any alteration zone development, but with calcitization of anhydrite) in the Fillmore area, indicates a genetic link between the dolomitization of the alteration zone and the dolomitic cement usually present within the Watrous redbeds. Where dolomitization in the altered zone is absent, so is dolomite in the immediately overlying Watrous sediments, suggesting that those locations where the alteration zone is anomalously absent are sites where dolomitization failed to occur in the uppermost Mississippian carbonates and in the overlying basal Watrous sediments. This further suggests that, when dolomitization has occurred (the usual case), it did so when both the uppermost Mississippian carbonates and the lowermost Watrous sediments could be affected (*i.e*., dolomitization, and formation of the alteration zone, occurred after deposition of the basal Watrous strata). The presence of dolomitized Watrous sediments above the lowermost calcitic interval therefore points to dolomitization having taken place during later Lower Watrous time and, perhaps, during deposition of the Upper Watrous evaporites.

Where a 'typical' alteration zone formed, but has subsequently undergone dissolution of the porosity-occluding anhydrite, as in the Parkman 101/12-16-9-33W1 well, the overlying Watrous strata has the expected dolomitic cement.

3. Formation of Green Watrous "Redbeds"

Reduction of basal Watrous redbeds has been observed where the alteration zone is absent beneath the unconformity surface. The usual red iron oxide coatings on grains have been reduced so that the sediments are now green. This situation occurs at the Manor Pool (Musial, 1995; Blair and Lake, 2002) and in the Fillmore area

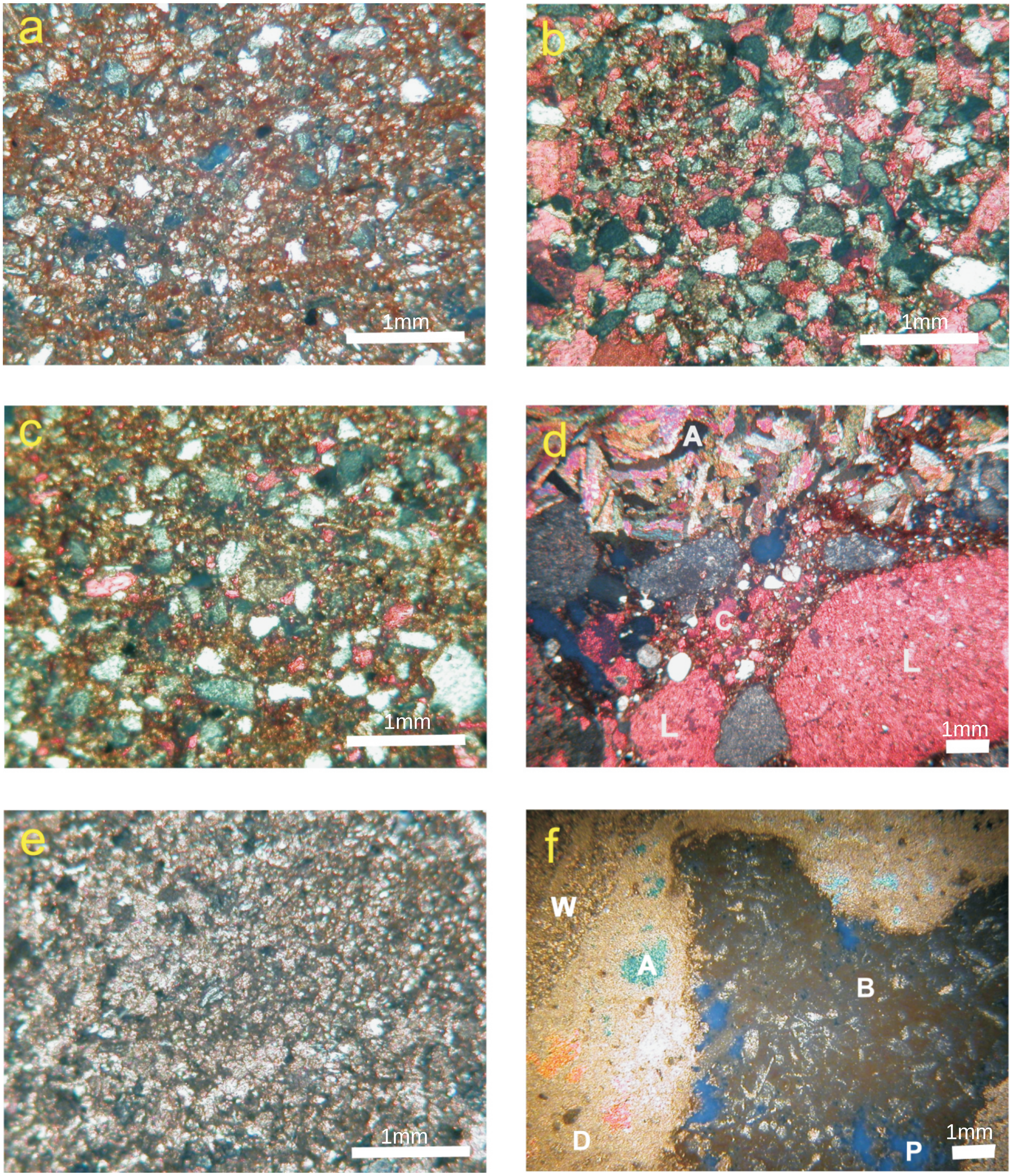

Figure 3 - Photomicrographs of Lower Watrous sediments and alteration zone in uppermost Mississippian strata (cross polars, scale bar 1 mm): a) 'typical' dolomite cement in red Watrous strata, with irregular quartz grains (101/12-34-3-31W1, 1071.37 m); b) calcite cement in reduced, green Watrous strata, alizarin red S stained (101/16-16-11-10W2, 1205.18 m); c) calcite cement in red Watrous strata, with no evidence for earlier dolomite rhombs, alizarin red S stained (101/16-16-11-10W2, 1201.60 m); d) calcite cement (C) in a red siltstone matrix, with limestone clasts (L) from the underlying Mississippian strata and primary anhydrite bleb (A), alizarin red S stained (141/15-18-10-30W1, 890.10 m); e) reduced, dolomitic green Watrous strata (101/12-16-9-33W1, 1056.13 m); and f) alteration zone with bitumen (B) staining dolomite (D) and porosity (P) where replacement anhydrite (A) once existed; with green dolomitic Watrous strata (W) (101/12-16-9-33W1, 1056.54 m).

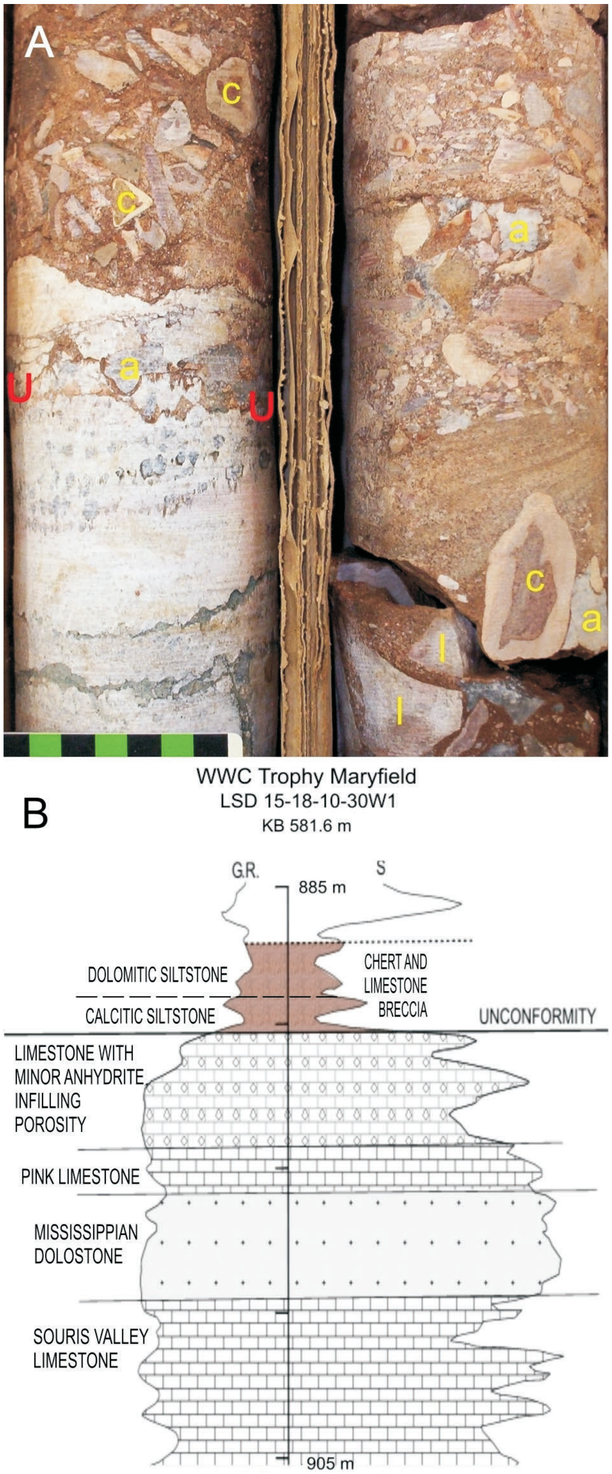

Figure 4 - Sub-Mesozoic unconformity, with redbeds overlying unaltered Mississippian limestone. A) Core slab (141/15-18-10-30W1) showing limestone (l) and chert (c) breccia, with primary, displacive anhydrite blebs (a), above the unconformity (U) at 890.80 m, scale units are 1 cm. B) Well section (141/15-18-10-30W1) identifying lack of alteration zone or calcitization. Abbreviations: G.R., gamma-ray log; and S, sonic log.

(Kendall, 2001) where petroleum has come into contact with the overlying Watrous redbeds. In the Manor Pool, this greening is not related to any late-diagenetic calcitization and therefore cannot be attributed to the redbed pigments reacting with hydrogen sulphide liberated during calcitization of anhydrite. In the Fillmore area, in the 101/16-16-11-10W2 well, the transition from calcitic to dolomitic cement lies many metres above the limit of reduction suggesting these two features are not directly related to each other (Figures 3b and 3c). The only link between them appears to be the absence of an effective caprock seal that has allowed an upward migration of hydrocarbons into the overlying basal (and calcitic) Watrous sediments.

Significant reduction of the redbeds to green strata is typically confined to the lowermost few metres of the Watrous, in close contact with the unconformity. Surdam *et al.* (1993) attributed the migration of oil into the redbeds to redox reactions producing organic acids that generated an increase in porosity within the reduced clastic sediments. This suggests the relative impermeability of the Watrous siltstones at the time that hydrocarbons were migrating.

In the Parkman Pool, the core taken in well 101/12-16-9-33W1 has green Watrous sediments that are directly underlain by an alteration zone which contains an anhydrite vein (after gypsum satin-spar) within pervasively dolomitized limestone (Figure 5). Dissolution of pore-filling anhydrite within the alteration zone (Figure 3f) occurred only after its formation, leading to an increase in permeability. Bitumen coats formerly anhydrite-filled voids in the alteration zone. Because the alteration zone failed to act as an effective caprock, hydrocarbons came into contact with the basal Watrous sediments, which, as a result, were reduced. Importantly, the basal Watrous sediments here are dolomitic (Figure 3e). This evidence is consistent with an interpretation involving 1) coeval dolomitization of the Lower Watrous Formation and the underlying alteration zone, followed by 2) partial dissolution of anhydrite from the alteration zone that allowed 3) hydrocarbon migration into the basal Watrous strata causing a colour change.

If we are correct in our interpretation that the alteration zone (and its dolomitization) formed at the same time as deposition (and early diagenetic alteration) of Lower Watrous sediments, then the absence of anhydrite veins (after gypsum satin-spar) from the Watrous sediments requires explanation. Shearman *et al*. (1972) convincingly argued that satin-spar veins are the product of hydraulic fracturing. This requires the presence of an overlying aquitard, in all probability provided by the overlying Watrous clastics. The lack of veins in this material may be due to the poorly lithified state of these sediments at this time; gypsum was introduced as early diagenetic displacive gypsum crystals rather than as fracture fills. The underlying Mississippian carbonates, on the other hand, were already lithified and failed in a brittle fashion.

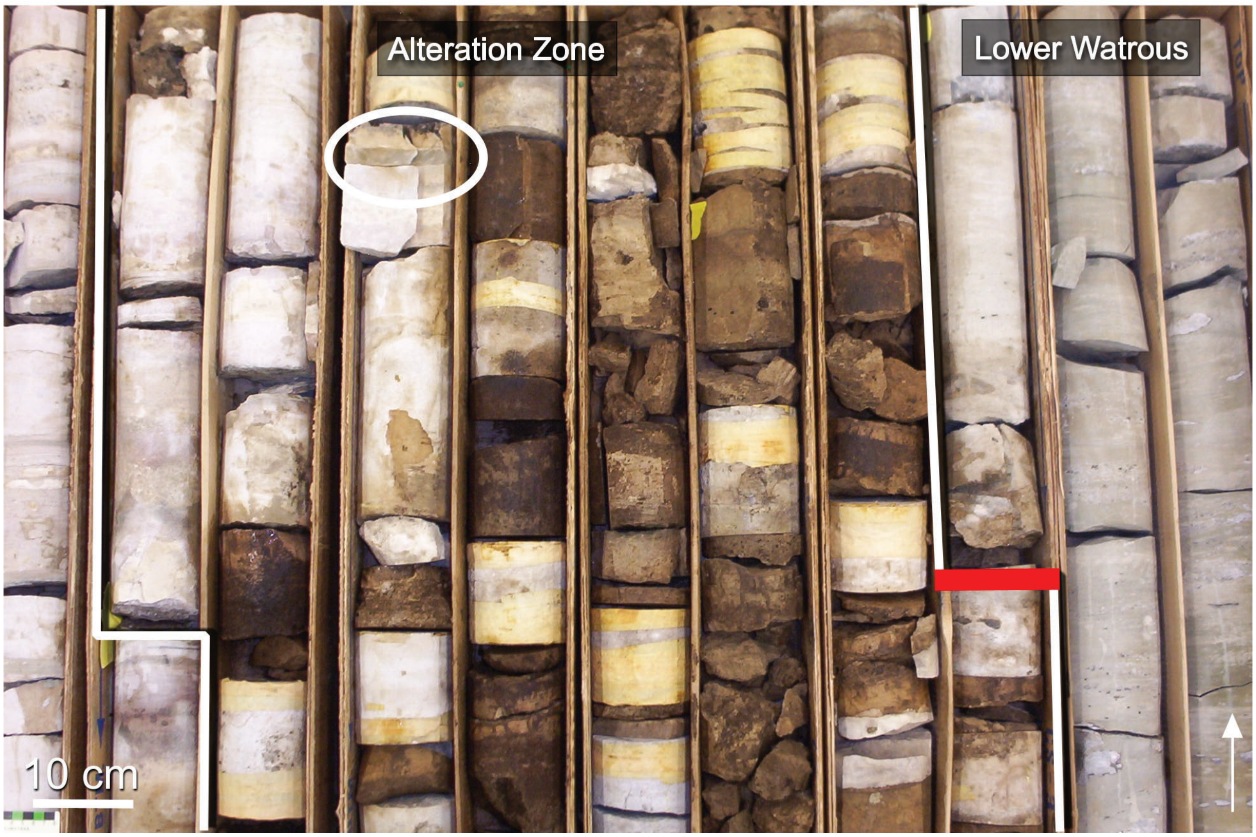

Figure 5 - Core identifying bitumen present within the alteration zone and reduction of the overlying Watrous sediments. Circled is an anhydrite vein after gypsum satin-spar. Arrow marks 'way-up'. Parkman Pool, 101/12-16-9-33W1, KB 652.2 m. Sub-Mesozoic unconformity (red line), 1057 m.

4. Strontium Isotope Evidence

Strontium isotope ratios were determined to assess the relative importance of seawater and other possible fluids (meteoric waters/basinal brines) that may have been responsible for precipitating sulphates within the basal Watrous strata, and the underlying alteration zones. Sulphate samples were taken stratigraphically through a 'typical' core (Parkman Pool, 101/4-34-8-33W1) where red, dolomitic Watrous sediments (containing depositional/early diagenetic anhydrite blebs after displacive gypsum crystals) unconformably overlie an alteration zone, which has been pervasively dolomitized and contains anhydrite void-fillings and horizontal veins after gypsum satin-spar. This alteration zone has an abrupt basal contact with underlying unaltered Mississippian limestones.

Strontium isotope composition was determined on a Thermo-Electron Triton mass spectrometer at the NERC Isotope Geosciences Laboratories, Keyworth, Nottingham, UK. Sixteen replicate analyses of the NBS987 standard gave a value of 0.710280 ±0.000010 (2-sigma). Results are quoted in Tables 1 and 2 relative to a preferred value of 0.710250 for this standard. Four analyses of standard seawater (normalized using the preferred value for NBS987, as above) gave a mean value of 0.709180 ±0.000004 (2-sigma).

Strontium isotope values were obtained from 13 anhydrite blebs in the Lower Watrous, near the unconformity. $^{87}Sr/^{86}Sr$ ranges from 0.708245 to 0.708638 (Table 1), and shows a broad trend of increasing value with core depth. The mean value of all 13 anhydrite blebs is 0.708475 ±0.000195 (2-sigma; Figure 6). Sulphur and oxygen isotope values from similar sulphates obtained by Qing *et al*. (2005) suggested precipitation from Triassic or Jurassic seawaters. If the interpretation of the oxygen and sulphur values is correct, then the anhydrite blebs have more radiogenic strontium than would be expected. This may indicate a hybrid water source for the basal units of the Lower Watrous, with Triassic seawater entering the basin through the Montana Trough (Figure 2), but with meteoric waters or brines introducing a stronger radiogenic input. A further possibility is that the brines that precipitated the original displacive gypsum crystals became more radiogenic by reacting with clastic feldspars within the Watrous sediments. Denison *et al.* (2001) obtained excellent strontium and sulphur isotopic consistency for evaporites of the Upper Watrous Formation (Figure 6). They argued that the mean strontium value of 0.708269

Table 1 - $^{87}Sr/^{86}Sr$ isotopic ratios and core depths from which samples were taken of anhydrite blebs within the Watrous redbeds.

Well (Lsd.)	Core Depth (m)	Distance above unconformity (m)	Watrous Cement	$^{87}Sr/^{86}Sr$	±2 S.E.	Sr (ppm)
111/8-9-10-30W1	856.60	0.70	Dolomite	0.708410	0.000004	919
141/15-18-10-30W1	890.10	0.70	Calcite	0.708245	0.000004	491
101/12-34-3-31W1	1071.30	1.90	Dolomite	0.708374	0.000006	1422
101/6-33-4-32W1	1087.07	2.93	Dolomite	0.708507	0.000006	1281
101/6-33-4-32W1	1090.08	-0.08 (karst)	Dolomite	0.708527	0.000006	853
121/2-11-5-33W1	1130.80	0.20	Dolomite	0.708452	0.000006	841
101/4-34-8-33W1	1056.31	0.39	Dolomite	0.708502	0.000004	935
101/4-34-8-33W1	1056.44	0.26	Dolomite	0.708490	0.000006	1011
101/12-16-9-33W1	1056.13	0.87	Dolomite	0.708455	0.000006	500
101/5-25-2-34W1	1251.97	0.03	Dolomite	0.708458	0.000006	1159
101/11-6-11-8W2	1180.34	0.06	Dolomite	0.708552	0.000004	n/d
101/16-16-11-10W2	1203.05	2.85	Calcite	0.708638	0.000006	1162
101/16-16-11-10W2	1205.80	0.10	Calcite	0.708569	0.000004	1381

Table 2 - $^{87}Sr/^{86}Sr$ isotopic ratios and core depths from which samples were taken; Parkman Pool, 101/4-34-8-33W1, KB 643.7 m.

Depth (m)	Area	Lithology	$^{87}Sr/^{86}Sr$	±2 S.E.	Sr (ppm)
1056.31	Watrous	Anhydrite bleb	0.708502	0.000004	935
1056.44	Watrous	Anhydrite bleb	0.708490	0.000006	1011
1057.55	Alteration Zone	Anhydrite vein	0.708428	0.000006	435
1058.83	Alteration Zone	Anhydrite vein	0.708214	0.000006	304
1060.17	Alteration Zone	Anhydrite vein	0.708220	0.000006	333
1061.14	Alteration Zone	Anhydrite vein	0.708232	0.000006	481

represents a Late Pennsylvanian age for this unit, although it could represent an Anisian or possible Norian stage of the Triassic period (Korte *et al*., 2003). Dow (1967), from a detailed well-log correlation across the Williston Basin, equates the Lower Watrous with the upper part of the Spearfish Formation that rests upon demonstrably Permian strata in the central part of the basin. This would preclude the Lower Watrous from being of Pennsylvanian age.

Strontium isotope values from anhydrite veins in the alteration zone of well 101/4-34-8-33W1 (Table 2) also show the influence of a fluid with a more radiogenic $^{87}Sr/^{86}Sr$ value than if it were reworked Mississippian (Visean) sulphate (Figure 7). Nickel and Qing (2004) obtained similar radiogenic values for anhydrite veins in the alteration zone and suggested the influence of deep-circulating basinal brines as the diagenetic fluid. However, we believe the strontium data from the overlying Watrous sediments (Table 2; Figure 7) suggest the more radiogenic waters could have originated from above the unconformity and penetrated down into the underlying limestone. The explanation suggested by Nickel and Qing (2004) for the radiogenic nature of the sulphates in the alteration zone (contamination from minor amounts of clay minerals and other silicates) is not inconsistent with our view that the diagenetic fluids responsible for the alteration zone originated within the Lower Watrous at the time these sediments were being deposited. Depositional anhydrite from a Mississippian siltstone (101/12-22-2-34W1; sample depth 1287.2 m) also gave a more radiogenic value ($^{87}Sr/^{86}Sr = 0.708129$) than is typical of the Visean (Figure 7), confirming that anhydrites in a clay and/or silicate matrix can give a more radiogenic $^{87}Sr/^{86}Sr$ ratio than the strontium seawater curve. As most of the strontium isotope values obtained for the Lower Watrous suggest more radiogenic formation waters than can be obtained for any Palaeozoic or Mesozoic seawater, the lowest isotopic values should therefore be closest to marine waters. The lowermost value obtained for the Watrous redbeds, $^{87}Sr/^{86}Sr = 0.708245$ (Table 1), falls within seawater values for the Triassic (Figure 6).

The strontium data can be explained by a mixing of two waters beneath the unconformity. Waters with more radiogenic strontium percolated down from the basal units of the Lower Watrous ($^{87}Sr/^{86}Sr = 0.708475 \pm 0.000195$; 2-sigma) into the underlying Mississippian carbonates and mixed with groundwaters which had dissolved Mississippian evaporites of Visean age ($^{87}Sr/^{86}Sr = 0.70765$ to 0.70795; values from McArthur *et al*., 2001). This generated anhydrite veins in the alteration zone with strontium isotope values in between the two, ($^{87}Sr/^{86}Sr = 0.708274 \pm 0.000206$; 2-sigma) for well 101/4-34-8-33W1.

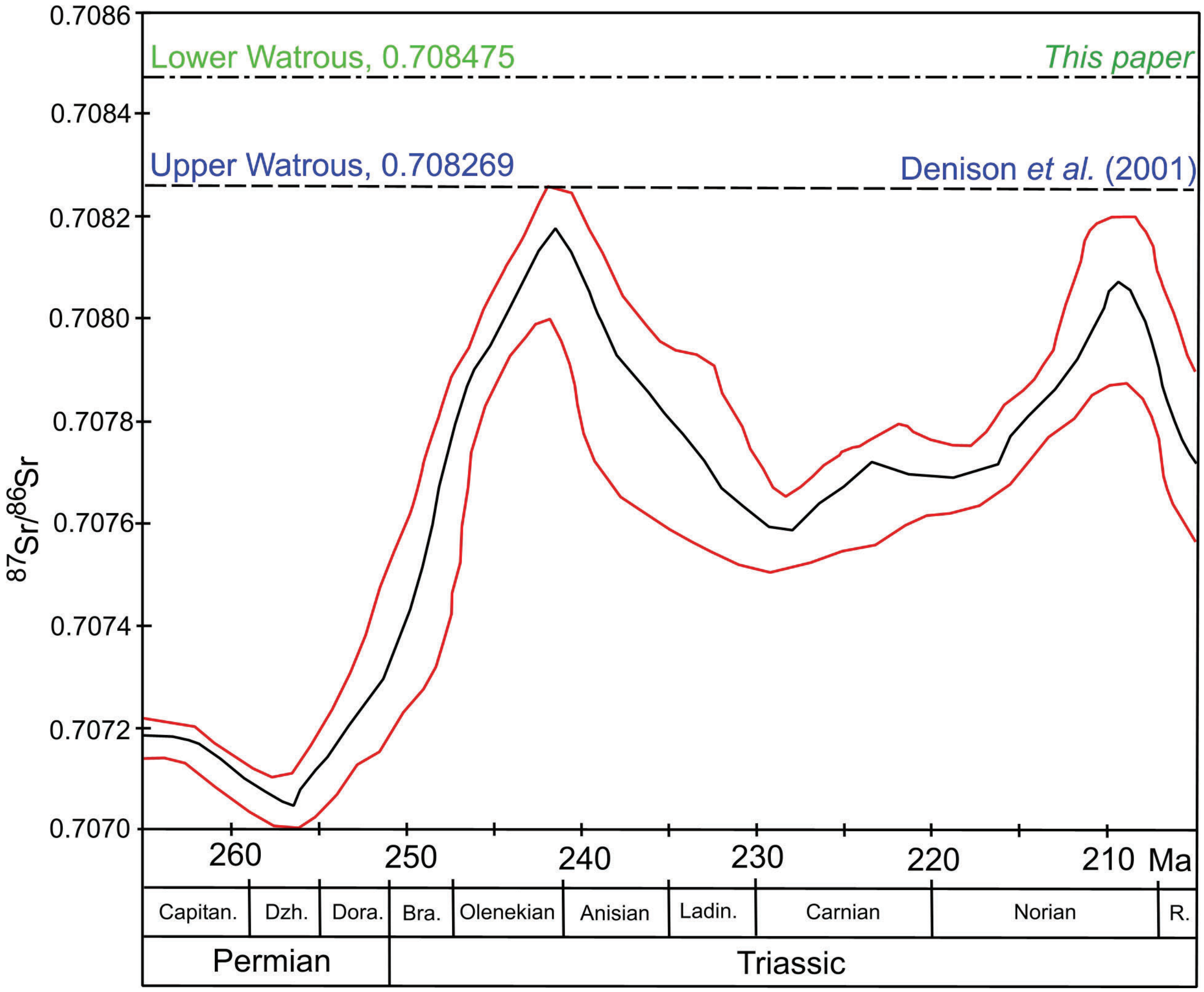

Figure 6 - Strontium curve for Late Permian and Triassic seawater, with mean value (black line) and sample envelope (red lines) (adapted from Korte **et al.*****, 2003).***

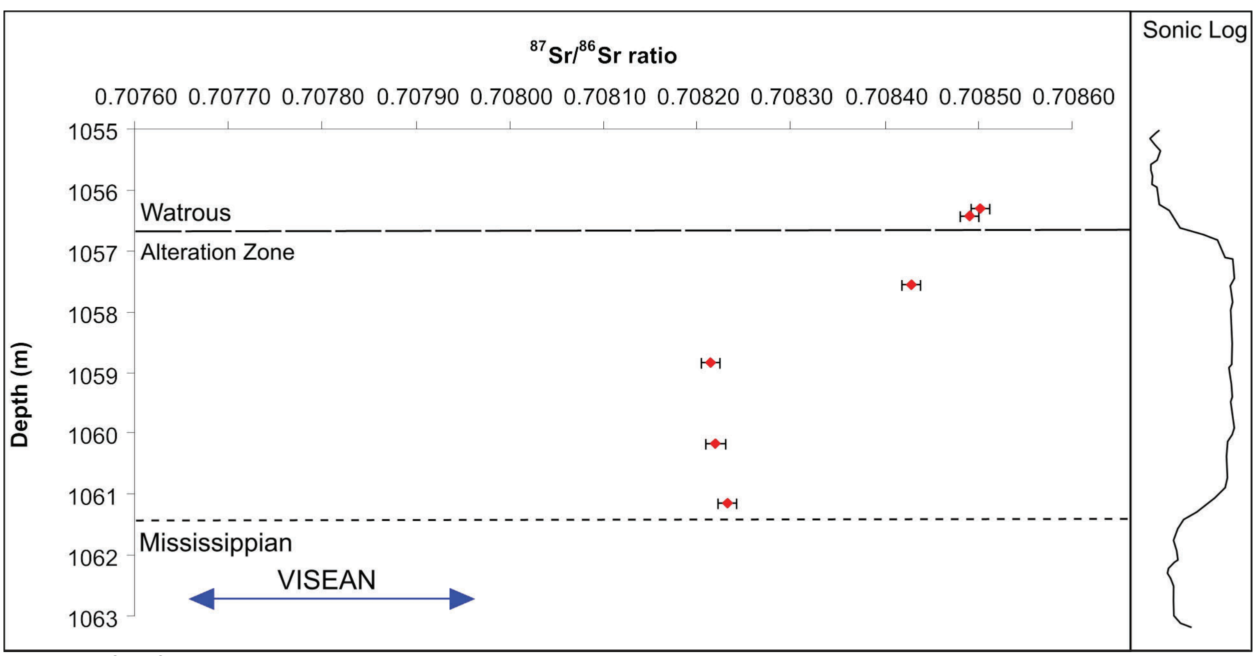

Figure 7 - $^{87}Sr/^{86}Sr$ isotopic ratios, through core 101/4-34-8-33W1, versus depth, with error bars based on external precision (±0.000010 2-sigma). Blue arrow indicating expected $^{87}Sr/^{86}Sr$ values for evaporites of Visean age.

5. Conclusions

We believe there is a genetic link between the dolomite in the basal few metres of the Lower Watrous and that within the alteration zone, a link suggested by the absence of both dolomites in anomalous wells. Greening of the basal Watrous sediments is explicable by reaction with hydrocarbons and is not associated with events related to the formation of the alteration zone and its redbed cover. Geochemical data do not confirm a Pennsylvanian age for the Watrous, but suggest mixing of waters from above and below the unconformity may have occurred which is consistent with the post-unconformity burial age of the alteration zone.

6. Acknowledgments

Staff at Saskatchewan Industry and Resources kindly allowed access to, and sampling from, the core archives. John Lake offered his time and expertise over particularly intriguing cores, and possible interpretations of geochemical evidence were discussed with Julian Andrews, University of East Anglia (UEA). Samples were analyzed for $^{87}Sr/^{86}Sr$ isotopes at NIGL, funded by an isotope research support grant awarded by the NERC Steering Committee. Trace element concentrations were obtained using laser-ablation ICP-MS with the help of Graham Chilvers (UEA). This paper forms part of a NERC-funded Ph.D. by Gemma Bates (grant number NER/S/A/2005/13587).

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