

# Appendix C

## Produced Water Geochemistry

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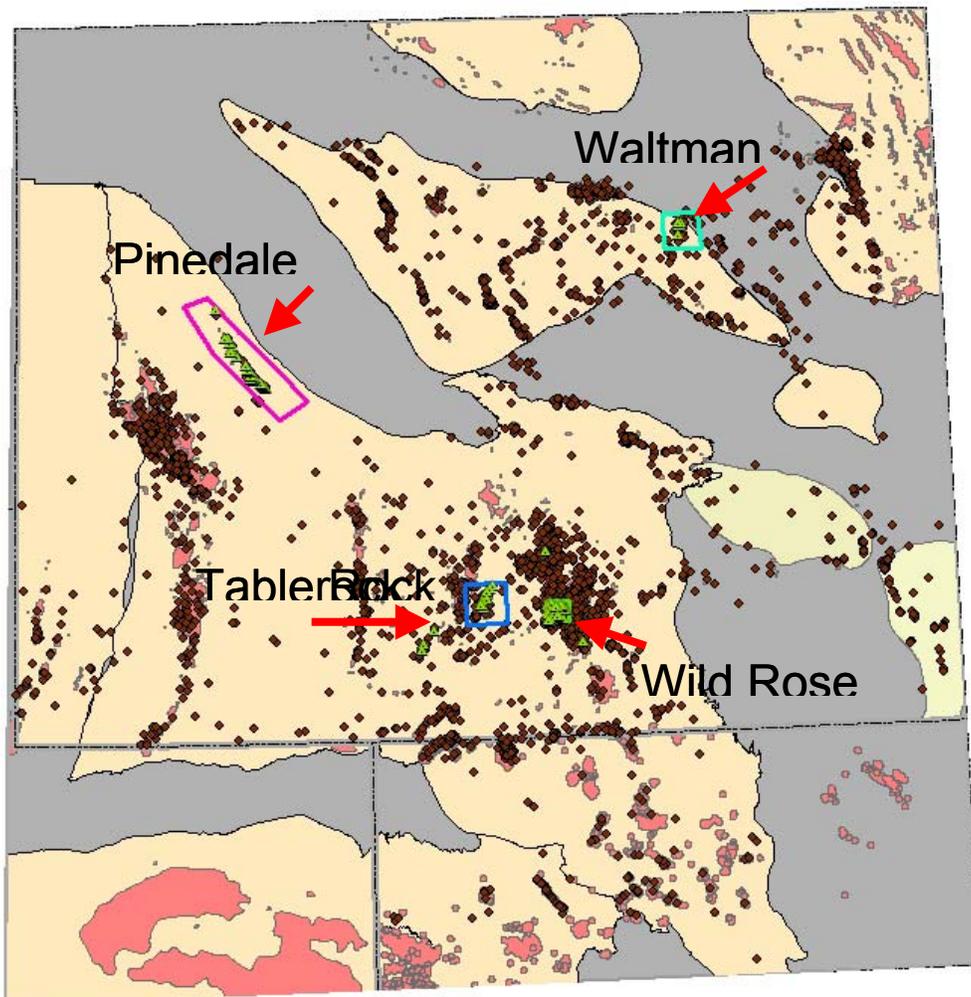
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## New Samples Collected for this Study

### *Methodology*

#### Sample Collection and Analysis

Water samples for this study were taken during the summers of 2003 and 2004 from around the Green River and Wind River Basins areas of Wyoming as shown in fig. C-1. Data for the new samples collected for this study are included in a spreadsheet linked to this appendix ([geochem\\_data\\_analysis\\_examples.xls](#)). This spreadsheet also contains examples of calculations and charts used by Dr. Leta K. Smith for some data analysis and interpretation tasks.



*Fig. C-1. Water samples taken summers of 2003 & 2004 from Green River & Wind River basins areas of Wyoming*

Most of the seventy-seven water samples were collected at the separator, although four were sampled at the collection tank. Wellhead samples could not be safely obtained for many wells due to low water production and high wellhead pressures.

Water samples collected for this study were analyzed for

- 1) Major and minor elements
- 2) Stable isotopes (oxygen and hydrogen)
- 3) Strontium radiogenic isotopes

Major and minor element analyses were performed at the University of Wyoming Rock Chemistry Laboratory. Dr. Carol Frost, Dept. of Geology and Geophysics, University of Wyoming performed the strontium radiogenic isotopic analyses. Isotech Laboratory in Champaign, Illinois analyzed stable isotopes.

### **Dilution by Dewpoint Water**

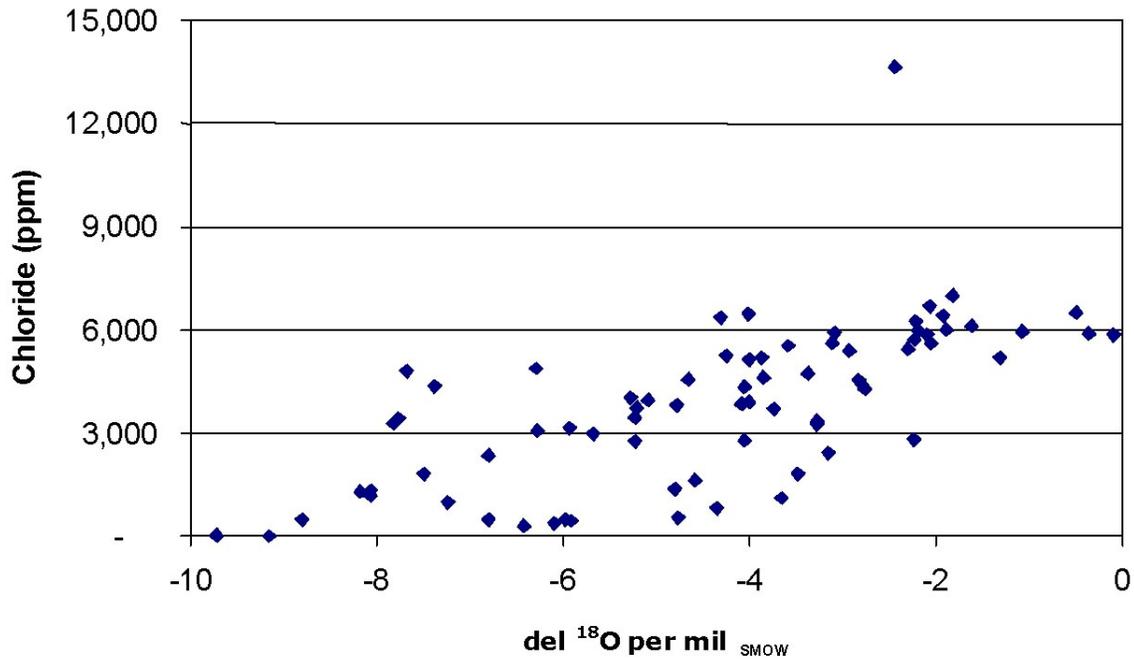
Prior to interpretation, water analyses were corrected for dilution according to a methodology outlined by Meshri (1981), using the chart of McKetta and Wehe (1958). This correction is for dilution caused by condensation of water vapor from the gas stream, which is commonly referred to as “dewpoint” or “vapor” water.

The correction was made in accordance with a factor by which analyses was increased in order for it to represent formation water. This factor was determined for each well based on differences in both bottomhole and separator temperatures and pressures. The correction factors for the samples varied between concentration factors of 1X and 1.84X with the average being 1.04.

*Note: The original “un-corrected” analyses are reported in the database so that correction factors other than the one used in this study can be applied to the raw data.*

Stable isotopic data provides additional evidence that the water samples are primarily formation water with little dilution by water condensing from the gas stream. In their study of the Frio formation in the Texas Gulf Coast (1996), Poulson, et al, found that  $\delta^{18}\text{O}$  correlated with chloride concentration and water production. They concluded that both of these correlations could result only from condensation of dewpoint water, not mixing of formation water with some other isotopically light water such as meteoric water.

A plot of  $\delta^{18}\text{O}$  vs. chloride concentration for samples from this study shows no correlation (fig. C-2). Lack of a strong correlation indicates that dilution by dewpoint water is not a significant factor in causing these samples to be relatively low in total dissolved solids (TDS).

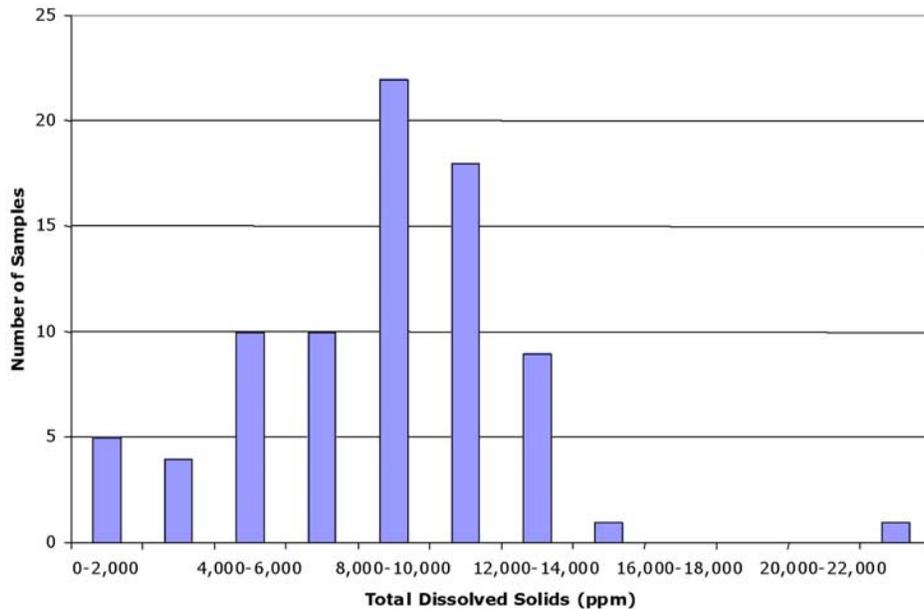


*Fig. C-2. Oxygen isotopic composition vs. chloride concentration*

A low calculated correction factor combined with the lack of correlation between  $\delta^{18}\text{O}$  and chloride concentration indicates that the sampled water is primarily formation water, not formation water diluted by vapor condensing from the gas stream.

## Salinity and Major Element Composition

All of the samples were relatively fresh, even after correction for dewpoint water dilution. The TDS ranges from less than 1,000 ppm to just over 23,000 ppm (fig. C-3). By comparison, seawater is 35,000 ppm and average river water is 100 ppm (1979 Meybeck).



*Fig. C-3. Range of TDS in new samples collected for this study*

The average salinity for sampled fields is given in Table C-1, which includes only those fields where more than one sample was taken.

**Table C-1. Average salinity for sampled fields**

| Field Name         | TDS (ppm) | No. Samples |
|--------------------|-----------|-------------|
| Cave Gulch         | 3,943     | 8           |
| Pinedale Anticline | 9,704     | 27          |
| Table Rock         | 5,765     | 4           |
| Wild Rose          | 8,221     | 36          |

Cave Gulch field samples have the lowest average salinity at 3,943 ppm, while samples from the Pinedale Anticline area have the highest TDS, averaging almost 10,000 ppm. The distribution and range of TDS for the individual fields is discussed later in this summary.

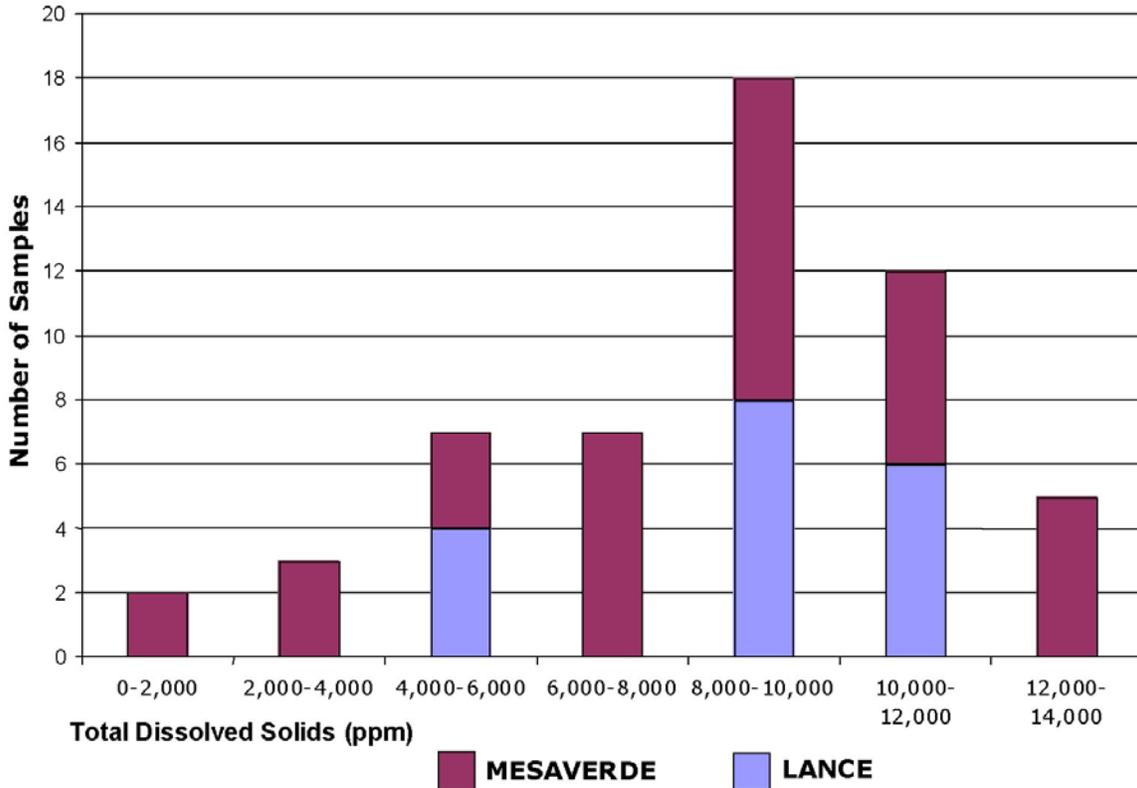
Samples that came from a single interval are shown in Table C-2 with the number of samples from each field and formation. Samples from multi-zone completions, of which there were 13, are excluded.

**Table C-2. Number of samples from each field and formation**

| <b>Single Interval Samples</b> | <b>Field Name</b>  | <b>No. of Samples</b> |
|--------------------------------|--------------------|-----------------------|
| Lance                          | Cave Gulch         | 4                     |
|                                | Pinedale Anticline | 14                    |
| Almond                         | Barrel Springs     | 1                     |
|                                | Unknown            | 1                     |
| Almond, Upper                  | Siberia Ridge      | 1                     |
| Blair                          | Unknown            | 2                     |
| Ericson                        | Pinedale Anticline | 1                     |
| Frontier                       | Cave Gulch         | 1                     |
| Ft Union                       | Cave Gulch         | 2                     |
| Lewis                          | Table Rock         | 1                     |
| Mesaverde                      | Wild Rose          | 36                    |
| Muddy                          | Cave Gulch         | 1                     |
| Nugget                         | Table Rock         | 2                     |

Except for the Lance formation and samples labeled as Mesaverde group, there were insufficient samples from any one formation to assess trends by formation.

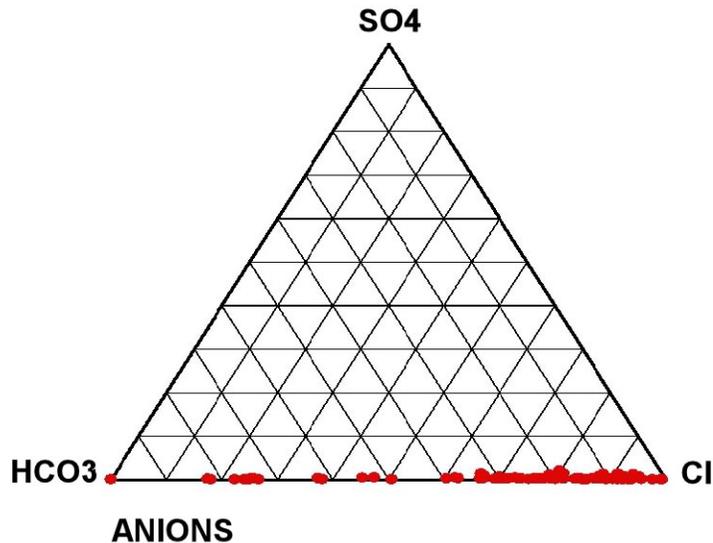
Fig. C-4 shows a comparison between the Lance and Mesaverde group samples. The salinity of both these groups is very similar, but the Mesaverde group samples exhibit a wider range. The Lance formation has an average salinity of 8,760 ppm and ranges between 4,000 ppm and almost 12,000 ppm. The Mesaverde group samples have an average salinity of 8,221 ppm, but ranges from less than 100 ppm to over 13,000 ppm.



**Fig. C-4. Comparison of TDS between Lance formation & Mesaverde group samples**

The range exhibited by the Mesaverde group samples is not surprising. The Upper Almond formation was deposited in a marine setting. The Lower Almond formation and older formations such as the Ericson were deposited in a coastal plain and estuarine environment where the original water deposited with the sediment would have been fresh or slightly brackish. Previous studies by Smith (1998) showed that formation water originating from the Upper Almond is generally more saline than water originating from the Lower Almond.

In terms of major element composition, most of the samples have a cation composition dominated by sodium (fig. C-5). Only two samples have calcium as their dominant cation. None of the samples are dominated by magnesium, and in fact, magnesium is generally less than 1% of normalized total cations. The highest percentage of magnesium is from a sample in Wild Rose field, which is the least saline of all samples.



*Fig. C-5. Major element composition of samples collected for this study*

Chloride is the dominant anion in more than 80% of the samples, but there is a range between samples that are chloride-dominated and samples that are bicarbonate-dominated (fig. C-5). This trend in anion dominance parallels the trend in salinity. Chloride-dominated samples have an average salinity of 9,936 ppm, whereas samples that are bicarbonate-dominated have an average salinity of 5,937 ppm.

The samples that have bicarbonate as the dominant anion are from one of four formations: Lance, Almond, Ft. Union, or the Mesaverde group. However, not all samples from those formations are dominated by bicarbonate. With the exception of the two samples from the Ft. Union formation the majority of the samples from the other three formations are dominated by chloride.

Table C-3 shows the number of samples from each formation that are chloride-dominated or bicarbonate-dominated. This table includes only those samples that are from single-zone completions.

The samples with bicarbonate dominating the anions are from formations having some portion of their strata deposited in a non-marine environment. This indicates that the present formation water originated with the deposition of the rock and that there has been no significant movement of water through the rock.

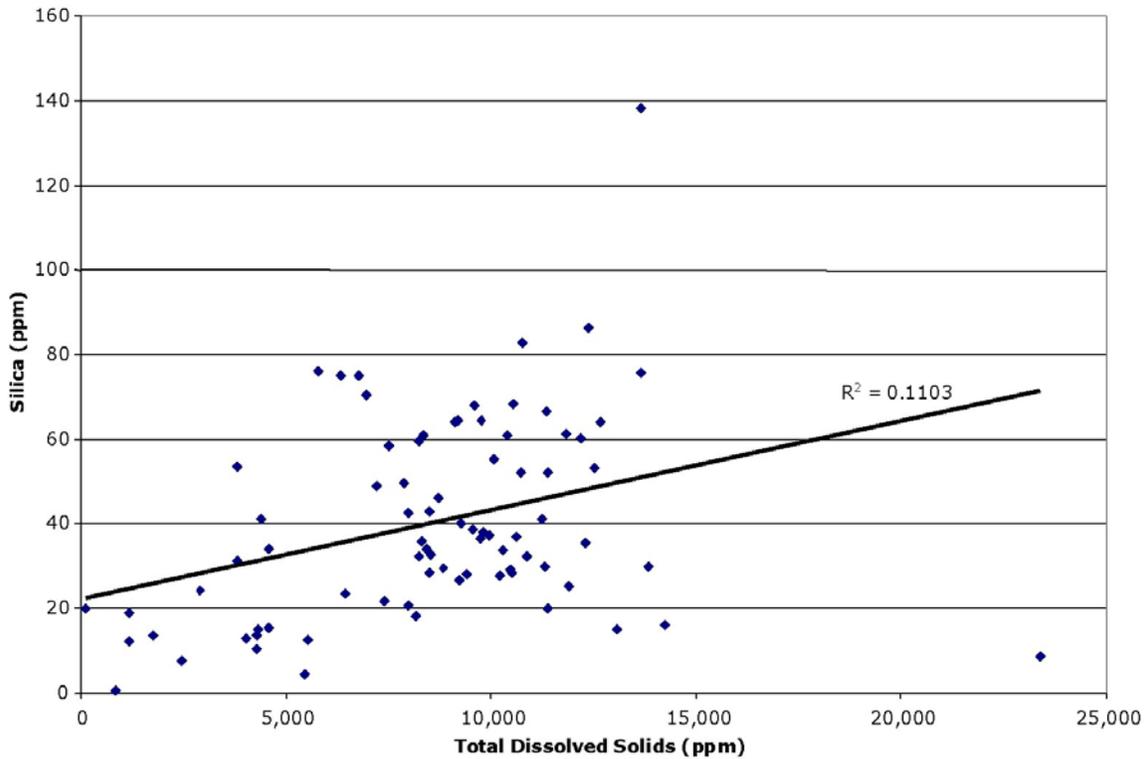
**Table C-3. Chloride or bicarbonate-dominated samples by formation**

| <b>Intervals Sampled</b> | <b>Number of samples that are chloride dominated</b> | <b>Number of samples that are bicarbonate dominated</b> |
|--------------------------|--|---|
| Lance                    | 14   | 4   |
| Almond                   | 1  | 1   |
| Almond, Upper            | 1  |   |
| Blair                    | 2  |   |
| Ericson                  | 1  |   |
| Frontier                 | 1  |   |
| Ft Union                 |  | 2   |
| Lewis                    | 1  |   |
| Mesaverde                | 32   | 4   |
| Muddy                    | 1  |   |
| Nugget                   | 2  |   |

## Minor Element Composition

The samples collected for this study were analyzed for silica, barium, bromide, strontium, and rubidium. The latter two elements are discussed in the section “Strontium Isotopes.”

Silica concentrations generally increase with increasing total TDS although the correlation is weak (fig. C-6).

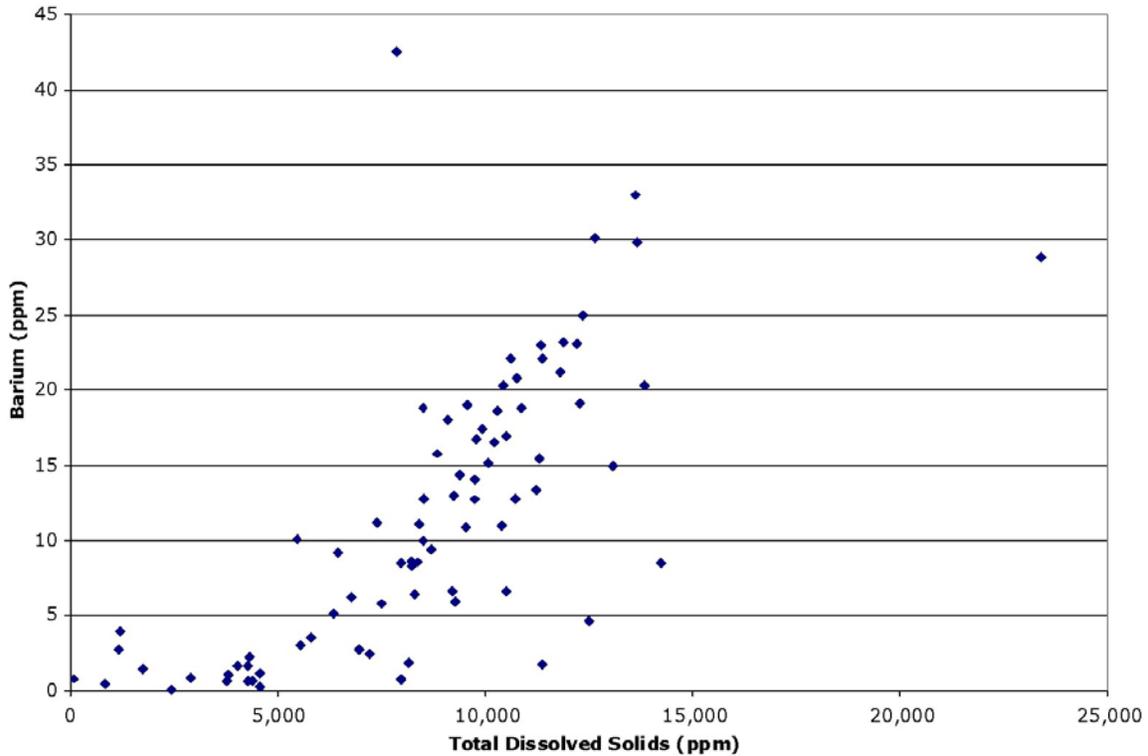


*Fig. C-6. Silica vs. TDS in samples collected for this study*

Samples from the Mesaverde group exhibit the largest range of concentration – between 14 and 138 ppm, while the Lance formation samples have concentrations between 12 and 55 ppm.

The Mesaverde group samples have an average silica concentration of 56 ppm, while the Lance formation samples have an average silica concentration of 30 ppm. No other formation had a sufficient number of samples to make any generalizations about trends.

Barium concentration increases with TDS (fig. C-7).

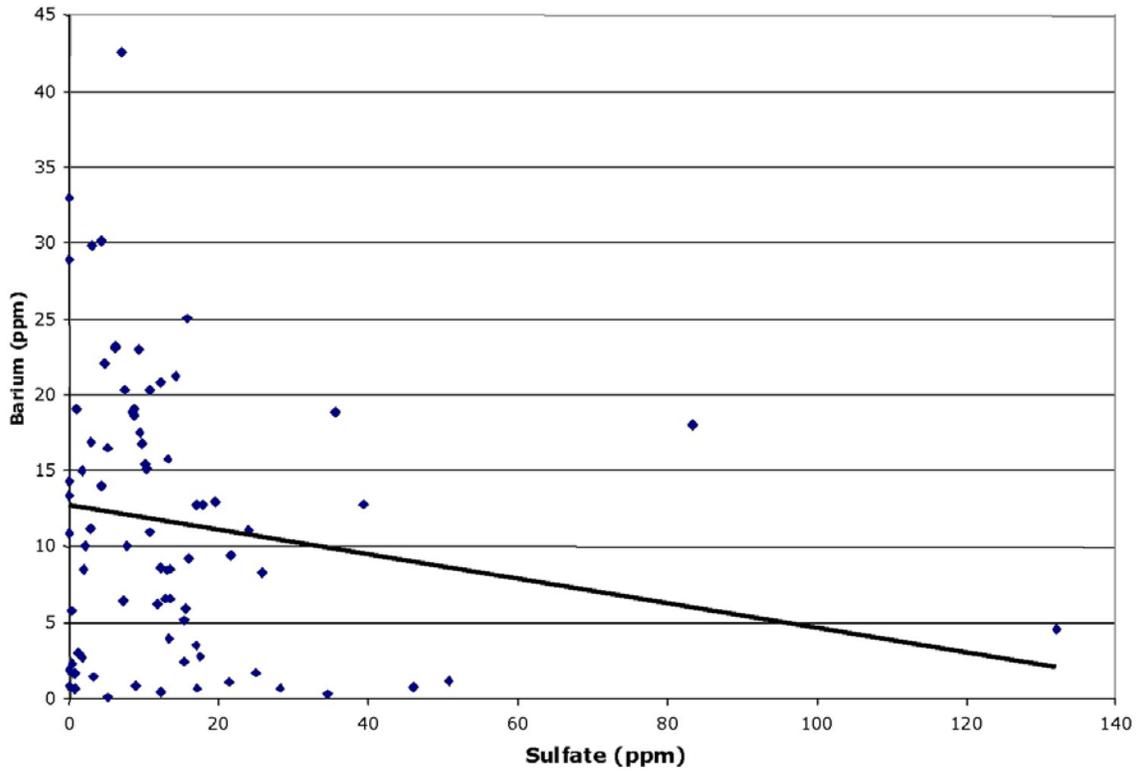


*Fig. C-7. Barium vs. TDS in samples collected for this study*

There is little distinction in barium concentrations between the Lance formation and Mesaverde group samples. Both have an average barium concentration of 12 ppm.

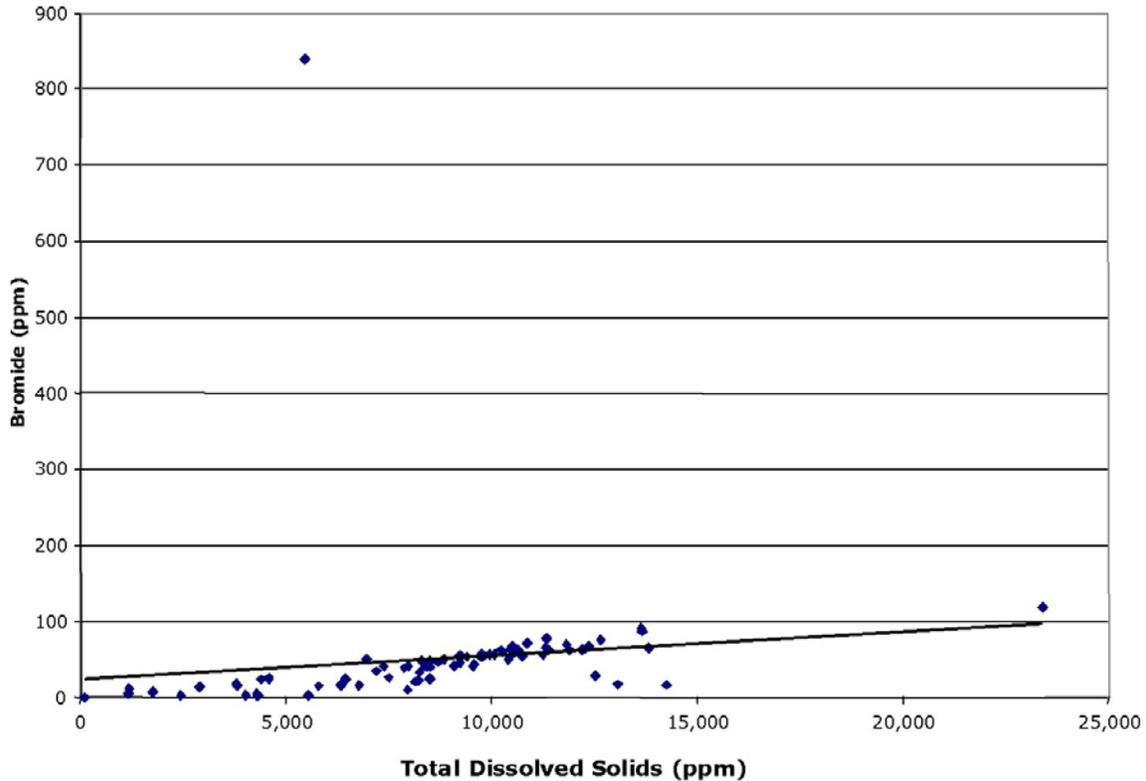
However, the Mesaverde group samples have a wider range of barium concentrations than the Lance formation samples. Barium concentration in Mesaverde group samples range from 0 to 43 ppm, while those of the Lance formation samples range from 2 to 23 ppm.

Barium concentrations have a weak inverse relationship to sulfate concentrations (fig. C-8). An inverse relationship can be expected. As sulfate increases, barium and sulfate will precipitate out as barite cement, and barium is used up before the sulfate is depleted. Barite cement, although not abundant, is a commonly observed cement in the Mesaverde in the Green River basin (1995 Dunn, et al).



*Fig. C-8. Barium vs. sulfate in collected for this study*

Bromide concentrations correlate strongly with salinity, with the exception of only one suspect outlier (fig. C-9). Nothing else about the sample analysis indicated that it should be removed from consideration. The charge balance was good, pH was within normal range, and there was no excess potassium or magnesium indicating contamination.



*Fig. C-9. Bromide vs. TDS in samples collected for this study*

Bromide:chloride ratios are higher than seawater. Seawater has a Br:Cl ratio of 0.004, whereas the average for these samples (excepting the outlier) is 0.01. A number of authors have examined excess bromide in formation waters, and there are two theories about its origin.

One theory is that organics are the source (1979 Carpenter and Trout; 1987 Means and Hubbard; and 1989 MacPherson and Land), while the other theory purports re-crystallization of potash (1987 Hanor and 1992 Moldovanyi and Walters). While the scope of this study did not lend itself to determining an origin of excess bromide for these samples,

Moldovanyi and Walters (1992) dismissed the organic origin because bromide concentrations did not correlation with the concentration of organic components in the water.

No analysis of organic components was performed on these samples, so the potash origin cannot be evaluated. Such a determination would require comparative samples from the same area from Paleozoic dolomite and carbonate formations and from Paleozoic eolian producing formations that have interbedded evaporite deposits.

However, a bromide concentration of 839 ppm is most typically found in formation water having chloride concentrations well over 50,000 ppm (1975 Collins). This sample is from a well in the Cave Gulch Field that produces from the Muddy formation. It is the deepest sampled formation in this dataset.

But another well from the same field producing from the Frontier formation just 1,000 feet above this well, produces water with only 11 ppm bromide, which is similar to the other samples taken from Cave Gulch. For these reasons, this bromide concentration is assumed to be due to a contaminant in the water.

## ***Stable Isotopes of Oxygen and Hydrogen***

Stable isotopes are useful tools in understanding geological processes because different isotopes of an element tend to behave in slightly different ways. This process of fractionation is the phenomena by which natural chemical, physical, and biological processes cause the relative abundances of isotopes to vary among different compounds. By detecting the relative proportion of the different isotopes of an element in different situations, we come to understand those geologic processes affecting the fractionation.

Fractionation results from slight variations in the physical and chemical properties of isotopes and is proportional to differences in their masses. In general, a molecule containing the lighter of two isotopes is more reactive than a similar molecule containing the heavier isotope.

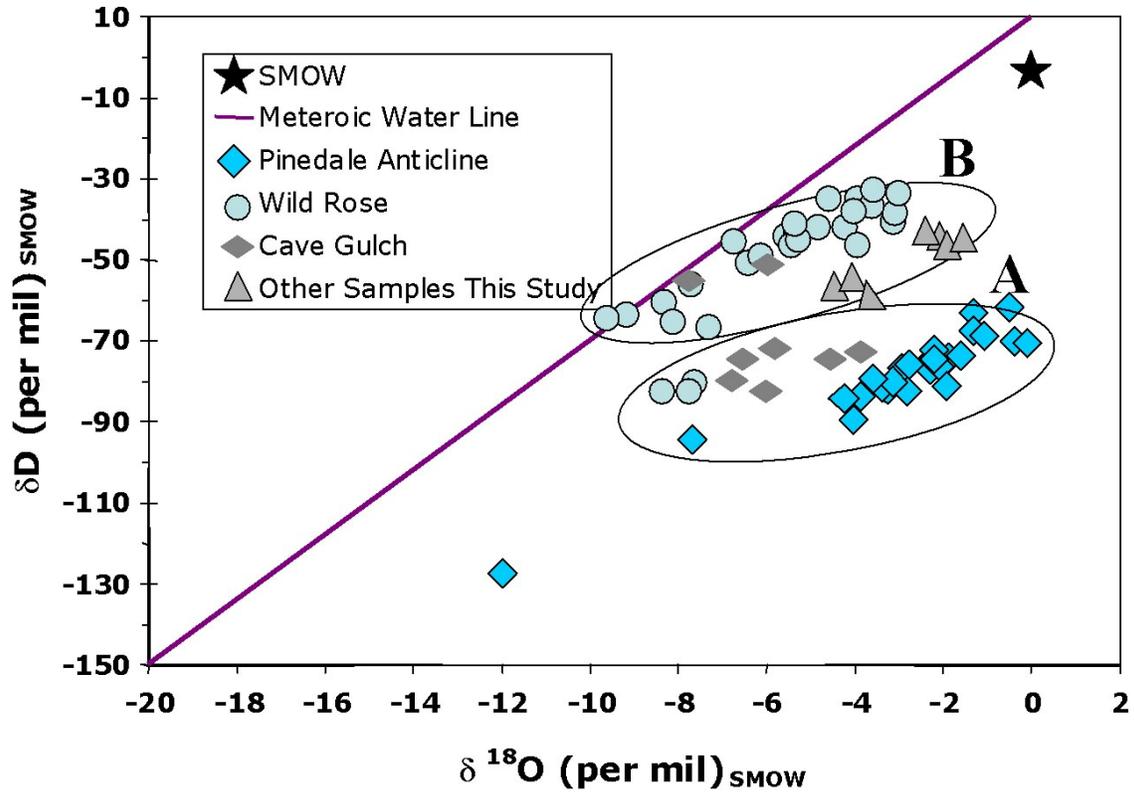
The processes affecting fractionation of oxygen and hydrogen in water include diagenetic reactions with minerals, temperature, and evaporation. During evaporation  $^{16}\text{O}$  and  $\text{H}$  preferentially enter the vapor phase, while  $^{18}\text{O}$  and  $\text{D}$  are concentrated in the liquid phase. Thus, water vapor formed by evaporation of liquid water is depleted in  $^{18}\text{O}$  and  $\text{D}$ , leaving the remaining water enriched. When the vapor re-precipitates as rain or snow, the resulting meteoric water is depleted in  $^{18}\text{O}$  and  $\text{D}$ .

Water that evaporates over the ocean tends to move toward the poles and inland before it precipitates. Successive cycles of evaporation and precipitation lead to variations in the isotopic composition of meteoric water relative to latitude, altitude and inland distance. Lower latitudes are generally more enriched in  $^{18}\text{O}$  and  $\text{D}$  and higher latitudes generally more depleted in  $^{18}\text{O}$ .

The isotopic composition of formation water is the sum of its origin in the depositional environment (either sea water or fresh water or a mixture), water-rock interaction in the subsurface, and mixing due to uplift or faulting. Thus formation water has a wide range of isotopic composition. Most diagenetic reactions tend to affect the oxygen:isotopic ratio without much effect on the hydrogen:isotopic ratio. This is due to the hydrogen budget in a rock water system being dominated by the water. Therefore, changes in  $\text{D}$  generally must be accounted for either through mixing or through isotopic exchange with hydrocarbons or hydrogen sulfide.

The rocks examined in this study include both marine and fresh water depositional environments. Also, there are both shale and coal source rocks. The various combinations of these parameters can yield unique isotopic signatures that allow us to understand the origins of the formation waters.

Fig. C-10 shows the stable isotopes of oxygen and deuterium for the samples. The samples fall into two groupings. Both have similar ranges of oxygen isotopic values but have different deuterium values.

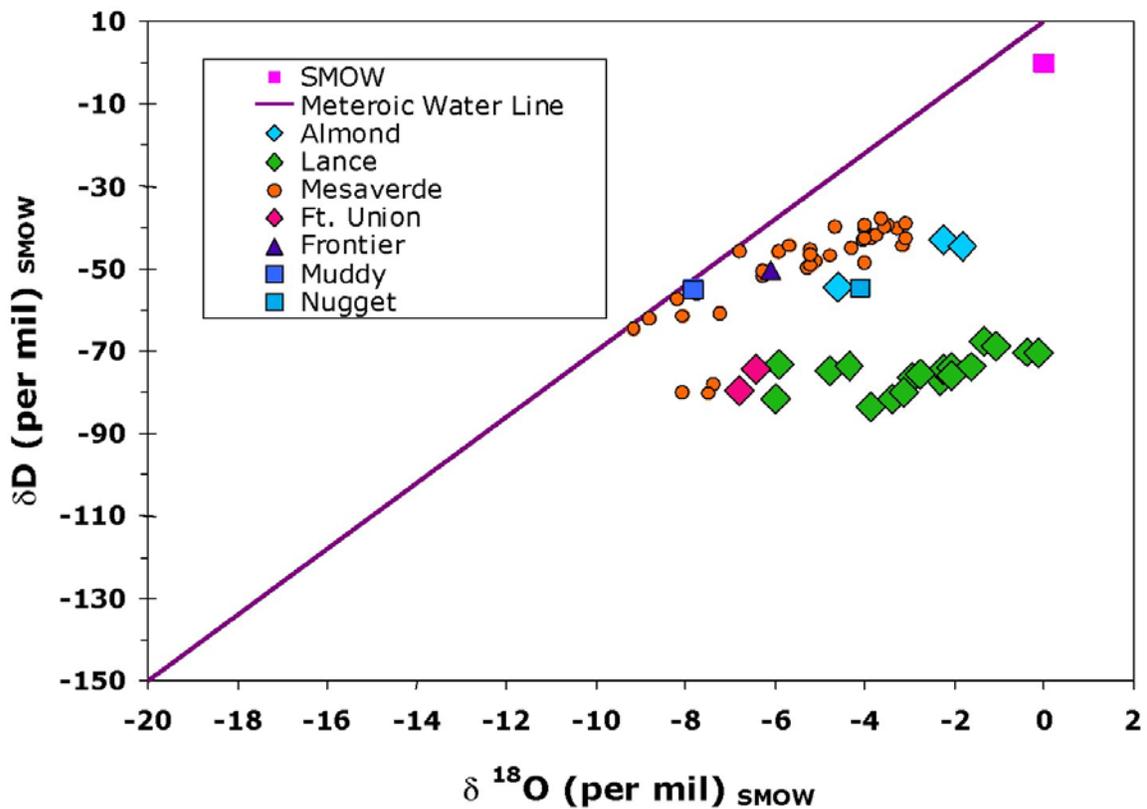


*Fig. C-10. Plot of stable isotopes of oxygen and deuterium, samples labeled by field*

Group A has deuterium values between  $-94\text{‰}$  and  $-62\text{‰}$ , and Group B has deuterium values between  $-64\text{‰}$  and  $-38\text{‰}$ . Group A samples include all those from Pinedale (except one outlier), three of the samples from Wild Rose, and all but two samples from Cave Gulch. Group B samples include all but three of the samples from Wild Rose, two samples from Cave Gulch and the remaining samples from this study.

With the exception of three samples from the Mesaverde group, the groups make more sense when plotted by formation of the completed interval. Fig. C-11 shows the same plot of oxygen and deuterium isotopes but this time with the samples labeled by formation. This plot includes only those samples that were from wells with completions in a single zone.

Samples in Group A are from the Lance formation, the Ft. Union formation, plus three from the Mesaverde group. Samples in Group B are from Muddy, Nugget, Frontier, Almond, and all the Mesaverde group samples except the three included in Group A. The A and B groupings, in general, appear to be controlled by the depositional environment and/or age of the formation that was sampled.



**Fig. C-11. Plot of stable isotopes of oxygen and deuterium, samples labeled by formation**

Smith (1998) showed that the origin of produced water at Standard Draw-Echo Springs could be determined, in part, from the stable-isotopic composition, which was controlled more by the depositional environment than the age. In that study, it was shown that water samples originating from the Lower Almond formation, which has high coal content, had a distinctly different stable-isotopic composition than the Upper Almond, which is a marine bar.

The Lower Almond samples tended to have more negative values for both oxygen and deuterium. Two samples from two Lower Almond coalbed methane wells had the most negative values. Taken together, this suggests that the greater the coal content, the more negative the stable isotopes.

For these reasons the three Mesaverde group samples falling in Group A are likely to be Lower Almond or Ericson, whereas the remaining Mesaverde group samples are more likely to be from the Upper Almond or from other strictly marine sections within the Mesaverde group.

### ***Strontium Isotopes***

Strontium isotope concentrations and ratios in produced waters are used primarily as indicators of past rock-water diagenetic interactions. There are two sources of strontium in sedimentary rock sequences: (1) seawater trapped during deposition and (2) detrital minerals. Most Sr-bearing detrital minerals have high Rb/Sr ratios or are very old relative to the host rock. Therefore, water in contact with these minerals will have higher  $^{87}\text{Sr}/^{86}\text{Sr}$  than contemporaneous seawater.

These differences can be used to identify the source of the strontium, which in turn can reveal much about the rock and its history. For example, marine carbonate rocks begin with  $^{87}\text{Sr}/^{86}\text{Sr}$  (the same as contemporaneous seawater) and even if dissolution of these rocks takes place, it will not change the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the pore water. Therefore, if the formation water strontium isotopic composition differs from the host rock, then that water had to originate elsewhere.

Strontium isotopic composition of cements in a rock illustrates this as well. If cements in a carbonate rock have a different isotopic composition from the host rock, then the water from which the cements precipitated also originated elsewhere.

Another use of strontium isotopes is to detect compartmentalization of an oil and gas reservoir into different hydrodynamic systems. If two sedimentary packages are in hydrodynamic communication, then they will fall along the same strontium isotopic mixing line (strontium isotopic composition vs. strontium concentration).

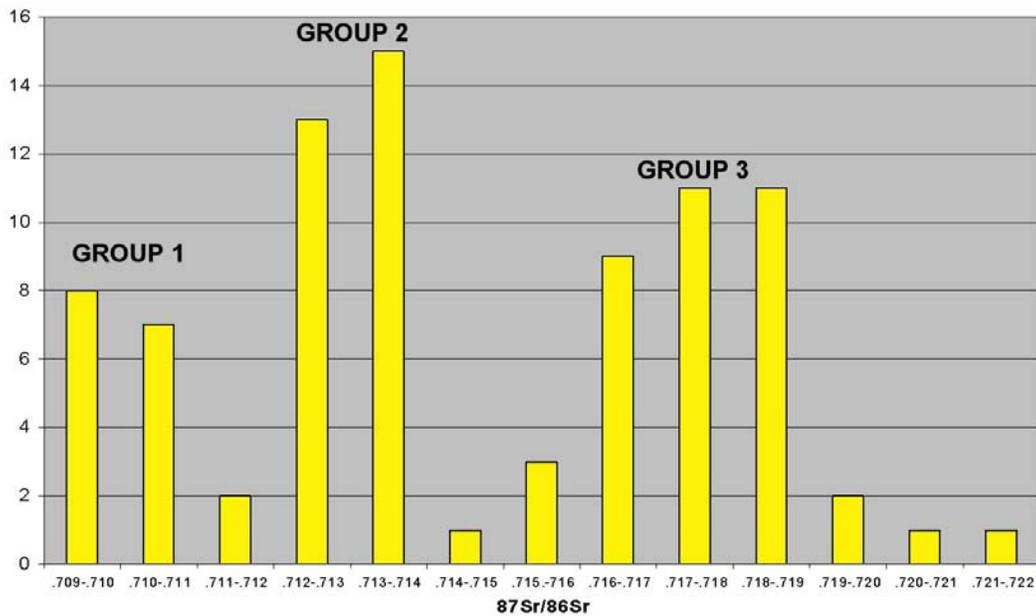
Isolation of two rock-water systems can result in different strontium isotopic mixing lines. Other than separation and isolation of the two systems, the reason cannot be explicitly determined, but some reasons for different mixing lines are:

- Amounts of strontium-bearing minerals
- Different diagenetic histories
- Deep basin fluids flowing through one portion of the reservoir and not the other
- Any number of other rock-water interaction scenarios

However, for oil and gas field systems, simply knowing that two parts of a reservoir are not in hydrodynamic communication can be the start of an improved recovery system for the field.

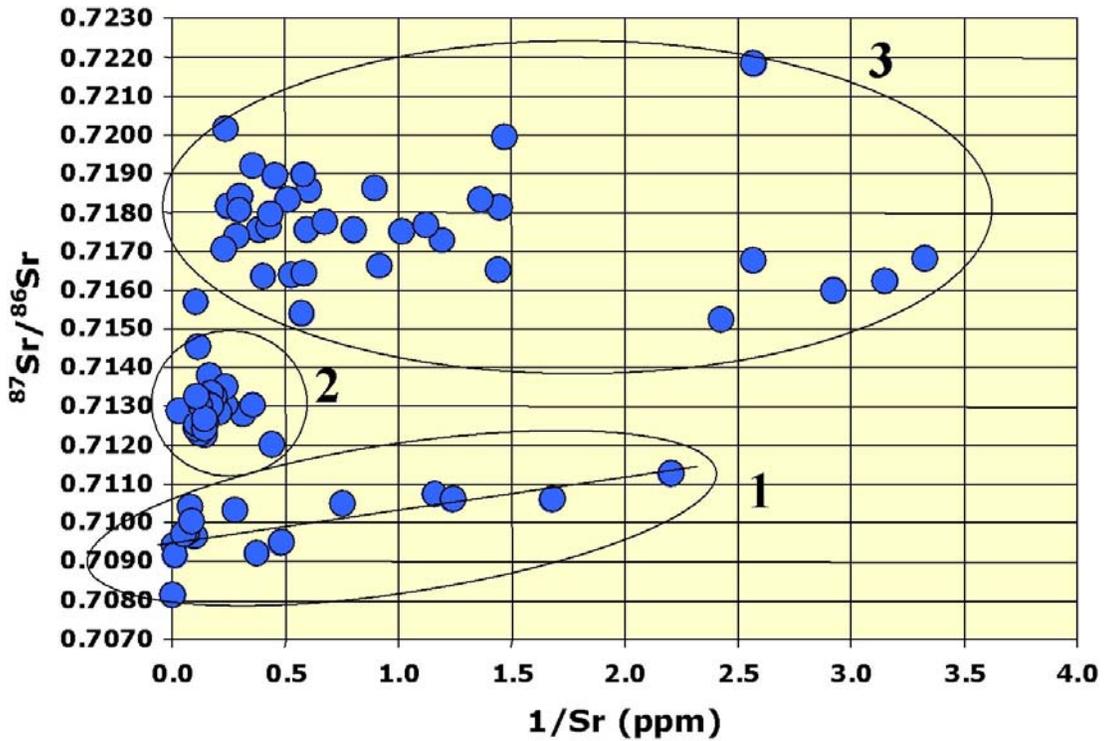
The range of strontium isotopic ratios for samples collected in this study is between 0.7092 and 0.7218. The range of strontium isotopic composition for contemporaneous seawater (Upper Triassic and Lower Cretaceous through Eocene) is approximately 0.7069 to 0.7082 (1982 Burke, et al). Present-day seawater has a strontium isotopic composition of 0.7091 (1982 Burke, et al). Therefore, these samples are all more radiogenic than either contemporaneous or present-day seawater.

Fig. C-12 is a histogram showing that the samples are tri-modally distributed. Group 1 has strontium composition less than 0.711, Group 2 has strontium compositions between 0.712 and 0.714, and Group 3 has strontium compositions between 0.716 and 0.719.



**Fig. C-12. Frequency distribution of strontium isotopic ratios**

These three groupings do not translate into three distinct mixing curves on a plot of strontium concentration vs. strontium isotopic composition (fig. C-13).



*Fig. C-13. Strontium concentration vs. strontium isotopic composition*

On a graph of this type, a mixture between two end-member components will plot as a straight line. Also, if there are two distinct lines, this can be taken as an indication of compartments that are isolated from one another. The groupings suggest a combination of original water composition and separate diagenetic histories.

Most of the samples from the same formation fall into the same group, but this is not always the case (fig. C-14). For example, while most Mesaverde group samples are in Group 3, two samples fall into Group 2.

All the Mesaverde group samples are from the same field, Wild Rose. The Lance formation samples are from the Pinedale Anticline and from Cave Gulch.

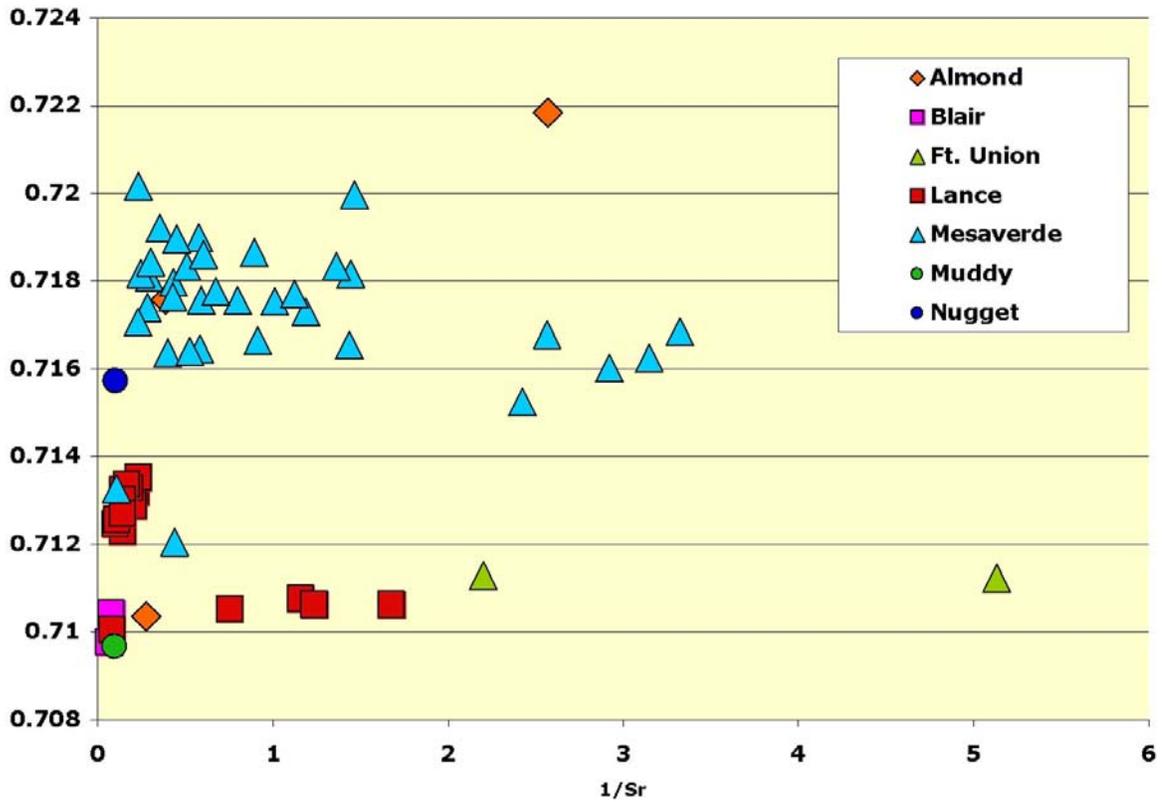
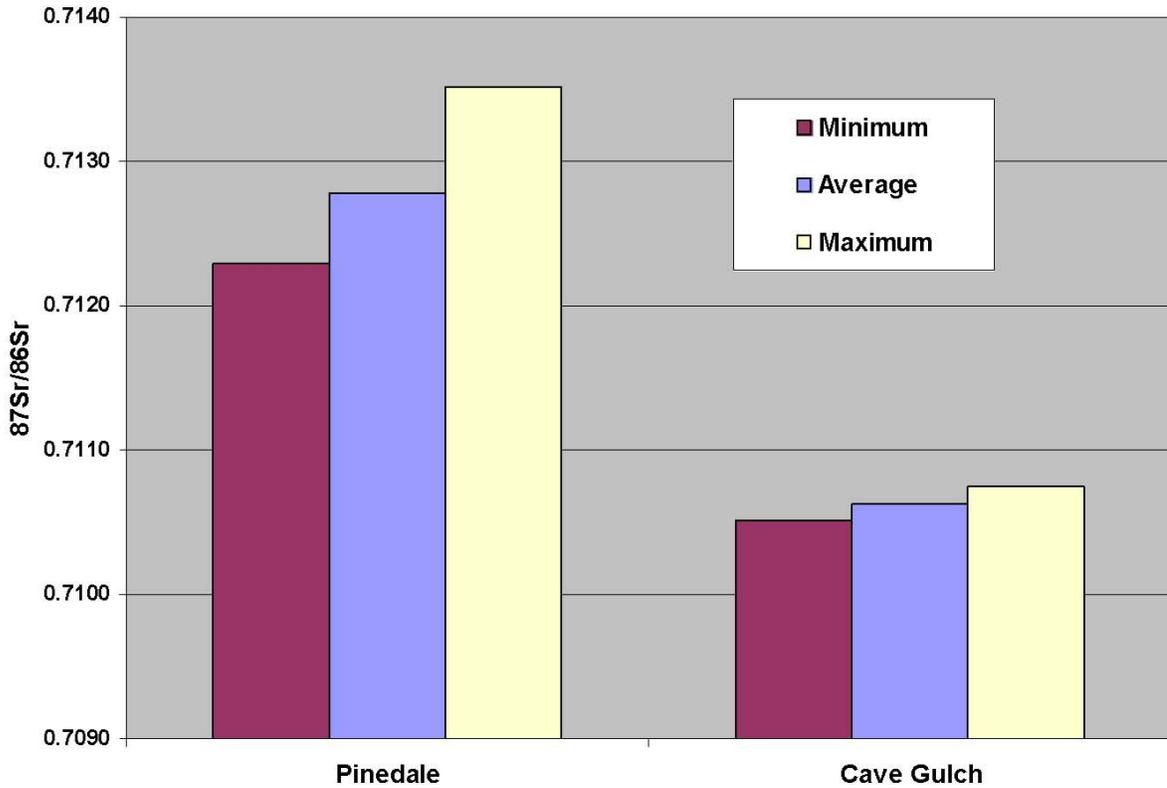


Fig. C-14. Strontium concentration vs. strontium isotopic composition, samples coded by formation

With one exception, all the Pinedale Lance samples fall into Group 2, whereas the Cave Gulch Lance samples all fall into Group 1 (fig. C-15). This is likely a diagenetic overprint onto original formation water as the Cave Gulch samples are shallower by about 3,000 feet. The average top depth for the Cave Gulch Lance samples is 5,510 feet, whereas that for the Pinedale Lance samples is 8,570 feet.

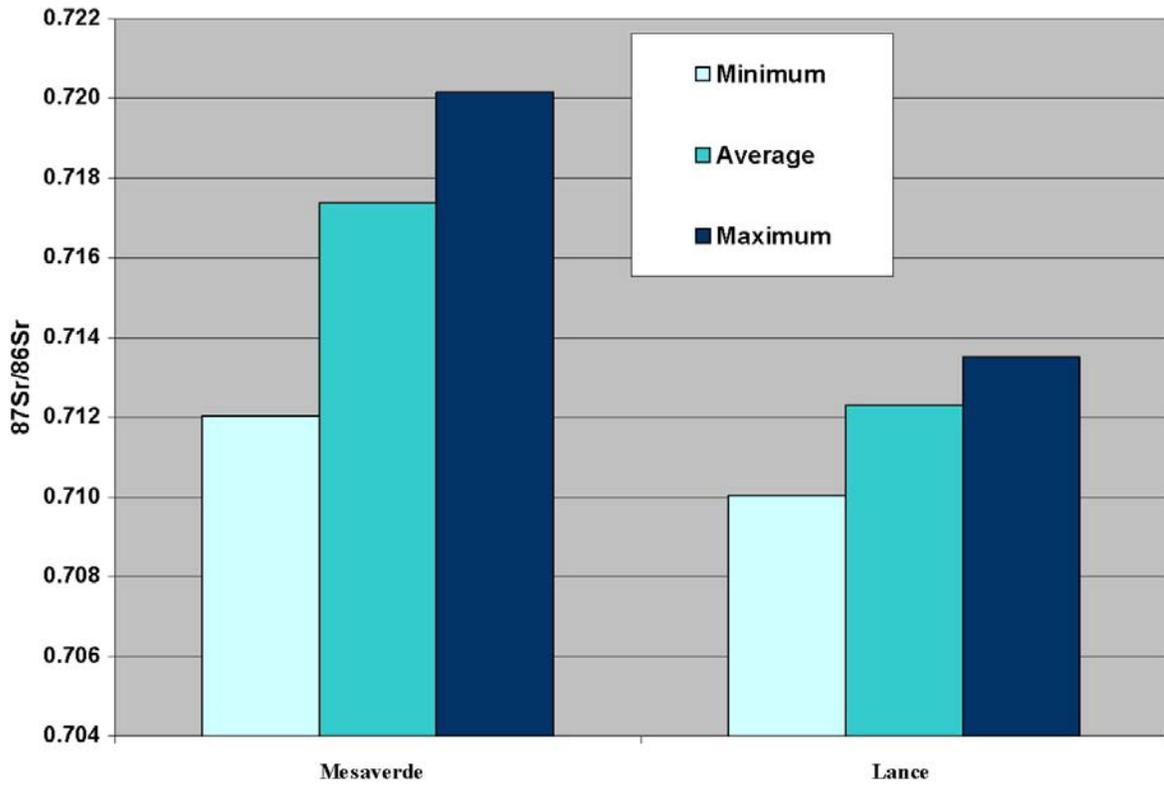


**Fig. C-15. Range and average of strontium isotope values for Lance formation samples—comparison of Pinedale & Cave Gulch**

A comparison of the Lance and Mesaverde samples indicates a trend that is the reverse of what might be expected based on age. Both the Mesaverde and the Lance are Upper Cretaceous. However, the Mesaverde group spans a longer time covering most of the Late Cretaceous whereas the Lance formation occurs at the very end of Later Cretaceous.

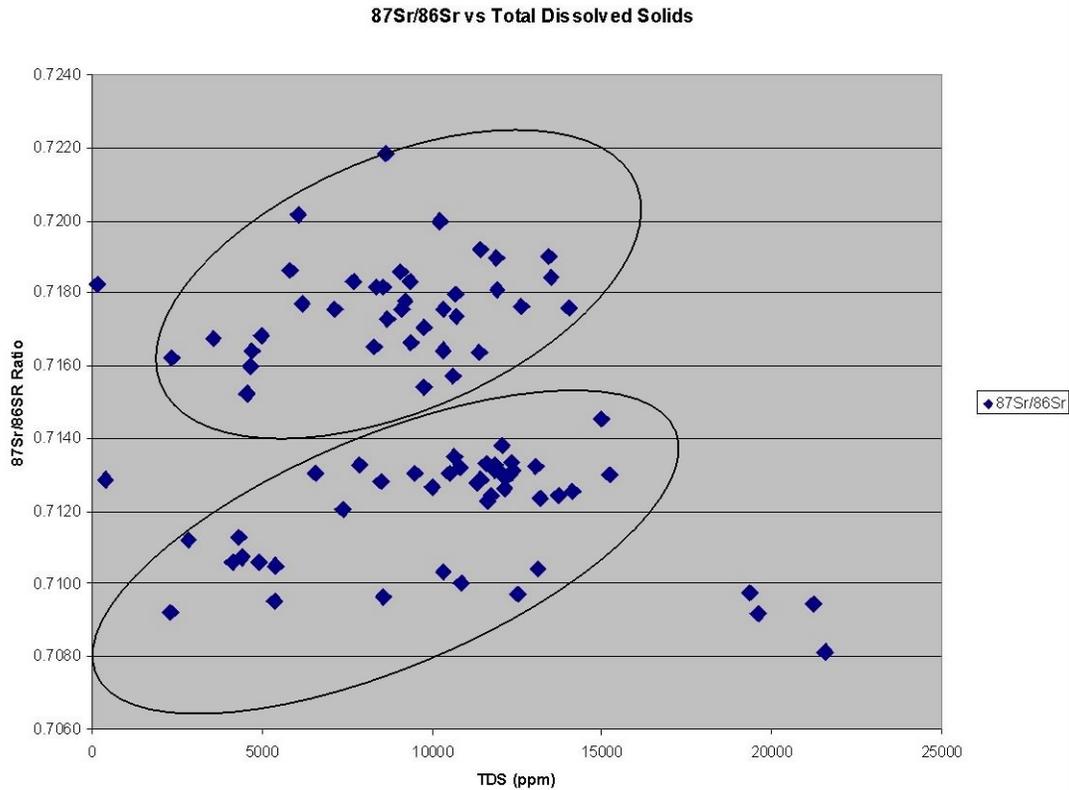
Throughout the Late Cretaceous, strontium isotopic composition of contemporaneous seawater became more radiogenic. Thus it might be expected that the Lance formation samples have a more radiogenic strontium signature than the Mesaverde samples, owing to the fact that it was being deposited at the very end of the Late Cretaceous.

However, as shown in fig. C-16 this is not the case. It is likely that this discrepancy is due to differences in depositional environment, as a significant portion of the Lance formation samples fall into the same groupings as the Ft. Union samples.



*Fig. C-16. Range & average of strontium isotope values for samples representing the Lance formation & Mesaverde group*

The relationship of  $^{87}\text{Sr}/^{86}\text{Sr}$  to other parameters was also examined. There is no relation to depth, although samples with Lewis production tend to exhibit a faint trend of becoming less radiogenic with depth. Strontium isotopic ratio vs. TDS shows increasing  $^{87}\text{Sr}/^{86}\text{Sr}$  with increasing TDS and roughly forms two diffuse clusters with slightly different slopes (fig. C-17).

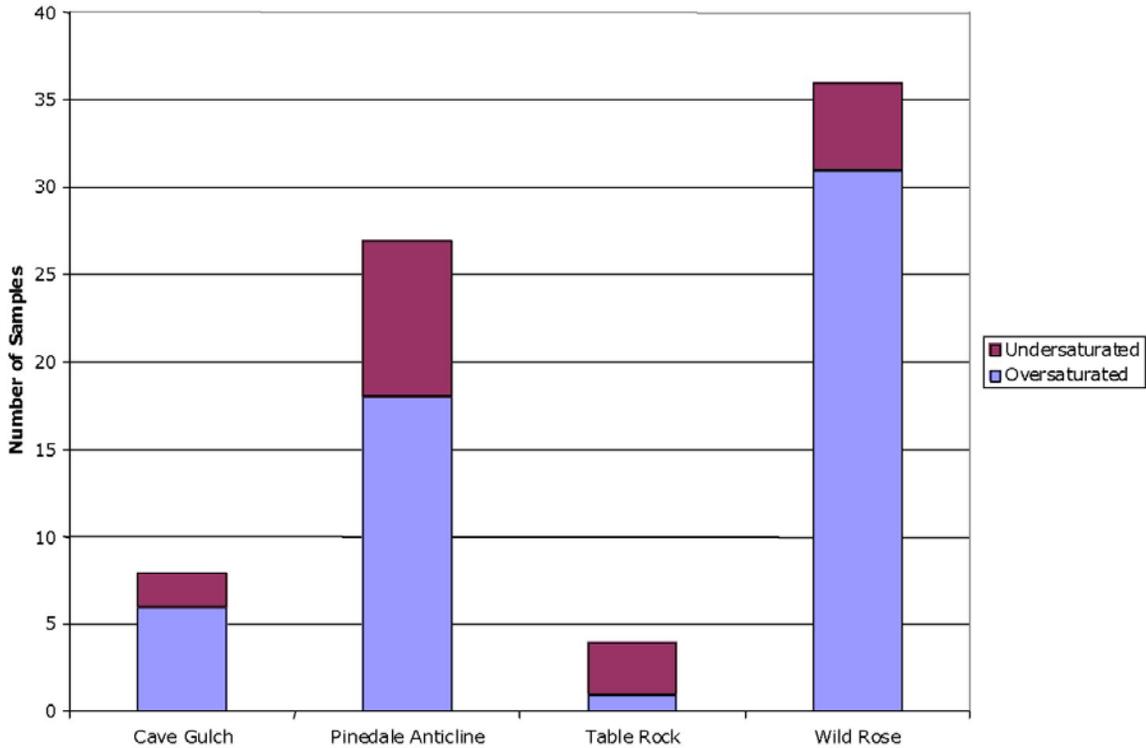


**Figure C-17. Strontium isotopic ratio vs. TDS shows increasing  $^{87}\text{Sr}/^{86}\text{Sr}$  with increasing TDS & roughly forms two diffuse clusters with slightly different slopes**

Data points immediately adjacent to the axes are suspect. Both groups show a positive relationship with TDS. The upper cluster is dominantly Mesaverde analyses and the lower group is dominantly Lance analyses. Their relative positions reflect their respective mean values as discussed previously. The process by which this relationship develops is yet to become clear.

## Chemical Modeling of Calcite Saturation

A calculation of the saturation state for calcite in the waters was performed using SOLMINEQ88 (1988 Kharaka, et al). All of the fields examined had some samples that were oversaturated and some that were undersaturated. Fig. C-18 shows the number of samples for each field that fell into each category.

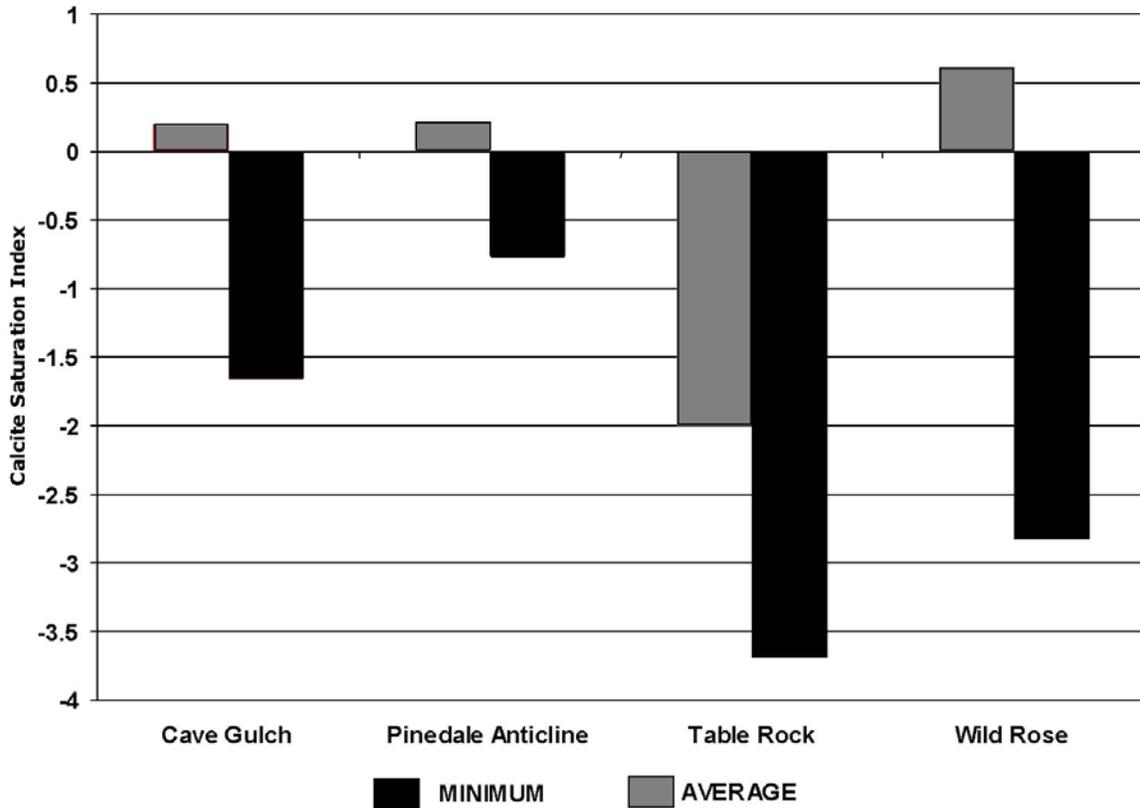


**Fig. C-18. Number of samples from each field over- or under-saturated with respect to calcite**

For most fields the number of samples that are oversaturated is more than the number of samples that are undersaturated.

That is not the case among the samples from Table Rock. Three of the four samples are undersaturated with respect to calcite. However, these four samples may not be representative due to the small sample set from that field.

It is interesting to note that the degree of undersaturation at Table Rock is also greater (fig. C-19), although it may be related to the small sample set.



Values shown for Standard Draw-Echo Springs are from Smith, 1998.

**Fig. C-19. Average & minimum calcite saturation index value for all samples from specified fields**

At the Standard Draw-Echo Springs field Smith (1998) found that areas of the field with the highest produced water were undersaturated with respect to calcite. The total gas produced from those areas was more than could be accounted for from a volumetric analysis of the perforated interval. So Smith hypothesized that gas was being produced from lower, uncompleted zones via open fractures connecting it to the completed zone.

The undersaturated state of the waters with respect to calcite does not indicate that fractures or matrix are free of calcite cements. It does suggest that compared to areas where the water is over-saturated with respect to calcite, there is increased likelihood that the fracture and/or matrix will be less cemented.

It was beyond the scope of this study to determine a correlation between gas production and calcite saturation state, although related detail is provided on the Wild Rose field in Appendices E and F.

## Historical Analyses

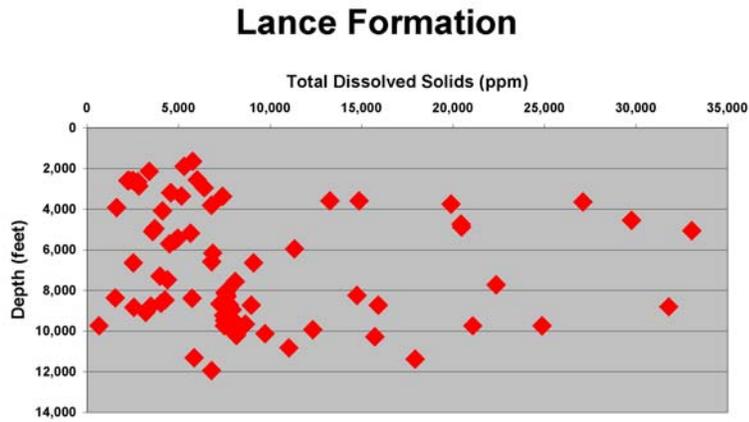
Three of the Upper Cretaceous formations (Almond, Lance and Frontier) were examined for trends in salinity with increasing depth using a high-graded subset of the historical data from the database. As can be seen on fig. C-20, while no trends are apparent (fig. C-20), there are some interesting comparisons between the formations.

The Almond and the Frontier formations exhibit the largest ranges in TDS, having waters between 1,500 and 42,000 ppm for the Frontier and between 1,700 and 50,000 ppm for the Almond. The Lance formation has water that ranges between 600 and 33,000 ppm. The overall lower TDS of the Lance formation, both in the average and the range, is in keeping with its non-marine origin as compared to the marine Frontier formation.

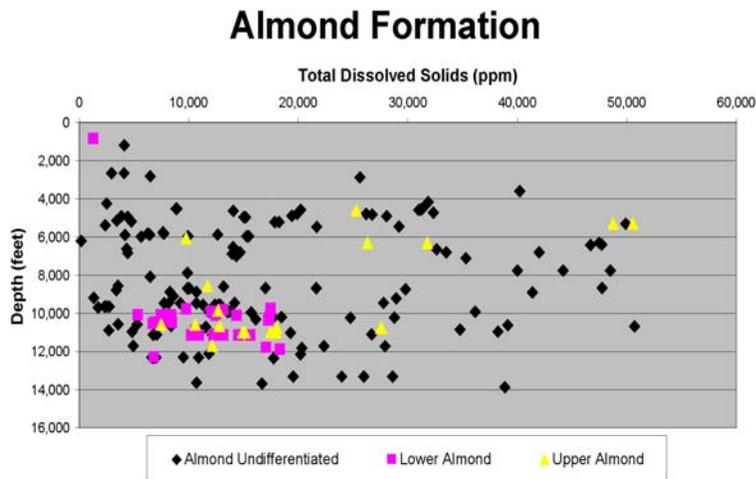
Where the Almond formation can be divided into Upper and Lower units, two distinct trends emerge. The Upper Almond, of marine origin, shows a wider range of TDS and a higher average TDS than the Lower Almond, which is predominantly of non-marine origin. The average TDS of the Upper Almond is 19,000 ppm, whereas that of the Lower Almond is 13,000 ppm.

This compares with the Lance whose average TDS is only 9,000 ppm. More discussion about the TDS ranges in the Frontier follows a discussion of the water composition.

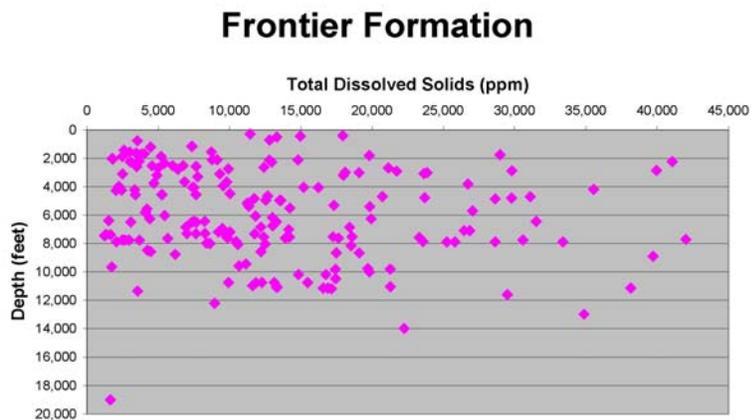
(a)



(b)



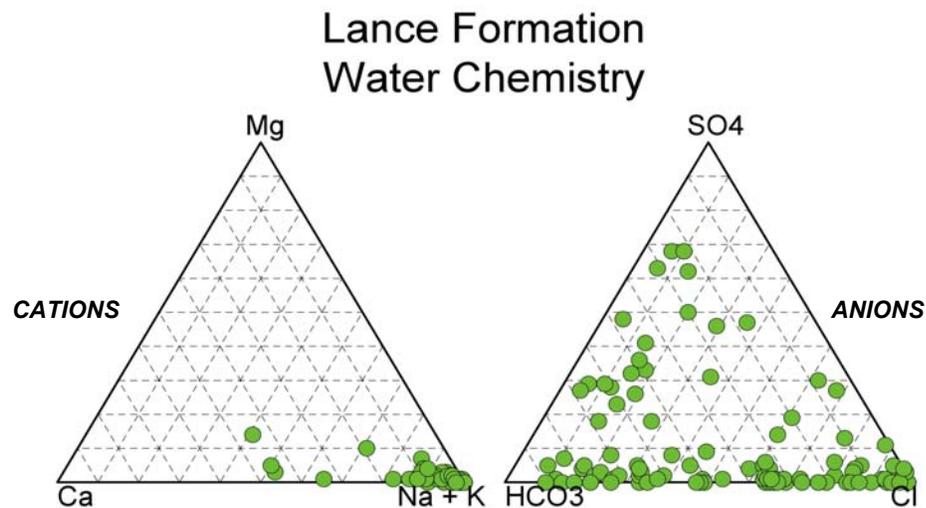
(c)



*Fig. C-20. Plots of TDS vs. depth for the (a) Lance, (b) Almond, and (c) Frontier formation samples in the database of historical water samples*

With a dataset consisting of over 3,000 analyses, the use of ternary diagrams allows the plotting of multiple points on a single diagram to look for larger trends in composition. Upper Cretaceous formations represented in the database were analyzed and compared with each other as well as with analyses representing Pennsylvanian and Permian reservoirs.

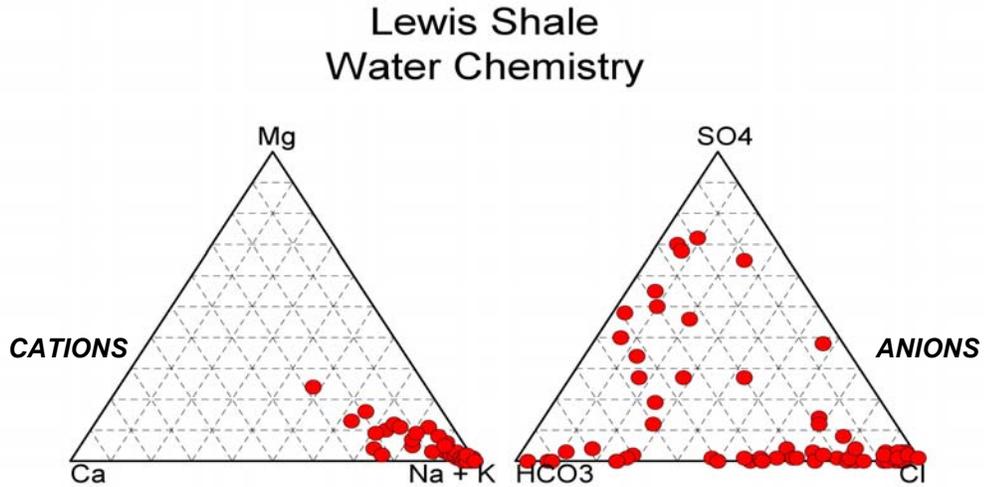
Lance formation water samples are all dominated by sodium and potassium for the cations (fig. C-21).



**Fig. C-21. Major element composition of Lance formation samples from database of historical analyses**

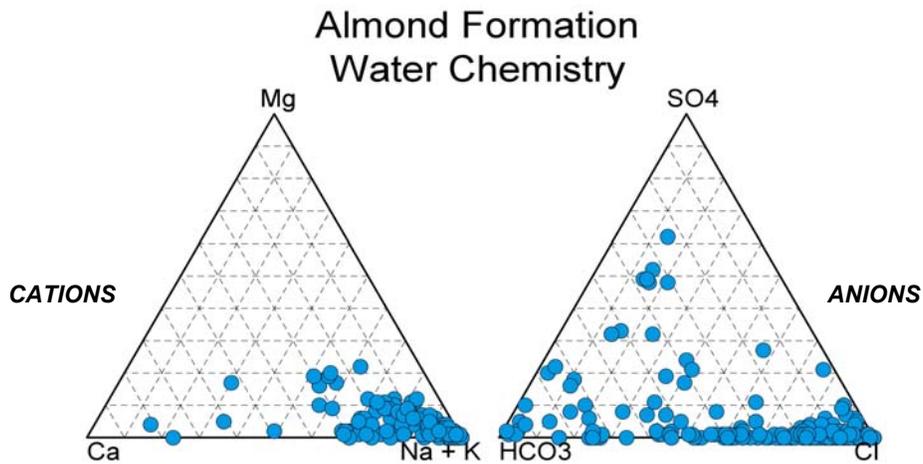
Although there is considerable scatter in the ternary plot for the anions, there is a tendency for the Lance formation waters to be dominated by bicarbonate. Fifty-nine percent of the samples have HCO<sub>3</sub> as the dominant anion, compared to only 27% for Cl and 14% for SO<sub>4</sub>. This reflects the overall non-marine origin of the Lance formation and the general tendency for the waters to be relatively fresh.

Cations in the Lewis formation water samples are all dominated by sodium and potassium (ternary diagrams in fig. C-22). Magnesium and calcium are present in roughly equal proportions. Cl generally dominates anions, although a high percentage of samples are dominated by  $\text{SO}_4$  (22%) or  $\text{HCO}_3$  (34%). The dominance of Na-Cl is expected from this marine shale sequence.



*Fig. C-22. Major element composition of Almond formation samples from database of historical analyses*

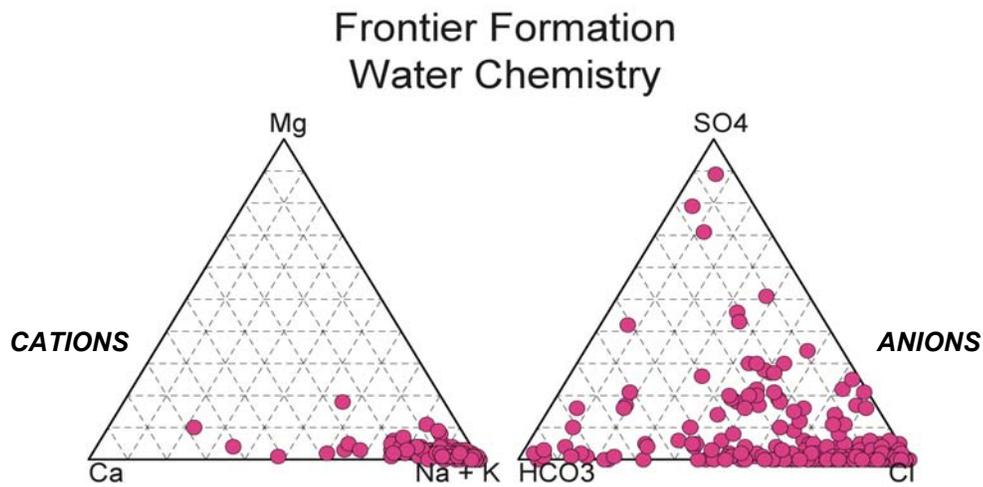
Na+K dominates the Almond formation water chemistry cations, with only a few samples dominated by Ca (ternary diagrams in fig. C-23).



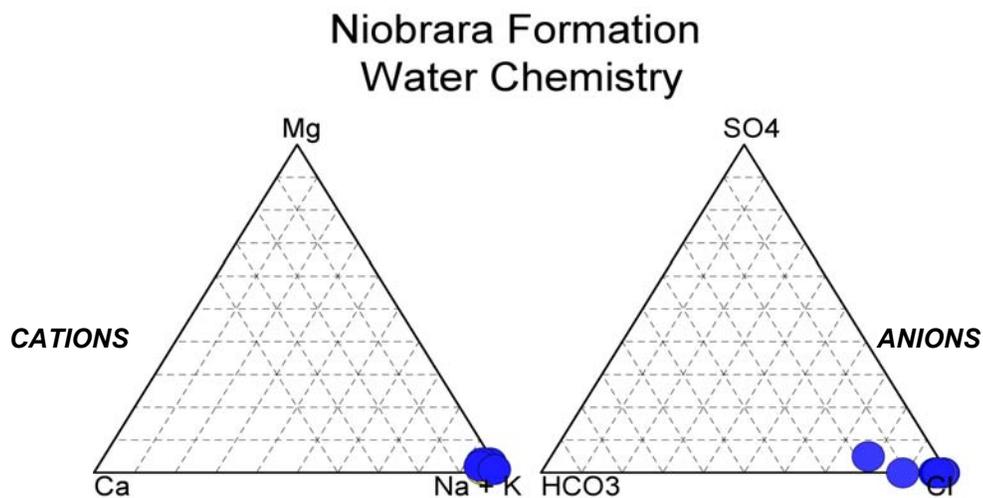
*Fig. C-23. Major element composition of Almond formation samples from database of historical analyses*

Although Cl dominates the majority of the water samples, the anions show considerable range between Cl- and HCO<sub>3</sub>-dominated waters. Just over 5% of the samples have SO<sub>4</sub> as the dominant anion. In general, the chloride-dominated samples are believed to be samples taken from the predominantly marine Upper Almond, while the bicarbonate dominated samples represent the non-marine sections of the Lower Almond.

The Frontier and Niobrara formation samples are also dominated by sodium and chloride (ternary diagrams in figs. C-24 and C-25). A small number of Frontier formation samples (3% of the total) have sulfate as the dominant anion. Although sodium-chloride brine is expected for the marine Niobrara formation, these samples may not represent the true diversity of the formation water. This formation has not been sampled extensively as there are only eight samples in the historical dataset from the Niobrara formation.

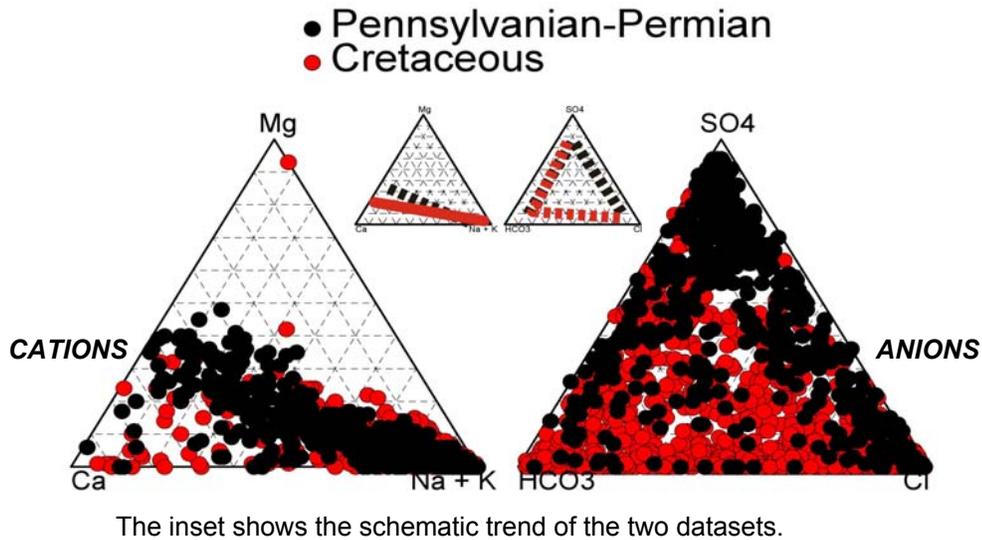


*Fig. C-24. Major element composition of Frontier formation samples from database of historical analyses*



*Fig. C-25. Major element composition of Niobrara formation samples from database of historical analyses*

Taken together, both the Cretaceous and the Pennsylvanian-Permian water samples show considerable scatter both in the cations and in the anions (ternary diagram in fig. C-26). This figure includes all Upper and Lower Cretaceous samples, not just those highlighted in the previous discussion. A couple of noteworthy trends emerge from this figure.



**Fig. C-26. Major element composition comparison of Upper Cretaceous formation samples with Pennsylvanian-Permian samples in database of historical analyses**

For the cations, both the Cretaceous and the Pennsylvanian-Permian samples fall along a trend between Na+K and with a relatively constant proportion of Ca and Mg. However, the Ca:Mg proportion is different for the two datasets. These are shown schematically in the inset. The Pennsylvanian-Permian samples generally have a Ca:Mg ratio that is 65:35, whereas the Cretaceous samples generally have a ratio that is 80:20. In both datasets there is also considerable scatter for the anions.

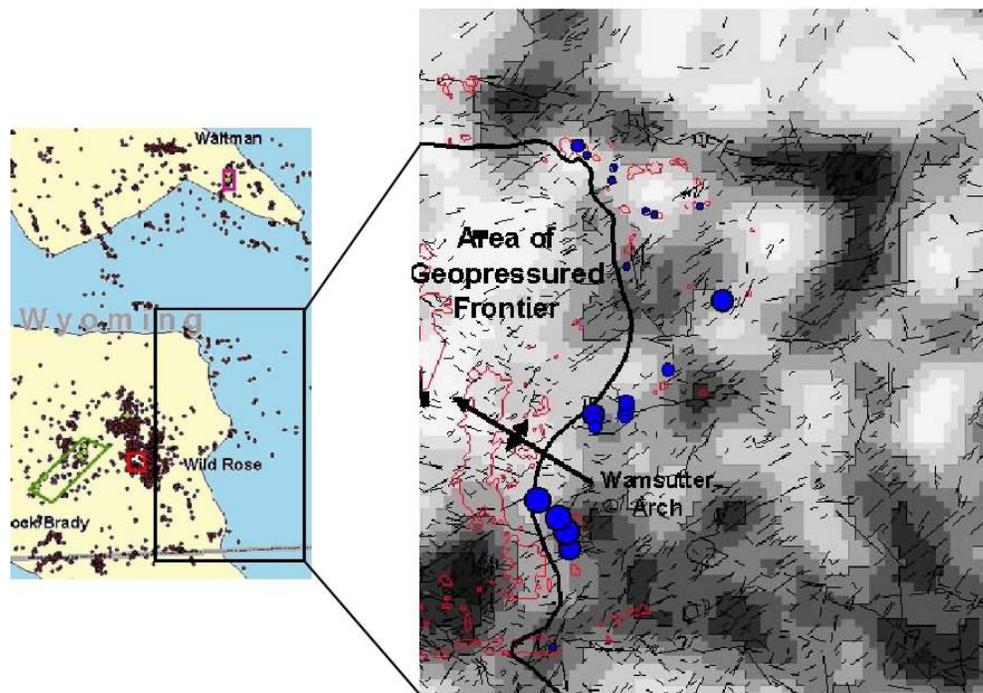
However, there are two distinct trends. The Upper Cretaceous samples generally fall along a line between Cl and HCO<sub>3</sub> or between HCO<sub>3</sub> and SO<sub>4</sub>. The Pennsylvanian-Permian samples, on the other hand, fall along a line between Cl and SO<sub>4</sub> or between SO<sub>4</sub> and HCO<sub>3</sub>. This is shown schematically in the inset of fig. C-26.

The presence of sulfate-dominated waters in the Pennsylvanian-Permian samples is expected due to the presence of evaporite deposits associated with the dune fields of the Pennsylvanian Tensleep formation. However, the presence of sulfate-dominated waters in the Cretaceous samples is more difficult to explain, as these formations are all marine and non-marine sandstones and shales.

From these interpretations we hypothesize that movement of water along major faults explains the local anomalies, and that the waters sampled from a particular formation may often not be native to that formation at all, i.e., water migrated into the sampled formation some time in the geologic past.

For example, the sulfate-dominated waters in the Cretaceous samples originated in an older, deeper formation. Detailed work at Standard Draw-Echo Springs field by Smith (1998), and an analysis of regional formation water trends (from historic water analyses) in the Green River basin in that same study, along with analysis of new samples collected for this study qualitatively, demonstrate an association between samples with high TDS and the proximity of major lineaments in the basin.

A small area along the east flank of the Greater Green River basin (fig. C-27) was evaluated for possible relationships between surface lineament densities and water compositional analyses. The Frontier formation is geopressed along the western margin of this small area. Frontier formation water analyses were derived from the database and mapped against surface lineament densities calculated from a previous study. Point values for the individual locations were extracted.



Map showing a small area along the western margin of the GGRB. The plunging black anticline symbol marks the Wamsutter Arch with the Mesaverde field outlined. The sinuous black line marks the approximate limit of geopressing in the Frontier. The solid circles are the locations of high quality produced water samples, size being proportional to TDS. The grayscale, pixelated background is surface lineament density, darker being higher, lighter being lower.

**Figure C-27. Possible relationships between surface lineament densities & water compositional analyses in GGRB**

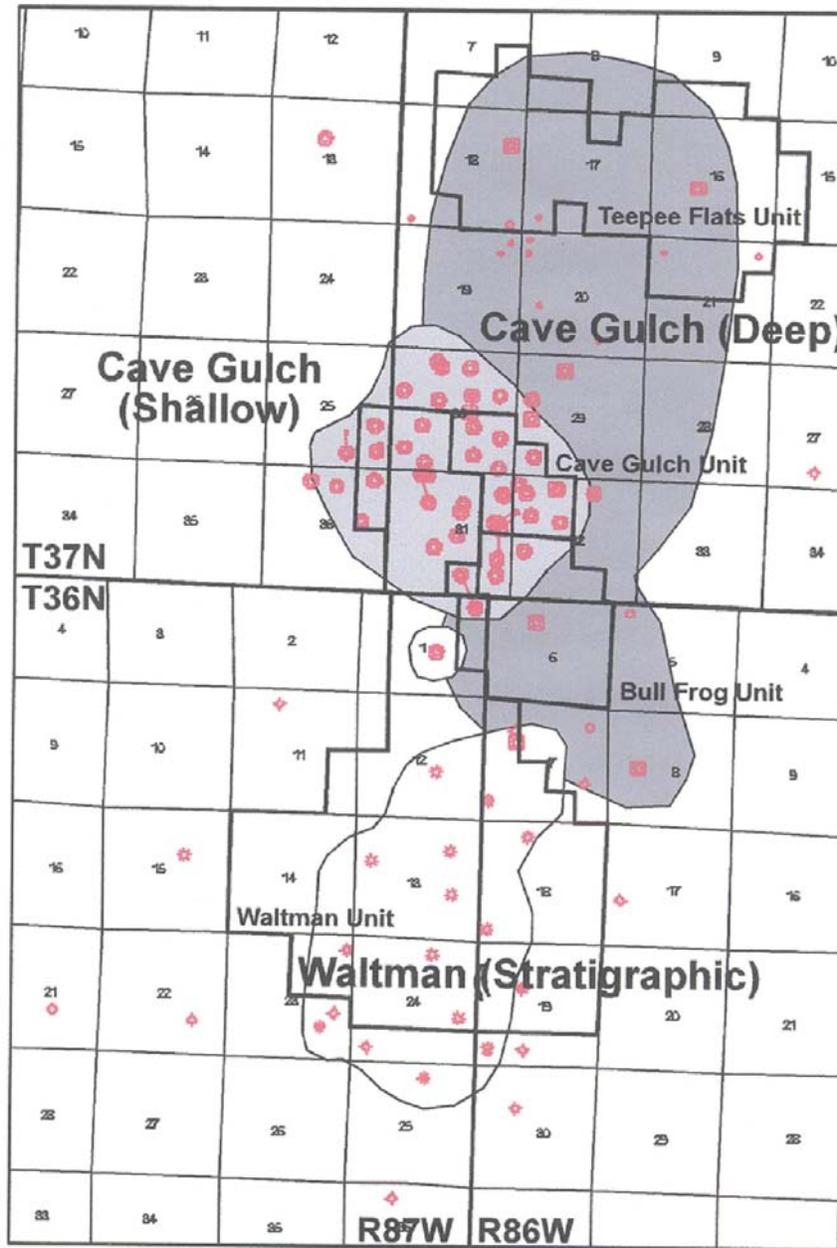


The reason for this discrepancy is that many samples in the historic database do not have an associated depth, so the samples shown in fig. C-20 are a subset of the total. Thus the very high salinity samples from the Frontier formation along with the strong positive correlation of TDS and lineament density strongly suggests that open fractures are conduits for higher TDS waters, probably from deeper in the basin, to migrate into the Frontier formation.

## Discussion of Individual Fields

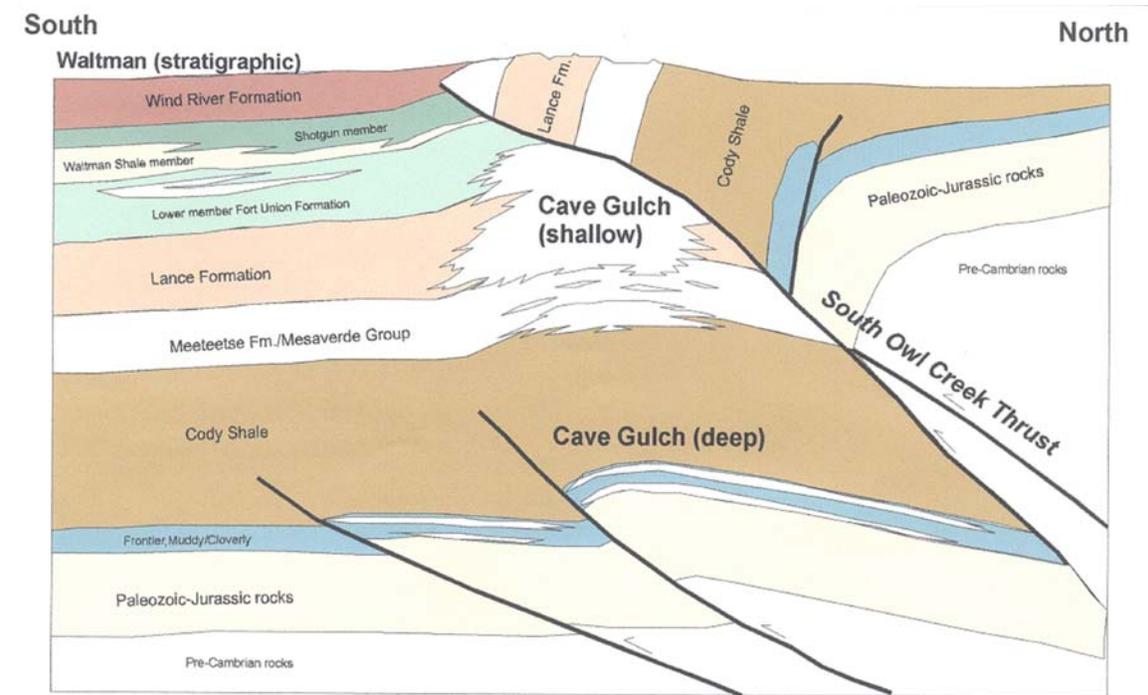
### *Waltman/Cave Gulch*

There are eight samples taken from the Waltman/Cave Gulch field complex along the Owl Creek thrust in the Wind River Basin (fig. C-29). These eight samples represent four formations: Ft. Union, Lance, Frontier, and Muddy.



*Fig. C-29. Waltman/Cave Gulch field complex location map*

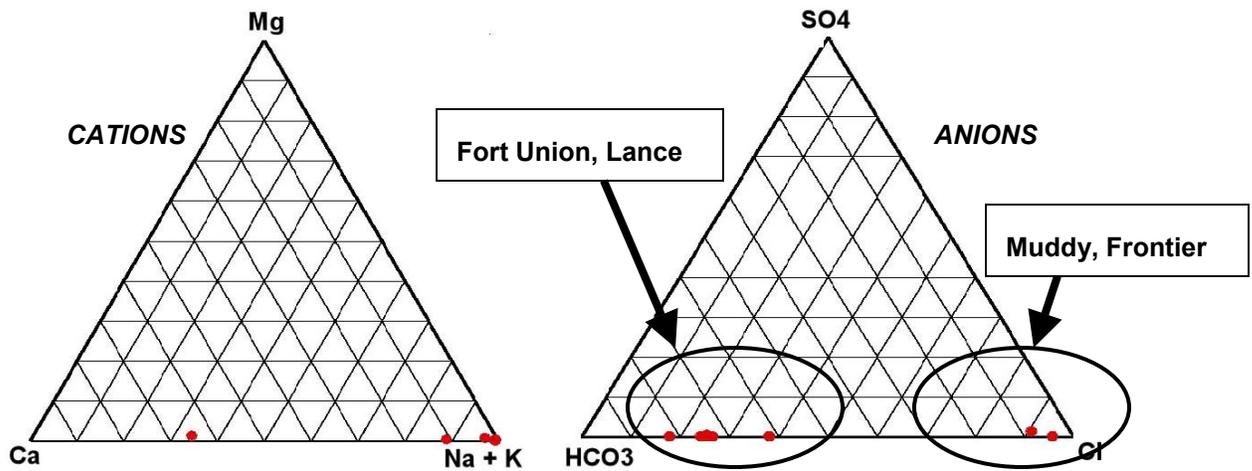
A north to south diagrammatic cross-section across of the area is shown in fig C-30. Production is from both “shallow” (3000 to 10,000-foot Ft. Union and Lance formations) and “deep” (17,000-to 23,000-foot Frontier, Muddy, and Lakota formations) targets.



**Fig. C-30. North to south diagrammatic cross-section of Waltman/Cave Gulch field complex**

Exploration and development within the deeper targets continues, with Barrett’s recent drilling of the Bullfrog #14-18, a 19,400-foot Lakota, Muddy and Frontier test. The Muddy tested 17.8 MMcfd and 30 barrels of water per day (bwpd), and 1 MMcfd of dry gas was tested out of the Frontier.

Because of the large number of formations represented, it is not surprising that there is a range in the observed compositions. The composition of these samples is shown on ternary diagrams in fig. C-31.



**Fig. C-31. Anions and cations showing samples from Cave Gulch field**

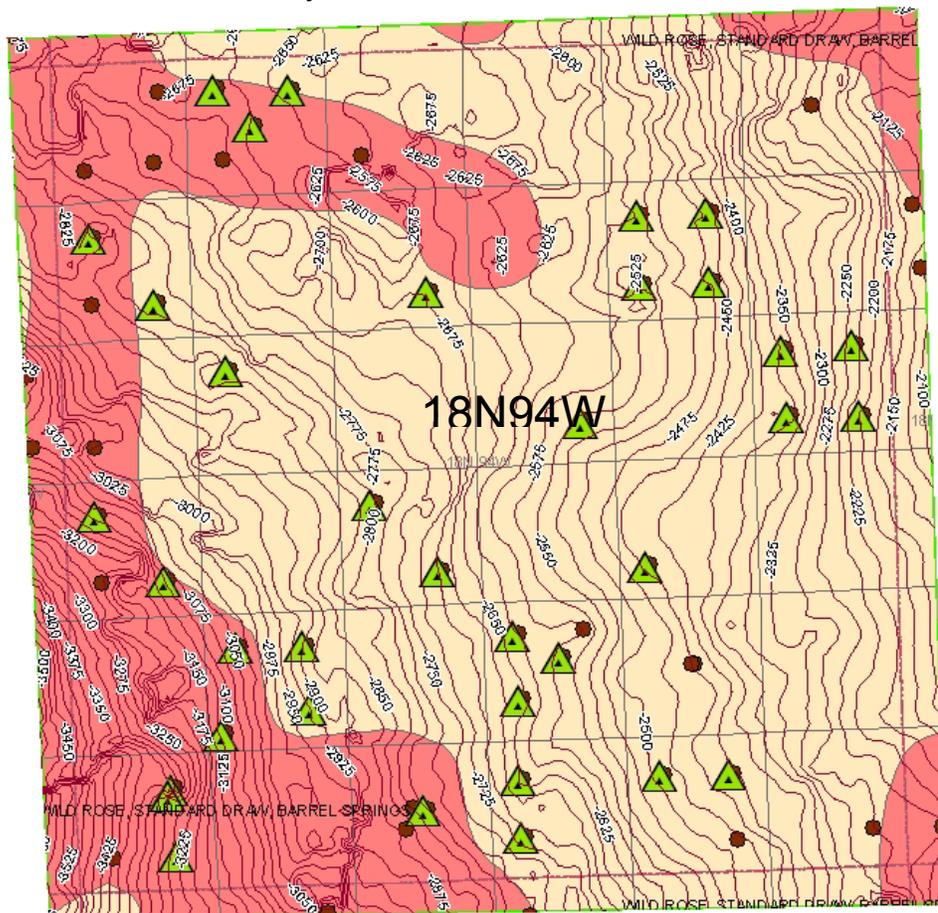
Ft. Union and Lance formations, both primarily non-marine in origin, are dominated by bicarbonate, whereas Muddy and Frontier formations, which are marine in origin, are chloride-dominated. The original depositional environment similarly controls stable isotopic composition. Ft. Union and Lance waters yield stable-isotopic compositions that fall into Group A (more negative deuterium composition), whereas Muddy and Frontier samples fall into the Group B (figs. C-10 and C-11).

Overall, the limited number of samples collected, analyzed and interpreted for the Waltman/Cave Gulch area reflects the depositional environments of their host reservoirs. There is no obvious geochemical evidence of large-scale vertical transport. A small proportion of the samples are undersaturated with respect to calcite. An expanded sampling program in the future may yield additional insights, particularly if the samples are collected over smaller intervals and the results integrated with petrophysical and borehole imagery interpretations.

## Wild Rose

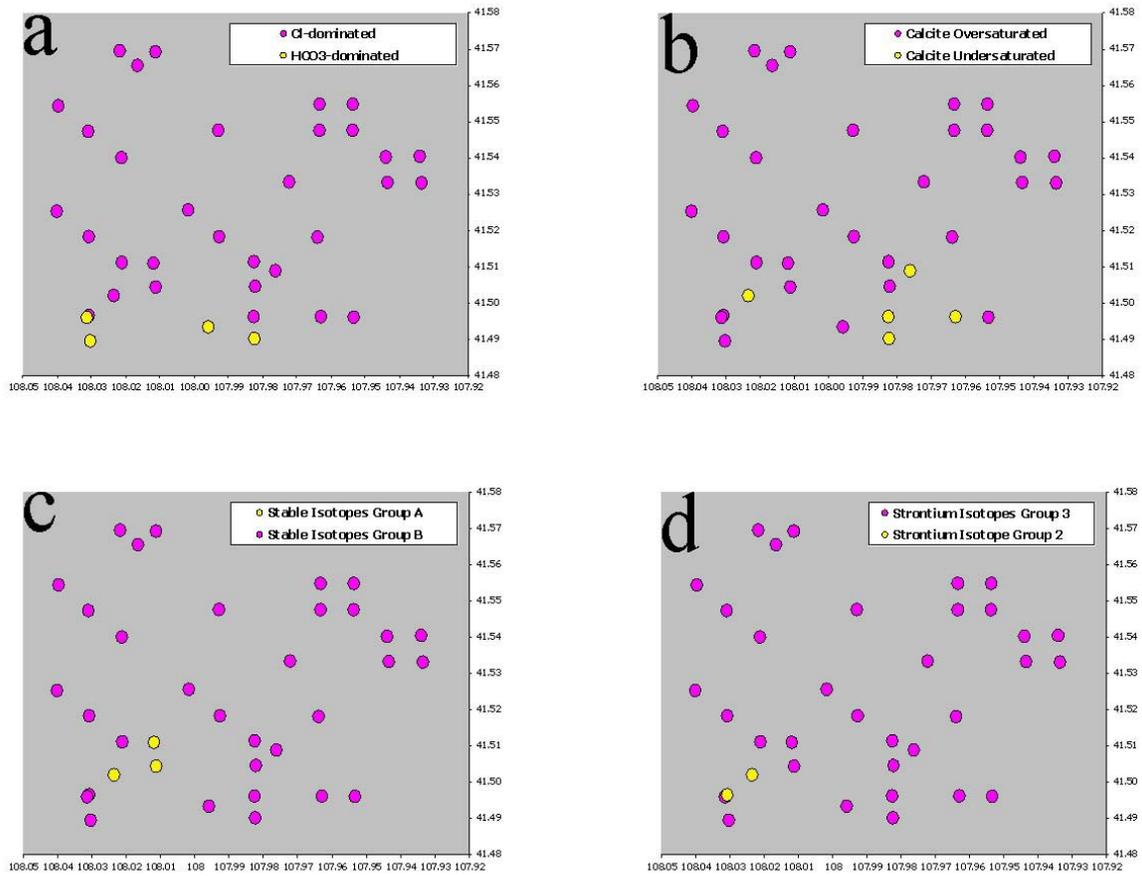
The Wild Rose field demonstration area (T18N, R94W) covers thirty-six square miles on the flank of the Wamsutter arch immediately west of the Echo Springs-Standard Draw producing area. Fig. C-32 shows the distribution of historical and recent water analyses in the township. Of the Mesaverde group, Wild Rose field is the only field where all the water samples were from wells reported completed.

As discussed previously, waters produced from the Mesaverde (Almond and Ericson members) can vary considerably in composition. This is due to the mixed marine and non-marine environments of deposition present within the uppermost Mesaverde. The potential stratigraphic variability notwithstanding, examining the geographic distribution of compositional variations reveals geochemical anomalies associated with major basement-controlled fault systems.



**Fig. C-32. Subsea structure contour map (feet) near the top of the Almond formation**

Fig. C-33 is a set of simple maps of the Wild Rose field area showing four components of water composition. The four maps include (a) the dominant anion (chloride or bicarbonate), (b) calcite saturation (whether the water is over- or undersaturated with respect to calcite), (c) stable isotope group (see fig. C-10 for explanation), and (d) strontium isotope group (see fig. C-14 for explanation).



**Fig. C-33. Maps of Wild Rose Field showing (a) dominant anion, (b) calcite saturation, (c) stable-isotope group, & (d) strontium isotope group**

Bicarbonate is the dominant anion in produced water from four wells in the field, all of which are along the southcentral and southwestern portion of the field in sections 31, 33 and 34 (fig. C-33a). Produced waters are generally fresher waters of a non-marine origin when bicarbonate is the dominant anion, suggesting that those four wells may have been completed in non-marine intervals of the Mesaverde. Five water samples from the southern portion of the field in sections 27, 29, 34, and 35 (fig. C-33b) were undersaturated with respect to calcite.

The stable-isotope groups generally indicate an affiliation with marine or non-marine origins for the formation water. Fig. C-33c shows three samples, all from section 29, with stable isotopes that fall into Group A, which is predominantly from non-marine depositional environments.

Fig. C-33d shows a map of the strontium isotope groups. Two samples fell into Group 2 and the remainder of the samples fell into Group 3. The Group 2 samples are in the southwest portion of the field in sections 29 and 31. Previously it was hypothesized that the dominant control on the strontium isotope signature was depositional environment of the rock. This is an outcome of the Lance and Ft. Union samples sharing similar characteristics, while being separate from the samples deposited in a marine environment (fig. C-14).

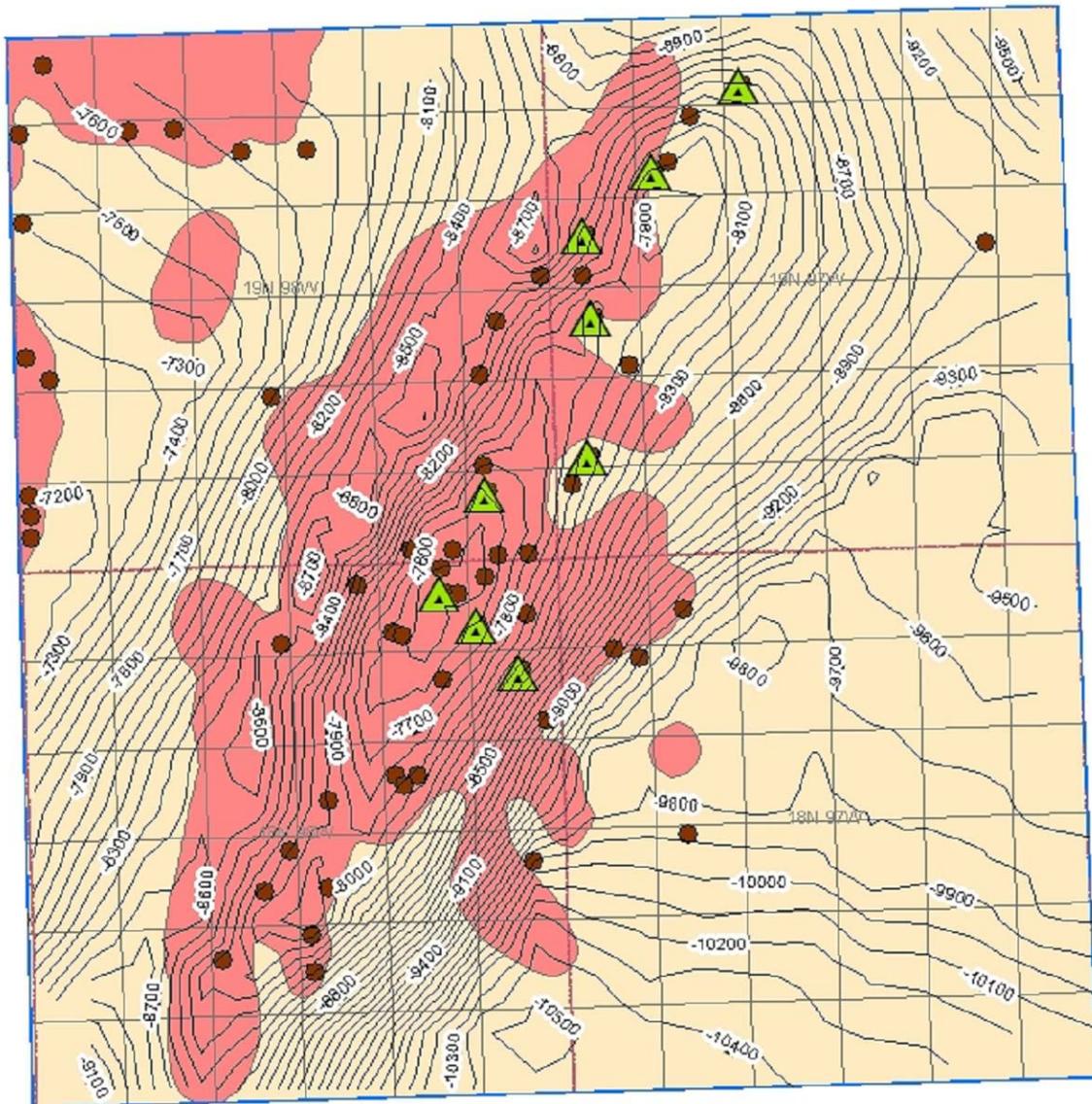
Close examination of the four maps makes it clear that the anomalies all tend to lie in the southcentral or southwestern portion of the field (sections 27, 29, 31, and 33-35), even though no single well exhibits anomalies for all four components. This clustering suggests that either one or both of two phenomena are occurring. One possible interpretation is that the wells in the southwest portion of the field are completed in the non-marine sections of the Mesaverde.

Alternatively, a similar clustering of anomalies was described by Smith (1998) in the Standard Draw-Echo Springs field, just to the east of Wild Rose. The anomalies corresponded to high gas production areas of the field. Smith hypothesized that the open fractures were conduits for gas and water from deeper horizons. One of the major through-going lineaments continues southwestward from Standard Draw-Echo Springs field through the Wild Rose field.

Since the majority of the wells in Wild Rose (not just the southwestern area) are completed through the entire Almond, it is probable that the clustering of anomalies is structurally controlled by the through-going basement fault.

## Table Rock

Table Rock field is a structurally controlled gas field located on the east flank of the Rock Springs uplift (fig. C-34). Production has been established from units ranging in age from Jurassic to Cretaceous. The area was the field demonstration site of the UPRR/DOE Greater Green River Basin Production Improvement Project in 1998-2000. Complete details of the project results and a thorough discussion of the local geology are contained in report DOE/MC/31063.



Subsea structure map (depth in feet) near Frontier horizon. Black circles are historical water analyses; triangles recent.

**Fig. C-34 Table Rock field area, Greater Green River Basin, Wyoming**

The objective of the project was to utilize horizontal wells to establish commercial production in the basin centered, naturally fractured Frontier formation. Anomalous production had been discovered in the center of the field itself. The goal was to extend production into poorer quality reservoirs of a continuous nature off the flanks of the structure using horizontal wells to specifically target the fractured Frontier formation. Samples collected from the Rock Island 4H and Sidewinders wells were analyzed but failed the quality control screening process. This was most likely due to contamination by workover fluids but was neither included in the database nor interpreted.

Four samples were taken from other wells in Table Rock field. One sample is from a well with Lewis through Almond completions. Another sample is from a well with only a Lewis completion. The remaining two samples are from wells with Nugget completions.

The sample from the Lewis-Almond completion is dominated by sodium and bicarbonate, whereas the other three samples are dominated by sodium and chloride. Salinities vary considerably among the four samples and do not relate to bicarbonate or chloride dominance in the anions. Table C-4 shows the completed interval and salinity of each Table Rock sample.

**Table C-4. Total dissolved solids of samples from Table Rock**

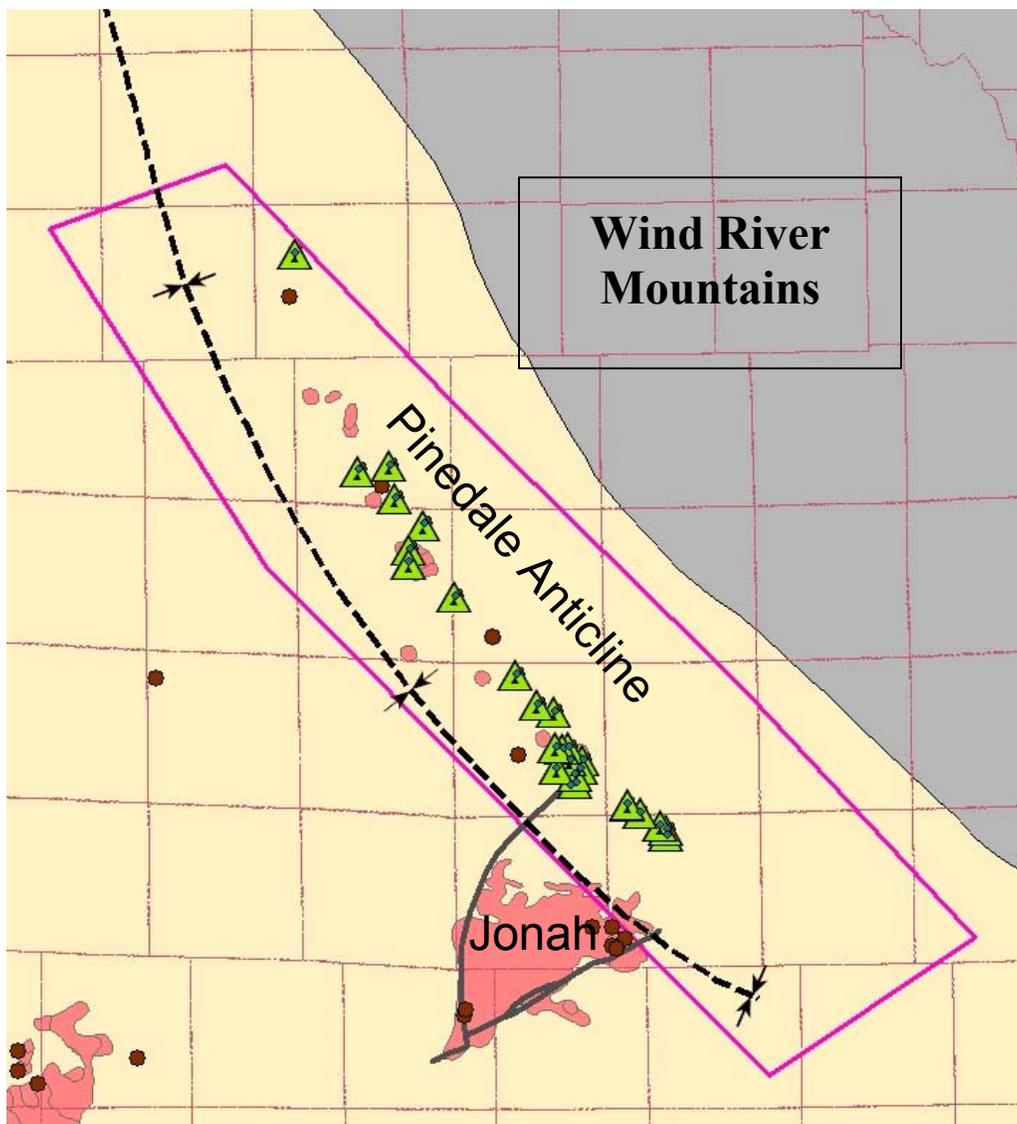
| <b>Complete formation</b> | <b>Total Dissolved Solids (ppm)</b> |
|---------------------------|-------------------------------------|
| Lewis through Almond      | 13,086                              |
| Lewis                     | 1,179                               |
| Nugget                    | 7,968                               |
| Nugget                    | 830                                 |

The contamination of the Rock Island 4H deep Frontier samples was regrettable. However, the degree of calcite undersaturation present in the water samples from other reservoirs that were valid is noteworthy. The Cretaceous reservoirs present along the east flank of the Rock Springs uplift are among the best in the area. A detailed water sampling program combined with core, thin section, and petrophysics studies might reveal the role of calcite undersaturated formation waters and secondary porosity development.

## ***Pinedale Anticline***

Pinedale anticline is located in the northern portion of the Greater Green River basin (fig. C-35). Production is primarily from the stacked low permeability sands of the fluvial Lance formation. The structure itself is a major hanging wall anticline 30<sup>+</sup> miles long with an estimated oil and gas in place of 40 tcf (Ultra Petroleum web site).

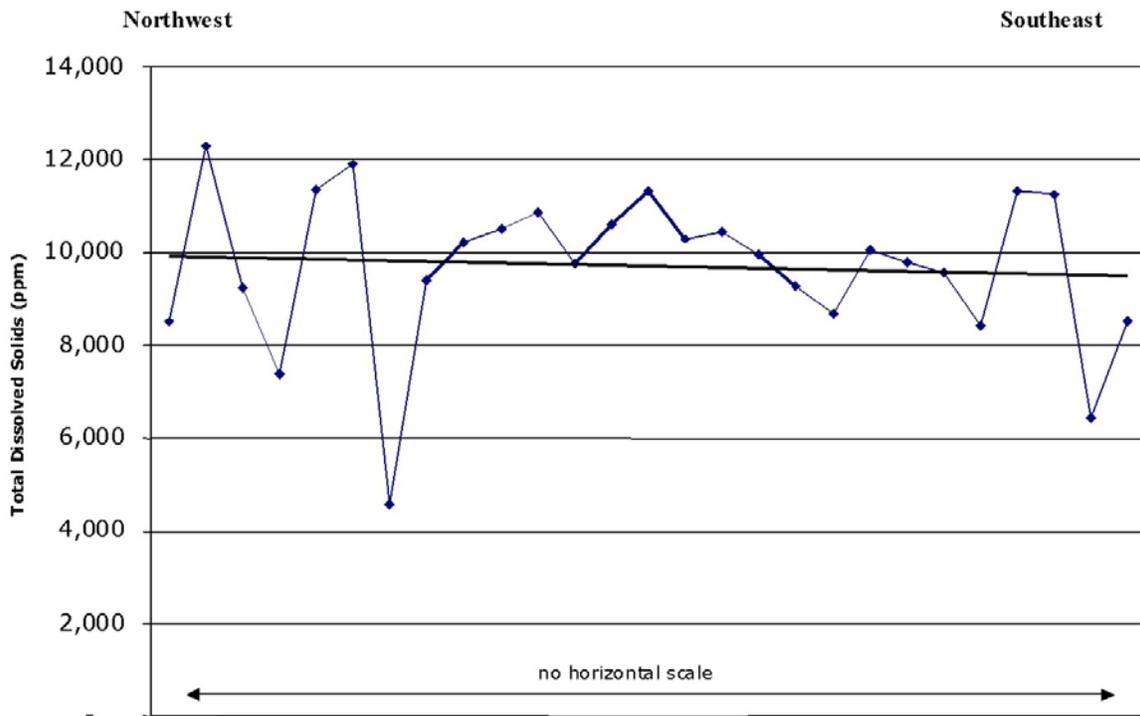
Production ranges from 8,000 feet to 14,000 feet and the gross pay interval is approximately 5,000-feet thick. The gas wells are completed and commingled over broad intervals using multi-stage hydraulic fracture treatments. The area is currently the subject of intense development activity.



***Fig. C-35 Pinedale area sample locations***

Samples collected as a result of this program are indicated with triangles in fig. C-35. The development program is focused on the axis of the anticline as was the sample program. Half of the samples from the Pinedale Anticline area are from wells with completions in the Lance formation. Two samples are from wells with Wasatch through Mesaverde completions. The remaining samples are from wells that have Lance through Mesaverde completions.

All the samples are sodium-chloride brines. The TDS ranges between 4,582 ppm to 12,288 ppm. There is a systematic decrease in salinity going from northwest to southeast, as shown in fig. C-36 on a cross-section plot. There is considerable scatter among the samples from the northwest end, but the general trend is freshening from northwest to southeast. At the same time, there is a slight increase in bicarbonate. This trend is irrespective of the completed interval.

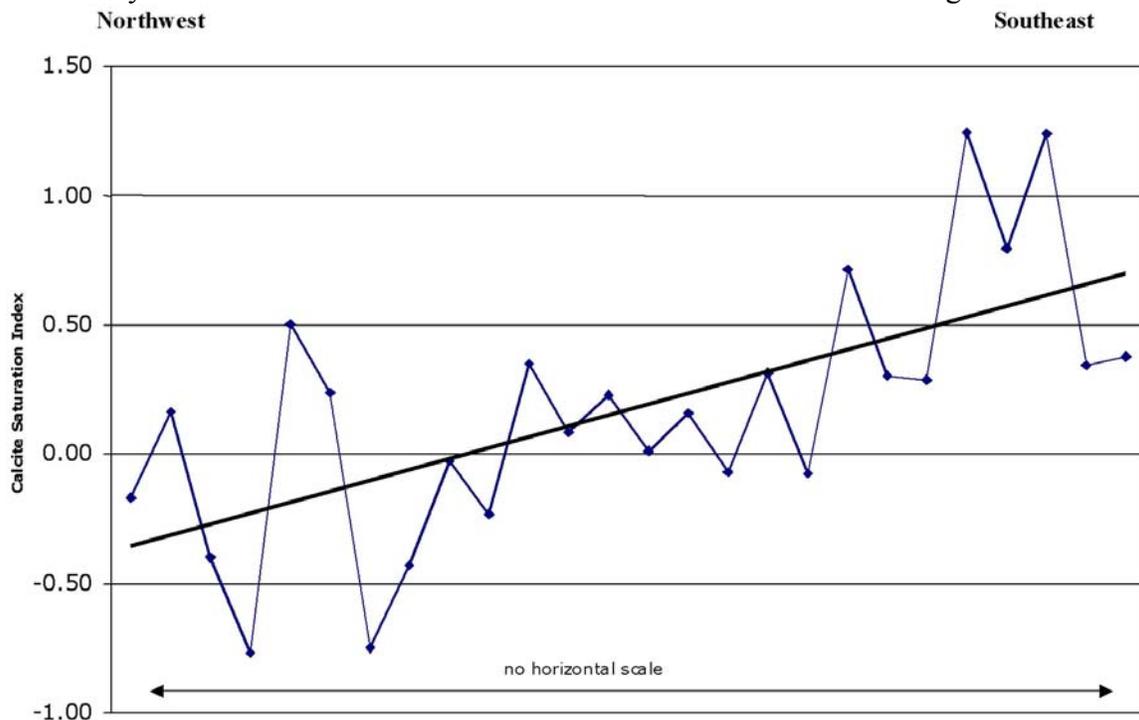


**Fig. C-36. The trend in TDS from northwest to southeast along the Pinedale Anticline**

All the Pinedale Anticline samples fall into the stable isotope Group A (fig. C-10), associated with more non-marine depositional environments. All the strontium isotopes are in Group 2 except one sample near the southeast end. The general trend of the strontium isotopes is a slight increase going from northwest to southeast.

However, there is one sample from the Rainbow 9-31 well that is considerably less radiogenic than the others, falling into Group 1. The reason for this anomaly is unknown. One well (Antelope 5-4), in the section adjacent to the Rainbow 9-31 well, exhibited a similar anomaly in the strontium isotopes. But when that well was re-sampled, the strontium isotopic value was more similar to the samples from other surrounding wells.

The Rainbow 9-31 was not re-sampled so it unknown if the anomaly is due to structural issues on the southeast end of the anticline, or the result of sampling contamination. In addition to the trend in TDS and strontium isotopes, the calcite saturation index also shows a systematic trend from northwest to southeast. This is shown on fig. C-37.



**Fig 37. Trend in calcite saturation index from NW to SE along Pinedale Anticline**

There is some scatter in the data, particularly on the far northwest end; however, the general trend is undersaturation to the northwest moving toward increasing oversaturation to the southeast. Similar to Wild Rose, this may indicate that there is less calcite cement in the matrix and fractures on the northwest end of the structure as compared to the southeast end.

The general trend in TDS, strontium isotopes, and calcite saturation index could not be correlated with any other phenomenon, such as depth. However, several things beyond the scope of this study are possible and worthy of future examination. These include, but are not limited to a detailed examination of the completed intervals, depositional environment and mineralogy, and a more detailed examination of the structure and fracturing.

## Conclusions and Recommendations

The primary conclusion of this study is that the main control on formation water chemistry is the original depositional environment of the host rock. This conclusion was reached from examination of the abundant samples in the historical database combined with the new more extensively analyzed samples from this study.

In general, those formations deposited in marine environments produce water that tends to have higher TDS, has chloride as its dominant anion, and whose deuterium isotopes are less negative as compared to formations deposited in non-marine environments. Those deposited in non-marine environments tend to produce water that is fresher, has bicarbonate as the dominant anion, and has deuterium isotopes that are more negative. In addition, historical samples from Pennsylvanian age rocks indicate that water from these formations are likely to have sulfate as the dominant anion.

Related to the primary conclusion is the observation that there are three types of events that affect the water chemistry, overprinting the signature of the original depositional environment. These events are diagenetic alteration, influx of meteoric water, and migration of water from other zones. The last event can be either a naturally occurring event that took place in the geologic past, such as during hydrocarbon migration, or a man-made event caused by the production of hydrocarbons.

Diagenetic alteration was not a component of this study, but has been the subject of literally hundreds of articles since the first studies of oilfield formation water in the 1960s. However, the effects of diagenetic alteration can be observed on the plot of stable isotopes (fig. C-10), which shows a wide range of  $^{18}\text{O}$  for each of the two groups. Suchecki and Land (1983) and Aplin, et al (1993) attributed this type of range to clay mineral re-crystallization. The plot of oxygen isotopes also provides evidence for meteoric influx. Group B samples intersect the meteoric water line. Hitchon and Friedman (1966) interpreted a similar pattern of formation water samples from the Alberta Basin as resulting from a mixing of diagenetically altered seawater with modern meteoric water.

The evidence for migration of waters between zones comes from exceptions to the general trends. This is most striking at Wild Rose field where anomalies in the dominant anion, stable isotopes, strontium isotopes, and calcite saturation indices all occur in the southwest portion of the field. Similarly, an anomaly was observed in the strontium isotopes in one well from the Pinedale Anticline. This does not conclusively prove mass migration, but earlier work by Smith (1998) showed that on a regional scale, the anomalies in TDS in the Green River basin coincided geographically with places where major lineaments had been mapped in the basin.

Also, results of this study indicate a correlation between TDS and surface fracture density (fig. C-28). Whether the phenomena observed in this study was naturally occurring migration or the result of hydrocarbon production is unknown. Smith (1998) demonstrated with a time series of water samples at Standard Draw Field that water was gradually being produced from a lower zone. Although originally proposed as a component of this project, no suitable locations were found for time series sampling.

The fact that trends related to depositional environment can be observed and that diagenetic overprints can be recognized leads to the second conclusion of this study, which is that there does not appear to be any wholesale movement of water throughout the Green River and Wind River basins. There is sufficient evidence, discussed in the preceding paragraph, to suggest that either local fracture swarms or major lineaments have provided conduits for vertical water movement. But these are localized events and are recognized as geographically related anomalies.

The final conclusion is that the study of formation water composition, certain components in particular, provides a means for assessing produced water origins, which is invaluable in developing a plan of remediation or avoidance. While it would be ideal to have a single component that provided each formation with a unique signature, petroleum systems have never been that simple.

Nevertheless, a few guidelines have emerged from this study. The main guideline to follow is the depositional environment of the host rock. However, it has been demonstrated that there are exceptions. One of the more important exceptions to note is that chloride-dominance is common in waters produced from formations that were deposited in a non-marine setting. However, the converse—bicarbonate dominated water production from a formation that was deposited in a marine setting—is rarely true, and this could point to a source of produced water outside the completed interval.

Stable isotopes back up other information in these situations, and it is recommended that analysis for these become routine. Strontium isotopes have the potential to become powerful source indicators, but more detailed studies that involve correlation with the rock chemistry will be required. Nevertheless, they have been shown in this study to be potential indicators of faulting and water movement, as indicated by the anomalies observed at Wild Rose field and at the Pinedale Anticline.

Trends emerged only with a sufficient number of sampled wells. In utilizing these guidelines, it is important to develop a complete picture of produced water composition using samples taken from numerous wells in the field. The wisdom of this was demonstrated in the Wild Rose field demonstration.