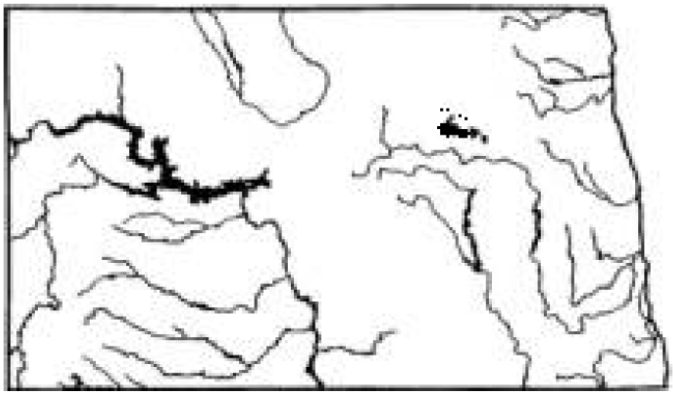

Technical Report No: ND08-09

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TABLE OF CONTENTS

LIST OF FIGURES 3

LIST OF TABLES 4

ACKNOWLEDGMENTS 5

ABSTRACT 5

INTRODUCTION 7

MATERIALS AND METHODS 13

RESULTS 15

X-ray Diffraction 15

Chemical Analysis 17

Inorganic Sulfide 19

Organic Sulfide 20

Organic Carbon 21

Ferrous Iron 22

Statistical Correlations 23

DISCUSSION 24

CONCLUSIONS 35

REFERENCES 36

LIST OF FIGURES

Figure Page

1. Generalized Stratigraphic Column of the Late Cretaceous Units Present in Eastern North Dakota with Associated Geochronologic Stages 11

2. Underlying bedrock and glacial direction near the Elk Valley Aquifer 12

3. Borehole Locations in Eastern North Dakota with Approximate Extent of Bedrock Subcrops 14

4. Average Weight % Abundance of e^- Donors by Formation 19

5. Distribution of Organic Carbon Within the Study Area 26

6. Distribution of Organic Sulfide Within the Study Area 27

7. Distribution of Inorganic Sulfide Within the Study Area 28

8. Distribution of Total Ferrous Iron Within the Study Area 29

9. Average Values by Formation for Each Donor 30

10. Map of Eastern North Dakota Aquifers with High Electron Donor Potential Based on Local Bedrock Formations 32

11. Map of Shale Formations in the Upper Midwest and the Extent of the Most Recent Glaciation 34

LIST OF TABLES

Table Page

1. Results of XRD Analysis 16

2. Results of Each Donor Test 18

3. Average Values and Standard Deviations by Formation 18

4. Results of Spearman Correlations and Associated Critical Values of Rho 24

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ABSTRACT

Research involving a network of in situ mesocosms (ISM) in North Dakota, Minnesota, and Iowa has revealed significant variation in the denitrification capacity of aquifers in different regions of these states. One aquifer in particular, the Elk Valley Aquifer (EVA) of east-central North Dakota, has the highest concentrations of electron (e^-) donors (organic carbon ~0.4%, pyrite as S ~0.4%, and ferrous iron ~0.3%) within its sediments and the highest rates of denitrification. The sediments at all of the ISM sites were deposited as outwash during the last Wisconsinan glaciation (~12ka), yet their e^- donor concentrations vary. We suggested that the e^- donor concentrations in the EVA are high because the local bedrock units that would have contributed sediments to it as glacial outwash also have high concentrations of e^- donors. The purpose of this study was to evaluate the amount of e^- donors available in the local Upper Cretaceous bedrock units.

Bedrock samples (n = 38) from 20 sites in eastern North Dakota were obtained by drilling during the summer of 2006 in conjunction with the North Dakota State Water Commission

(NDSWC). Samples were frozen before analysis for mineralogical content by X-ray diffraction, organic carbon, pyrite as inorganic sulfide, organic sulfide, and ferrous iron concentrations. It was hypothesized that the Niobrara, Carlile, and Greenhorn Formations would contain higher concentrations of e^- donors than the Pierre Shale.

Organic carbon concentrations in the Pierre (0.3% to 0.7%) are relatively low while concentrations in the Niobrara (~2.9%) and Greenhorn (~3.7%) are significantly higher. Pyrite as inorganic S concentrations in the Pierre (0.01% to 0.5%), Niobrara (~0.2 to 0.9%), and Greenhorn (~1.1%) are similarly distributed. Ferrous iron was generally present in concentrations of 1.0% to 2.0% over the entire study area with some high concentrations measured in Greenhorn (2.2%) and Niobrara (3.5%) samples. Organic sulfide was generally insignificant, but was present in measurable amounts (0.1% to 0.8%) in samples that were also rich in organic carbon. The Pierre showed the least variation of the formations tested, while the Niobrara showed the greatest. This is likely the expression of two distinct Niobrara members, a calcareous shale and a chalky shale.

Regional bedrock maps of shale formations and ice movements of the late Wisconsinan glaciation are used to show that there are likely other aquifers in North Dakota, and indeed other regions in the Upper Midwest, that contain aquifers rich in e^- donors just as the EVA is. These potentially reactive aquifers may play an important role in groundwater quality as the redox conditions within these aquifers are likely very different from that of others. It is suggested that future research focus on identifying other aquifers composed, at least in part, of glaciated shale.

INTRODUCTION

Ongoing denitrification research with in situ mesocosms (ISMs) (Korom et al., 2005) in aquifer sediments at 13 sites in three states (Iowa, Minnesota, and North Dakota) indicate that the site in the Elk Valley aquifer (EVA), east-central North Dakota (ND), (Korom et al., 2005) has the fastest denitrification rates and the sediments have the greatest concentration of electron (e^-) donors (organic carbon, inorganic sulfide, and ferrous iron) (Tesfay, 2006). Schuh et al. (2006) estimated that the supply of e^- donors in the EVA, an unconfined aquifer underlying cultivated land and used as a major source of drinking water, may be sufficient to reduce nitrate concentrations at current loading rates for centuries. The aquifers hosting all of the ISM sites are of the same geologic age, being formed of outwash deposits during the retreat of the late Wisconsinan glaciation, 20,000 to 11,600 B.P. (Fenton et al., 1983), yet, the e^- donor concentrations in the sediments vary. We proposed that the e^- donor concentrations in the EVA are high because the local bedrock units that would have contributed sediments to it as glacial outwash also have high concentrations of e^- donors. To verify my hypothesis, bedrock samples of east-central ND were analyzed for common e^- donors. Analytical results, coupled with bedrock maps of eastern North Dakota and known glacial movements, are used to predict other aquifers in eastern ND that, like the EVA, may also have high concentrations of e^- donors, and, therefore, high denitrification capacities. A bedrock map of the Upper Midwest showing directions of the ice movements of the late Wisconsinan glaciation is also used to show that there are other regions in the US with similar geological features, thereby predicting likely locations of other aquifers rich in e^- donors.

Nitrate, one of the most prevalent forms of groundwater pollution (Freeze and Cherry, 1979), predominantly originates from anthropogenic sources such as agricultural and livestock

production (Rivett et al., 2008), which are prevalent activities across North Dakota. Excess nitrate inputs can cause eutrophication of surface water as well as reduce the quality of subsurface supplies (Aravena and Robertson, 1998). The primary natural nitrate attenuation process is denitrification. This process requires an oxygen-limited environment, the presence of nitrogen digesting bacteria, and the availability of e^- donors (Korom, 1992; Starr and Gillman, 1993; Rivett et al., 2008). According to Korom (1992) the three most common e^- donors are organic carbon, sulfide (typically as pyrite, FeS_2), and ferrous iron minerals. Research has also shown that the controlling factor in this reaction has typically been the availability of suitable e^- donors within the aquifer sediments (Korom, 1992; Rivett et al., 2008).

Igneous derived sediments are not likely to contain significant quantities of e^- donors, and, of the common e^- donors, only iron could be present in significant quantities. Ferrous iron could originate from several igneous minerals including amphibole (grunerite), pyroxene (ferrosilite), biotite, olivine, glauconite, chlorite (chamosite / clinochlore), magnetite, or ilmenite (Appelo and Postma, 1996). One, if not several, of these minerals could be found in a variety of igneous settings. Organic matter is not likely to be found in igneous derived sediments although it could be entrained during the sedimentation process.

Of the common sedimentary rocks, sandstones and other clastic rocks likely reflect the character of their parent rock(s), while limestone and other chemical sedimentary rocks may contain e^- donors. If fact, denitrification has been observed and e^- donors have been measured in limestone and dolomite aquifers (Lawrence and Foster, 1986; Rivett et al., 2007). However, shale has the greatest potential to contain e^- donors due to its environment of deposition.

Shale underlies more of Earth's land surface than any other rock (Pettijohn, 1957) and as such its geochemistry in regards to e^- donors is fairly well known. Organic carbon is common in

shale and a major component of black shales, typically averaging > 3% in black shales and about 0.65% in gray shales (Vine and Tourtelot, 1970). The organic matter can accumulate in a variety of ways and will be preserved provided its depositional rates outweigh decompositional rates (Tourtelot, 1979). While most shales are marine in origin, the preserved organic carbon likely represents both terrestrial and marine sources and may or may not be associated with high inorganic carbon (calcite) concentrations (White and Arthur, 2006).

Pyrite and other sulfur forms (such as organic sulfur) are commonly associated with organic carbon in shale, and form early in the diagenetic process (Tourtelot, 1979; Pratt and Brassell, 1994). Pyrite is the only iron sulfide mineral to form in marine environments (Schoonen, 2004). Paytan et al. (2004) report that pyrite forms in sediments by reduction with organic carbon serving as the oxidant. Typically, the limiting factor in pyrite formation is the supply of buried organic carbon (Shultz, 2004). Pyrite also serves as a significant source of ferrous iron in shale and may be oxidized to iron oxide or gypsum (Schultz et al., 1980; Tourtelot and Cobban, 1968). Other sources of iron may include clay minerals, goethite/hematite, jarosite, detrital biotite, or some carbonate minerals (Tourtelot,1962; Cole et al., 1978; Fischer and Gaupp, 2005).

The bedrock of eastern North Dakota predominantly consists of a series of shale and related rocks deposited during the Late Cretaceous period (Bluemle, 1986a). These Cretaceous strata dip slightly to the west and subcrop beneath glacial till (Hanson and Kume, 1970). The sequence of stratigraphic units is summarized in Figure 1. The Greenhorn Formation and the Carlile Formation are both dark-gray shales, while the Niobrara Formation is generally lighter in color and is highly calcareous (Carlson, 1964; Merewether and Cobban, 1981; MacDonald and Byers, 1988). The Niobrara has been described as containing two unnamed members in eastern

North Dakota: a lower, dark gray, calcareous shale and an upper, chalky member (Carlson, 1964; Shurr and Reiskind, 1984; Reiskind, 1986). Most of eastern North Dakota's bedrock consists of the Pierre Formation, a thick, gray, noncalcareous shale which unconformably overlies the Niobrara. The Pierre contains several members including a dark-gray to black member known locally as the Pembina Member and elsewhere in the United States as the Sharon Springs Member (Schultz et al., 1980). The relatively high organic carbon and pyrite contents of this member are well established (Tourtelot, 1962; Gill and Cobban, 1965; Schultz et al., 1980; Kulp and Pratt, 2004). Due to their westerly dip, the lowest members of the Pierre and Niobrara Formations subcrop at the easternmost extent of each formation (Figure 2).

The EVA mentioned above lies in close proximity to all of these formations (Figure 2). Its sediments were deposited as an underflow fan and much of its sediment originated from the nearby or underlying Pierre, Niobrara, and Carlile Formations (Clayton and Moran, 1981; Hansen and Kume, 1970; Schuh et al., 2006). Similar glacial processes in North Dakota and other northern states have likely created other aquifers composed of shale-rich sediments that may also contain high quantities of e^- donors.

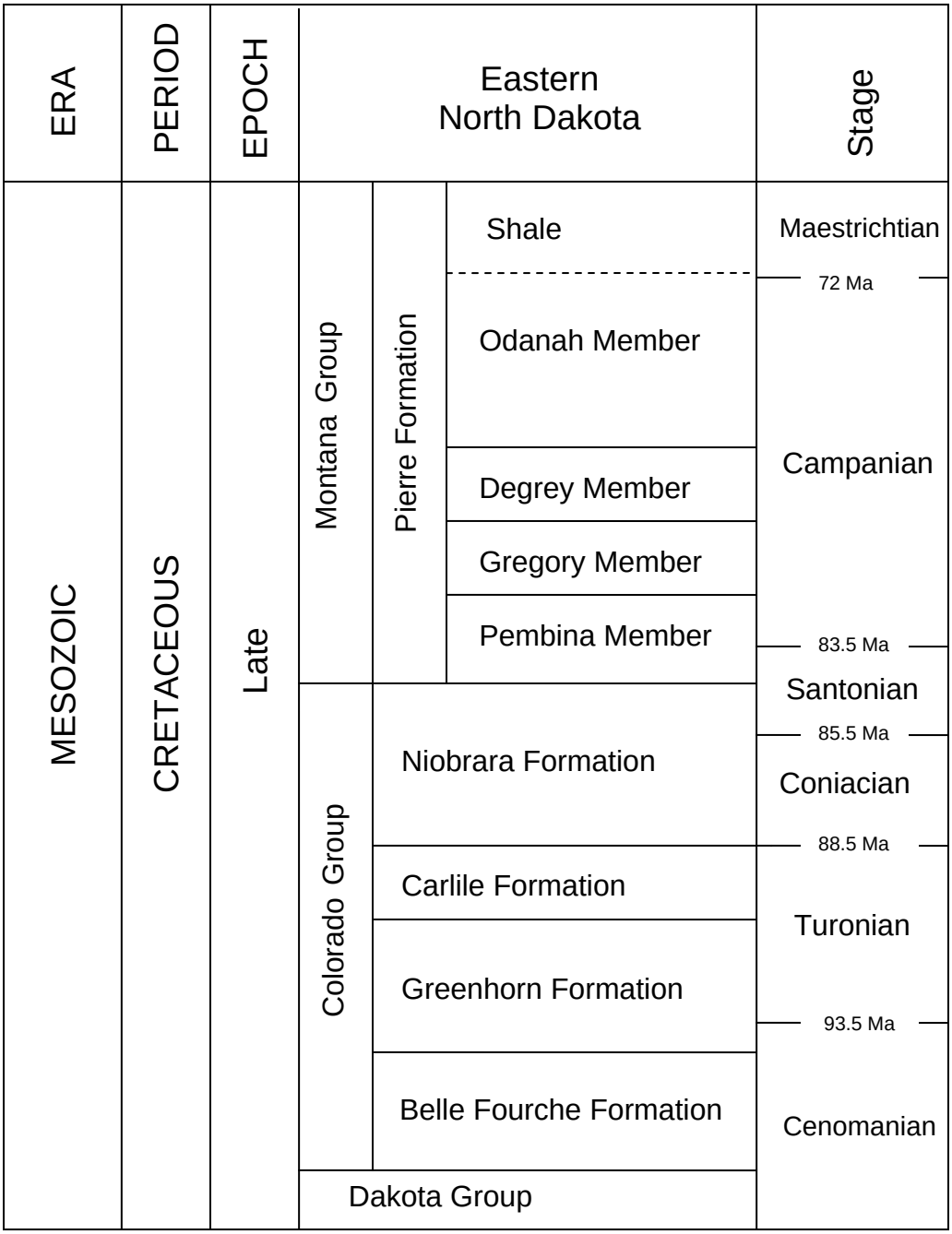

Figure 1: Generalized stratigraphic column of the Late Cretaceous units present in eastern North Dakota with associated geochronologic stages (Modified from Wosick, 1977, Gill and Cobban, 1965, and Bluemle et al. 1981). Stage dates are from Roberts and Kirschbaum, 1995.

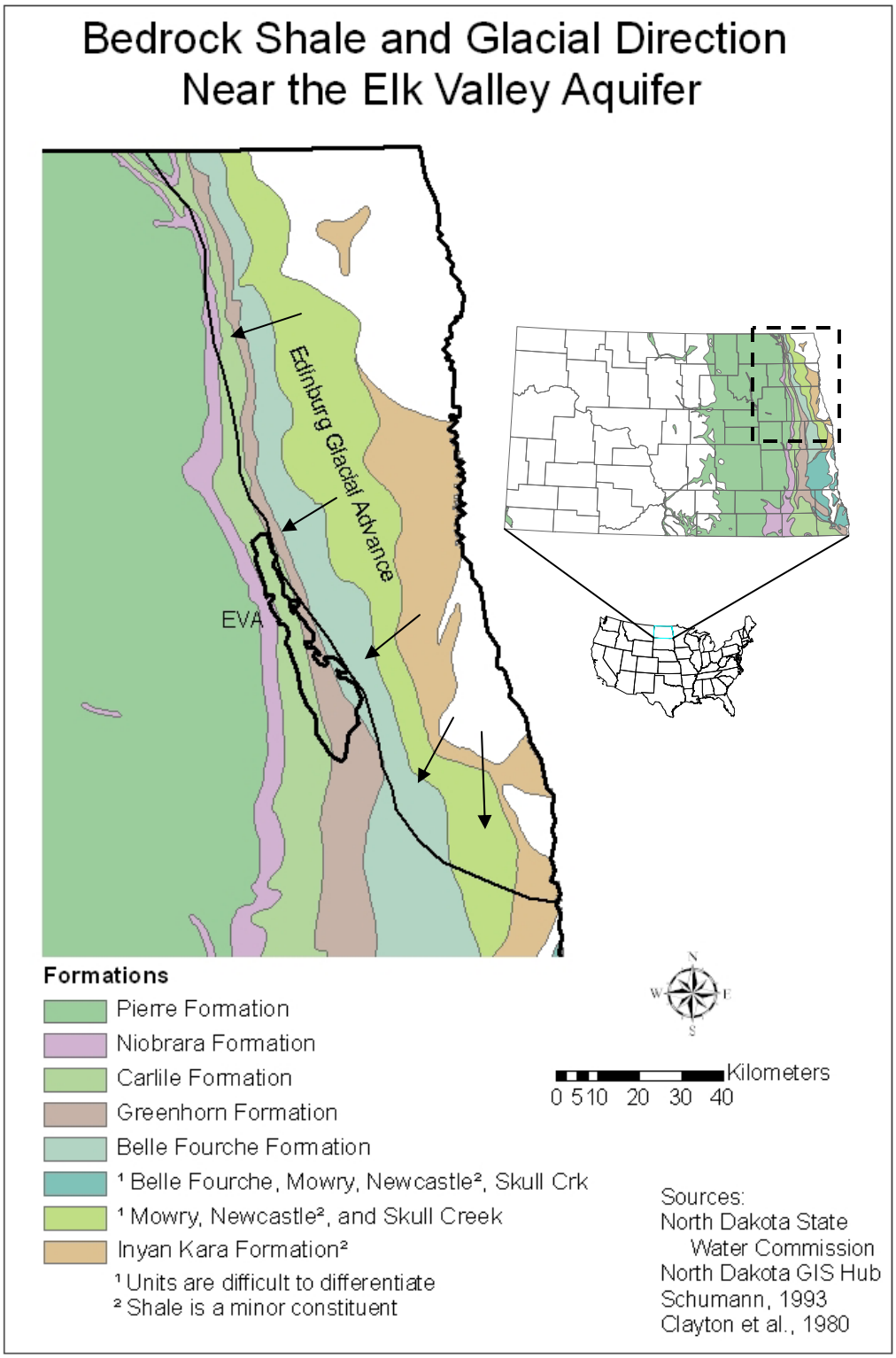

Figure 2: Underlying bedrock and glacial direction near the Elk Valley Aquifer. Deposition of the EVA was constrained on the east by the Pembina Escarpment and on the west by the Edinburg Glacial Lobe. The EVA is seen in close geographic proximity to several shale units that are potentially rich in electron donors. The inset shows the geographic extent of Cretaceous shale in eastern North Dakota.

MATERIALS AND METHODS

Samples were collected in June 2006 by drilling to the bedrock in seven eastern North Dakota counties (Figure 3). Upon extraction from the subsurface, lithologic cuttings were rinsed to remove drilling fluid, vacuum sealed in plastic bags, and frozen until needed for analysis. After sampling was completed, the holes were plugged with bentonite. Two to three samples were collected from each site in 3.05 – 6.10 m intervals; 20 sites yielded 36 samples. Formations were identified in the field and later reviewed in the laboratory. The field identification was checked against the reported lithologic descriptions (Bluemle, 1986a) and the X-ray diffraction (XRD) analysis. Samples that did not clearly exhibit properties of one formation or another were assigned to the formation that more closely matched its properties. Existing bedrock maps proved unreliable for formation identification based solely on location. Confident stratigraphic identification of Pierre members was not possible.

Analyses consisted of XRD analysis for mineralogy, total organic carbon analysis (Churcher and Dickout, 1987), inorganic sulfide analysis (Canfield et al., 1986), ferrous iron analysis using a modified method of Kennedy et al. (1999) (S. Klapperich, 2008), and a method for organic sulfide adapted from Tabatabai (1996) and LaCount et al. (1997). Our method for organic sulfide involves first removing various soluble sulfur forms and pyrite and then combusting the sample at a temperature low enough ($T < 650$ °C) not to combust other insoluble sulfate minerals, such as barite ($BaSO_4$). Tests showed the method was not sensitive to barite, a common marine shale mineral (Payton et al., 2004) most likely to survive the digestion phase (S. Klapperich, 2008). All chemical analyses were carried out at UND's Environmental Analytical Research Laboratory (EARL).

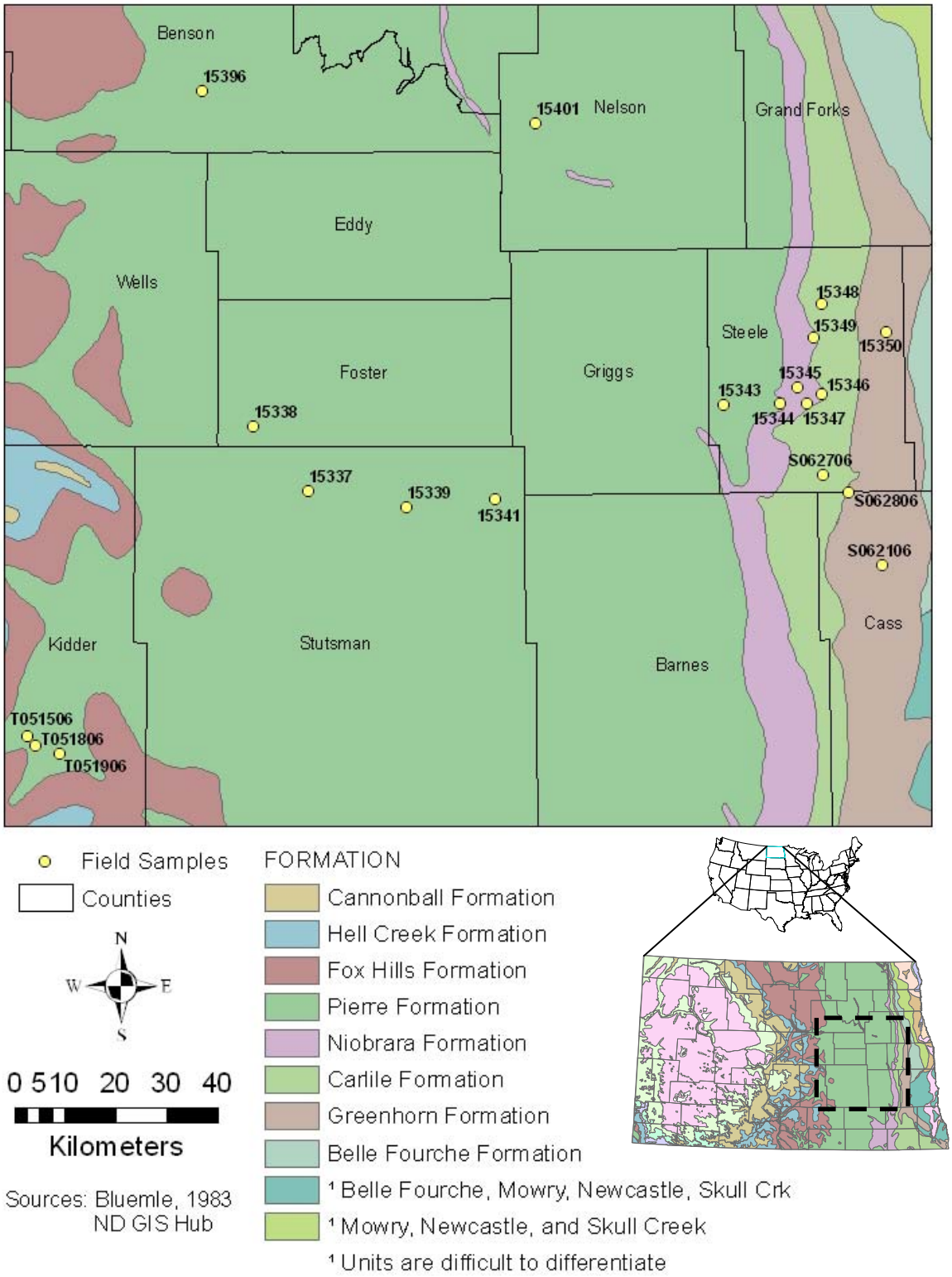

Figure 3: Borehole locations in eastern North Dakota with approximate extent of bedrock subcrops.

Since quantification limits varied on a daily basis, reported instrument detection limits are not always the most effective way to establish reliable data. As such, duplicate analyses of all samples herein were standard procedure for the combustion methods of organic carbon and organic sulfide. Duplicate analyses were also performed, although less frequently, for the other analytical techniques and all were evaluated by Equation 1.

$$\%\ difference = \left(\frac{value\ 1 - value\ 2}{value\ 1 + value\ 2} \right) \times 100 \qquad (1)$$

When the result of Equation 1 was less than 25%, the results were assumed to be reproducible and both values were kept. If the result of the formula was > 25% the results were discarded for this analysis (S. Klapperich, 2008).

RESULTS

X-ray Diffraction

XRD analysis was able to differentiate between samples from the different shale formations. Generally, results of the XRD yielded significant quantities of quartz and calcite as well as a variety of clay minerals, such as smectite and illite (Table 1). Pyrite was also present in each of the formations sampled and was generally found in samples of a medium to dark gray color, which is typically also an indication of higher organic carbon content (S. Klapperich, 2008). XRD analysis also showed that the curves from different depth intervals in the same borehole differed primarily in the peak intensity, but differed little in peak distribution. Characteristic features were identified within the curves that were used to help differentiate the different samples (S. Klapperich, 2008).

Table 1: Results of XRD analysis. Q - Quartz, Cal - Calcite, Pyt - Pyrite, Plag - Plagioclase Feldspar, I - Illite, Mus - Muscovite, Semc - Smectite, Crt - Cristobalite, Dol - Dolomite

Sample ID	Depth interval (ft)	Formation	Q	Cal	Pyt	Plag	I	Mus	Smec	Crt	Dol
T051506	390-400	Pierre	X		X	X	X				
T051806	140-160	Pierre	X		X	X	X				
T051905	101-111	Pierre	X		X	X					
15337A	66-80	Pierre	X		X	X	X				X
15337C	90-100	Pierre	X		X	X	X				
15338A	15-20	Pierre	X					X			
15338B	25-30	Pierre	X					X			
15338C	35-40	Pierre	X			X		X			
15396	96-100	Pierre	X	X		X					
15401	20-40	Pierre	X	X		X	X				
15339A	20-25	Pierre	X		X					X	
15339C	37-40	Pierre	X		X				X	X	
15341A	265-270	Pierre	X	X						X	
15343A	40-45	Pierre	X	X		X				X	
15344A	40-45	Pierre	X	X					X		
15345A	12-18	Niobrara	X	X							
15345C	15-20	Niobrara	X	X							
15347A	60-65	Niobrara	X	X							
15347C	75-77	Niobrara	X	X							
15346A	60-65	Niobrara	X	X	X						
15346C	70-75	Niobrara	X	X	X						
15349A	43-48	Niobrara	X	X	X						
15348A	70-100	Carlile	X	X	X						
15348C	80-100	Carlile	X	X	X						
S062706	245-260	Carlile	X								
15350A	131-140	Greenhorn	X	X	X						
15350B	142-150	Greenhorn	X	X	X		X	X			
15350C	150-160	Greenhorn	X	X	X						
S062106	379-400	Greenhorn	X	X	X						
S062806	300-320	Greenhorn	X	X	X	X					X

The samples from the Pierre Formation showed the most variation in mineral composition. Five of the 11 boreholes contained calcite while in the other six pyrite was positively identified. Plagioclase was also found in seven of the borehole sites. Clay minerals and mica were positively detected in all the boreholes in some combination of smectite, illite, or

muscovite. A broad cristobalite peak characterized samples from three of the boreholes, which is indicative of a silica-rich sample.

The Niobrara Formation was distinctive in that the dominant mineral was calcite instead of quartz. All samples contained predominantly calcite and quartz, and in the two western-most boreholes, those two minerals could account for nearly major every peak. Not surprisingly, these samples tended to be lighter in color. Samples from the more eastern boreholes contained more peaks, although the only additional mineral identified was pyrite.

The Carlile Formation samples also contained quartz, small amounts of calcite, and pyrite. The Carlile Formation is described as non-calcareous with abundant gypsum (Bluemle, 1986a); however, gypsum was not detected. The Greenhorn Formation samples also contain quartz, a large amount of calcite, and pyrite. Plagioclase, illite, and muscovite are also present in some samples. The relative heights of the quartz and calcite peaks are diagnostic of this formation in this study.

Chemical Analysis

Summary results for each donor are reported in Table 2. Summary results by formation are also reported in Table 3 and Figure 4. Depth within a borehole did not seem to be a factor as the upper section (0 to 6.10 m below the bedrock contact) was just as likely to produce a higher donor value as the lower section (6.10 – 12.20 m below the contact). As a result, values from each depth interval were averaged into a single value for each borehole tested.

Table 2: Results of each donor test. The results of the individual samples from each borehole have been averaged together to produce one value per location. All results are reported by weight %. Results for the organic donors represent values adjusted for Pre-Treatment (PT) weights. All OS tests for T051906 exceeded the 25% difference standard and were exclude. The values for Total Ferrous Iron are those referenced throughout the report.

Field ID	Formation	$\%S^-$	OS (PT Eq) (%)	OC (PT Eq) (%)	Fe(II) (%)	avg Pyrite Fe %	Total Ferrous Iron %
			NR – Not reproducible		Extraction method		
T051506	Pierre	0.51	0.006	0.654	1.04	0.45	1.49
T051806	Pierre	0.54	0.007	0.552	1.03	0.47	1.49
T051906	Pierre	0.41	NR	0.485	1.07	0.36	1.42
15337	Pierre	0.48	0.003	0.731	0.94	0.42	1.36
15338	Pierre	0.49	0.008	0.606	1.32	0.42	1.74
15339	Pierre	0.36	0.011	0.442	0.59	0.31	0.90
15341	Pierre	0.26	0.008	0.505	0.82	0.23	1.04
15343	Pierre	0.44	0.010	0.347	0.91	0.38	1.29
15344	Pierre	0.39	0.008	0.521	1.73	0.34	2.07
15345	Niobrara	0.32	0.007	0.427	3.26	0.28	3.54
15346	Niobrara	0.90	0.586	5.557	0.67	0.79	1.46
15347	Niobrara	0.22	0.004	0.451	1.29	0.19	1.49
15348	Carlile	0.87	0.105	1.967	0.86	0.76	1.62
15349	Niobrara	0.73	0.795	5.306	0.67	0.63	1.31
15350	Greenhorn	2.09	0.611	4.856	0.45	1.82	2.27
S062106	Greenhorn	0.56	0.533	3.804	0.58	0.49	1.07
S062706	Carlile	1.16	0.038	1.566	1.18	1.01	2.19
S062806	Greenhorn	0.59	0.094	2.478	1.07	0.52	1.58
15396	Pierre	0.47	0.013	0.327	0.86	0.41	1.27
15401	Pierre	0.07	0.007	0.710	1.32	0.06	1.38

Table 3: Average values and standard deviations by formation.

Formation	n	IS	stdev	OS	stdev	OC	stdev	Total Fe	stdev
Pierre	11	0.40	0.14	0.008	0.003	0.53	0.13	1.41	0.31
Niobrara	4	0.54	0.33	0.348	0.405	2.94	2.88	1.95	1.06
Carlile	2	1.02	0.20	0.071	0.047	1.77	0.28	1.90	0.40
Greenhorn	3	1.08	0.88	0.412	0.279	3.71	1.19	1.64	0.60

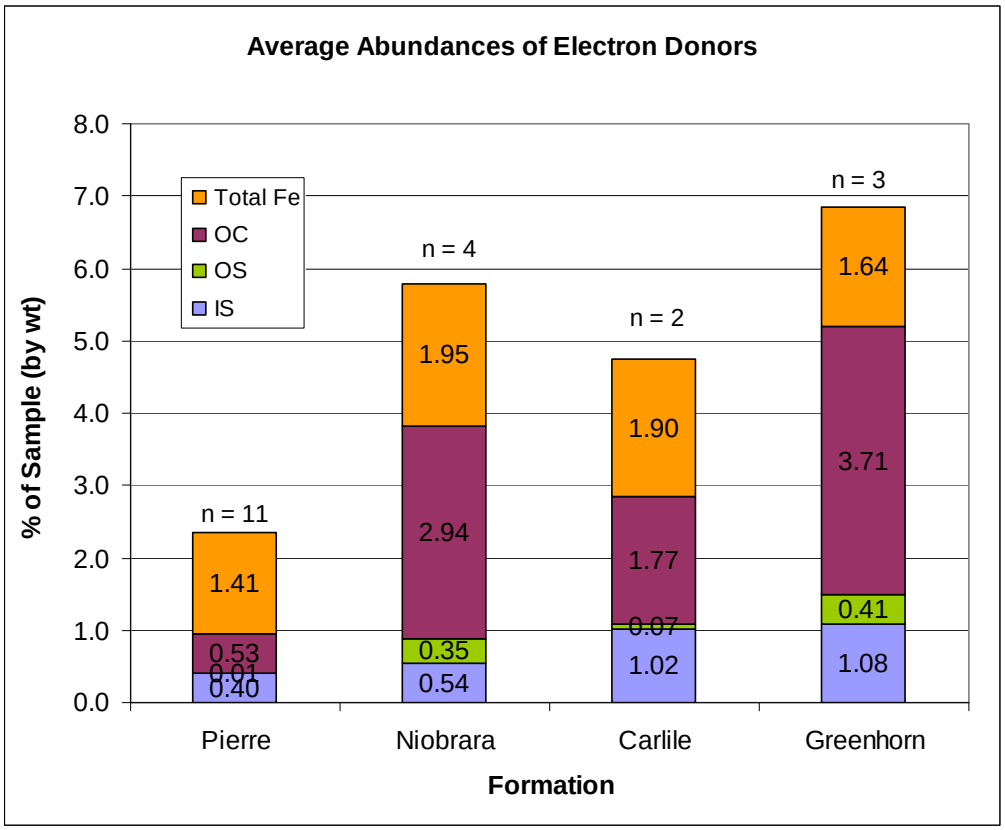

Figure 4: Average weight % abundance of e^- donors by formation. N represents the number of boreholes from each formation.

Inorganic Sulfide

Inorganic sulfide (IS) was the most thorough analysis conducted in this study. It was determined that the IS methodology could be used for organic sulfide analysis (S. Klapperich, 2008) and thus the IS test was repeated on nearly every sample (72 individual analysis). The samples showed excellent reproducibility among all the duplicate tests.

Overall, IS accounts for about 15% of the total donors present in all the tested samples. Values ranged from 0.067% by weight in a Pierre sample (15401) to 2.39% in a Greenhorn sample (15350C). All of the inorganic sulfide measured in this test was assumed to be in the form of pyrite, as it was the only sulfide mineral identified by XRD and it is the most commonly occurring sulfide mineral (Schoonen, 2004). IS was measured above the detection limit in all the

samples and was present in all the formations. Pyrite flecks were observed in some sample cuttings during collection (S. Klapperich, 2008).

Inorganic sulfide within the Pierre samples averaged about 0.4% by weight and appears evenly distributed within the study area. IS accounts for about 17% of the e^- donors present in the Pierre samples (Figure 4). Within the Niobrara Formation, the occurrence of pyrite as IS is not as uniform. In a pattern that is repeated with other donors, the highest concentrations were measured in the easterly Niobrara boreholes, 15346 and 15349, with an average of 0.82% by weight. The highest measured concentration in this formation of 1.16% occurs in borehole 15346. The two more westerly boreholes, 15345 and 15347, contain lower concentrations of IS and average 0.32% by weight. The lowest measured concentration of 0.18% in this formation occurs in borehole 15347.

The Carlile and Greenhorn samples both average about 1% IS by weight, which accounts for 21% of the donors in the Carlile Formation and 16% in the Greenhorn samples (Figure 4). Two of the Greenhorn sites averaged about 0.6% IS while a third borehole, 15350, averaged 2.1% pyrite, which is by far the highest IS value of any individual site.

Organic Sulfide

Overall, the test for organic sulfide (OS) yielded the lowest values of the e^- donors tested. The highest value of 0.79% came from a sample identified as Niobrara Formation (sample 15349), while several samples came in at close to or below detection. As a result, OS accounts for approximately 4% of the total available e^- donors within the study area. It would not be unreasonable to state that OS should not be considered a significant donor within the Pierre or Carlile Formations. Within the other two formations, OS accounts for approximately 6% of the available donors and is a minor contributor at best.

The test for organic sulfide revealed that very little OS is present in samples identified as Pierre Shale. All 11 boreholes had concentrations of less than or equal to 0.01% by weight. The average value of samples from the Pierre was 0.008%. Within the Niobrara Formation, samples from the two westerly boreholes, 15345 and 15347, were among the lowest reproducible values. On the other hand, the remaining two eastwardly boreholes yielded values that were among the highest of any of the boreholes tested. Not coincidentally, these samples were darker in color and also high in OC.

A measureable quantity of OS was found in samples identified as Carlile, with ~0.1% in boreholes 15348 and about 0.04% from borehole S062706. In comparison to the other donors available within the Carlile Formation, OS is not a significant contributor. OS within the Greenhorn was also among the highest measured amounts, averaging about 0.41% for all samples in the formation. The borehole S062806 had an average of about 0.09% OS and may represent a transitional zone between Carlile and Greenhorn.

Organic Carbon

Seventy-two organic carbon (OC) analyses were preformed on 36 individual samples. The highest OC concentrations were measured in a Niobrara and a Greenhorn sample, which each had 6.4% pre-treatment equivalence by weight. The lowest value from any sample, 0.29%, was also from the Niobrara. OC accounts for approximately 45% of the e^- donors available in the sampled material. Organic carbon is also a dominant donor within each formation. Duplicates show excellent reproducibility well below the 25% difference standard for Equation 1 (S. Klapperich, 2008).

Pierre samples contained relatively low amounts of organic carbon, ranging from 0.35% to 0.73%. Organic carbon accounts for about 23% of the donors available within the Pierre

samples. Niobrara samples are all highly calcareous, but are split between organic carbon-rich and organic carbon-poor samples. As with OS, the two westward Niobrara boreholes averaged 0.44% by weight, while the two eastward boreholes averaged 5.43% organic carbon. OC is the dominant donor within the Niobrara accounting for just over 50% of the available donors in the formation.

Organic carbon is the dominant donor in the Carlile and Greenhorn Formations as well. Values ranged from 1.6% to 2.1% in the Carlile sample and 2.5% to 6.4% in the samples identified as Greenhorn. The Greenhorn samples also contained higher amounts of inorganic carbon than the Carlile.

Ferrous Iron

The results for ferrous iron resulted from two tests: the wet chemical extraction technique (S. Klapperich, 2008) and the Fe(II) associated with pyrite as measured by the method for inorganic sulfide. Ferrous iron does not follow the pattern of the other e^- donors, that being low in the Pierre and higher in the other three formations. Instead Fe(II) is the dominant e^- donor present in the Pierre samples and the second most abundant in the other formations. Of the 44 analyses conducted, the highest value by a wide margin came from borehole 15345 with an average value of 3.45%. Iron nodules were observed in the drill cuttings of this borehole, so the high concentration is not surprising. The lowest iron value, 0.9%, was from a Pierre sample (15339).

Ferrous iron is relatively more abundant in the Pierre Formation than the other donors tested. The highest average value from any single borehole was 2.1% with an overall average for the formation of 1.4%. Although it is not clearly defined, the Fe(II) values tend to increase towards the east within the Pierre samples. Aside from the previously high Niobrara site, the

remaining three sites average 1.4% by weight as well. There was not an east – west difference as observed with the other donors. The Carlile and Greenhorn Formations each have a site with greater than 2% Fe(II) and overall average 1.9% and 1.6%, respectively. Fe(II) is 2.7% more abundant in the Carlile than OC and is the second most abundant donor in the Greenhorn.

Statistical Correlations

Statistical analysis was carried out on the data from 20 boreholes for the IS, OC, and Fe(II) donors with 19 boreholes representing the OS data, as the OS data from one of the boreholes were not reproducible. Before the donor distributions could be compared, the normality of their individual populations was tested. This was accomplished using the Shapiro & Wilk "W-test" (Gilbert, 1987). Both the lognormal transformed and non-transformed populations were tested for each donor. The results show that the entire suite of donors could not be considered to be normally distributed whether they are log transformed or not (S. Klapperich, 2008). Thus, the nonparametric Spearman Rho test (Conover, 1971), which does not assume an underlying distribution, was utilized for statistical comparisons.

Correlations were tested between the different donors at the individual formation level and across the entire study area. Correlations with longitude were also tested for each donor. The one-tailed version of the test was employed to determine if positive or negative correlations existed between the donors using critical values corresponding to $\alpha = 0.05$ (Table 4). Correlations were also checked within the 11 Pierre boreholes and the 9 remaining boreholes. However, the reduced sample size resulted in only a few correlations that were determined to have limited implications for this research.

Organic carbon, organic sulfide, and inorganic sulfide are all positively correlated with longitude. As expected, the test failed to correlate the ferrous iron with longitude. The test also

showed that the donors correlated well with each other. Organic carbon, organic sulfide, and inorganic sulfide all correlated with one another with an alpha value of 0.05 and ferrous iron correlated with inorganic sulfide with an alpha value of 0.1, but not with the other e^- donors.

Table 4: Results of Spearman correlations and associated critical values of Rho. All correlations with OS involve 19 instead of 20 points due to eliminated values. Critical values represent α = 0.05 and are from Table 10 in Conover (1971).

Spearman Rho test for positive correlation

Ho: There is not a positive correlation of the two donors' average values.

	IS	OS	OC	Fe
IS	x	Ho rejected	Ho rejected	Ho NOT rejected*
OS		x	Ho rejected	Ho NOT rejected
OC			x	Ho NOT rejected
Fe				x
Longitude	Ho rejected	Ho rejected	Ho rejected	Ho NOT rejected

* rejected at α = 0.1

Spearman Rho test statistic ($-1 < \rho < 1$)

	IS	OS	OC	Fe
IS	x	0.6327	0.7474	0.3323
OS		x	0.5825	0.0741
OC			x	0.2045
Fe				X
Longitude	0.4752	0.6895	0.6045	0.2496

Critical values of ρ, α = 0.05

	IS	OS	OC	Fe
IS	x	0.3895	0.3789	0.3789
OS		x	0.3895	0.3895
OC			x	0.3789
Fe				x
Longitude	0.3789	0.3895	0.3789	0.3789

DISCUSSION

There is clearly a trend toward eastern prominence of e^- donors among the samples and formations investigated. If the samples are averaged among the formations, the more eastern Niobrara, Carlile, and Greenhorn Formations contain higher quantities of all e^- donors tested than the Pierre Formation (Figure 4). This is particularly evident of the organic species, which are

nearly three times more prevalent in the eastern formations. Not coincidentally, samples of these formations were generally as dark or darker than samples from the Pierre. Inorganic sulfide, presumably as pyrite, was also twice as abundant in the eastern formations as the sampled Pierre. Ferrous iron, was also more abundant in the eastern formations, although only slightly so, with an average of 1.8% by weight to 1.4% in the Pierre.

When the results are broken down by borehole, further variation is observed. Organic carbon occurs in the highest concentrations in two of four Niobrara boreholes (the two eastern-most sites) and two of three Greenhorn boreholes. More organic carbon is present in the Carlile boreholes than the Pierre, although the difference is small (Figure 5). A similar overall trend can be seen in organic sulfide results, although the effect is less dramatic due to much lower overall concentrations (Figure 6). Inorganic sulfide has its highest values in one of two Carlile boreholes and one of three Greenhorn boreholes (Figure 7). The remaining boreholes are generally higher in concentration than those of the Pierre. Ferrous iron is much more evenly distributed, as noted previously (Figure 8). In fact, the highest values of ferrous iron come from the most eastern Pierre borehole and the most western Niobrara borehole. Similarly high values occur in boreholes across the study area. These observations were confirmed with the Spearman Rho test which shows statistically significant, positive correlations with more eastern values of longitude and all donors except for ferrous iron (Table 4). Clearly these organic-rich shale formations in eastern North Dakota have relatively large supplies of e^- donors.

However, the variation within formations is somewhat unexpected (Figure 9). The standard deviations are considerably higher for certain donors in both the Niobrara and Greenhorn formations. The reason for this is obvious for the Niobrara as the two western samples were much lighter in color and had a composition of a chalky shale and were over 50%

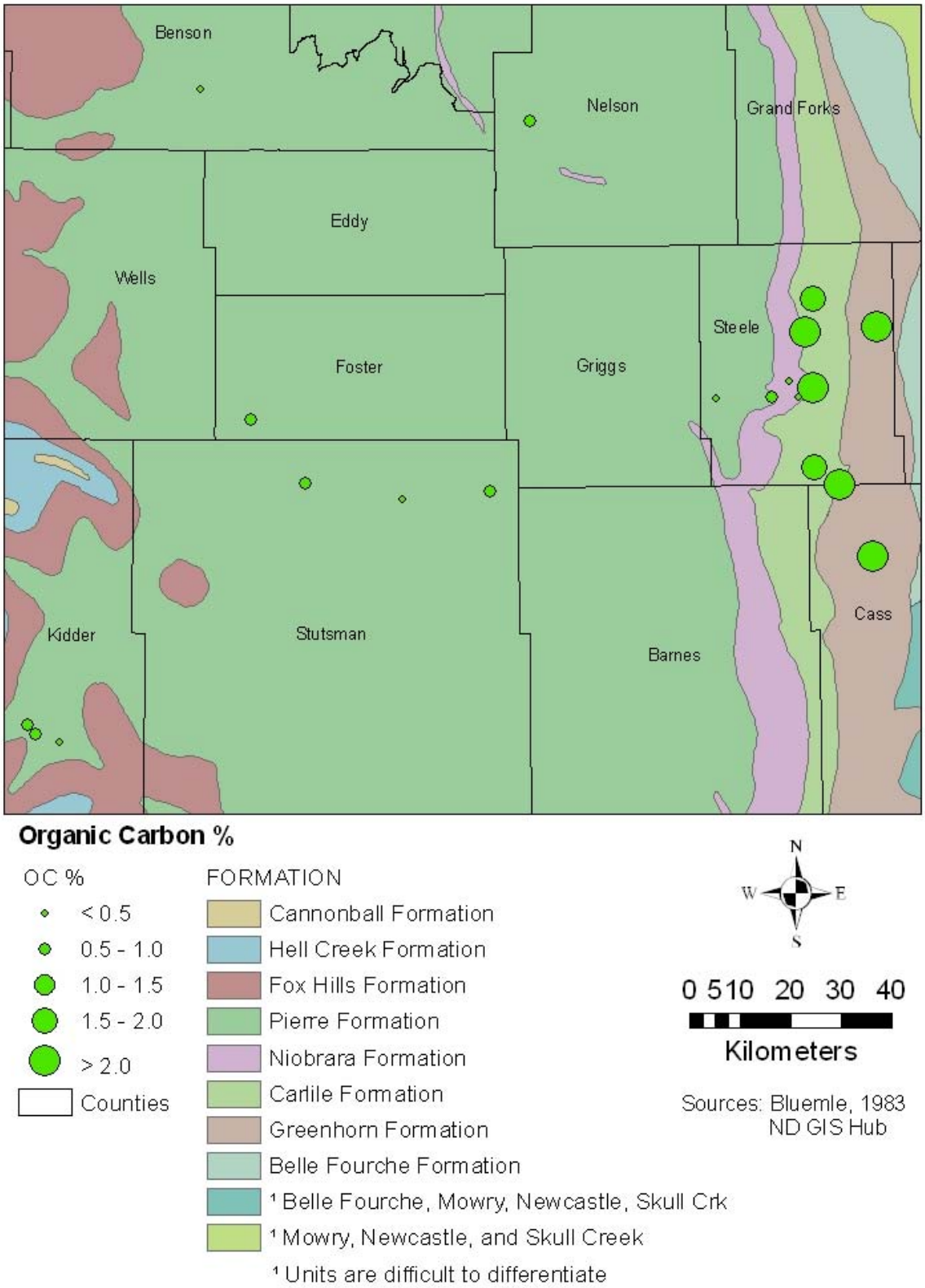

Figure 5: Distribution of organic carbon within the study area.

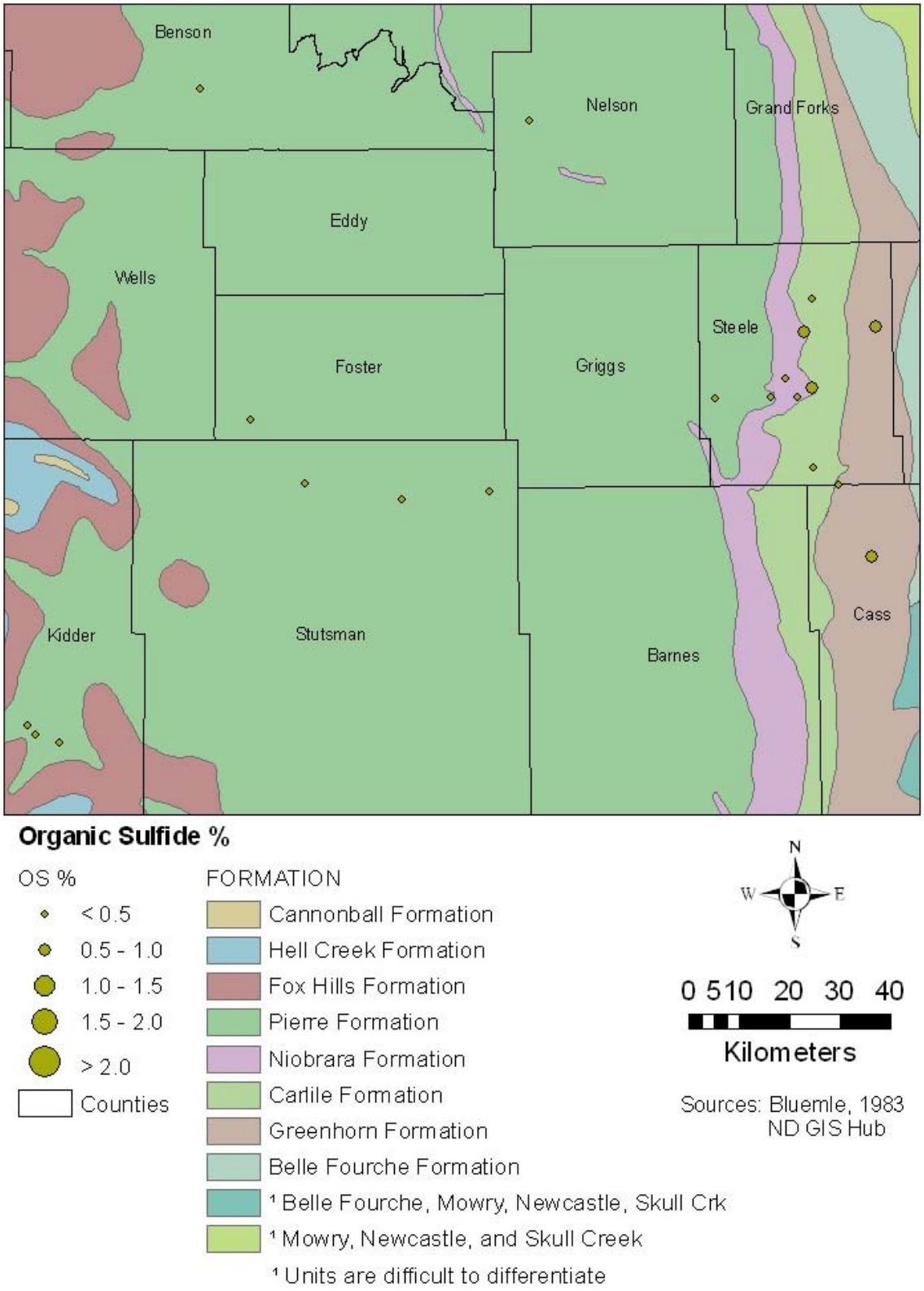

Figure 6: Distribution of organic sulfide within the study area.

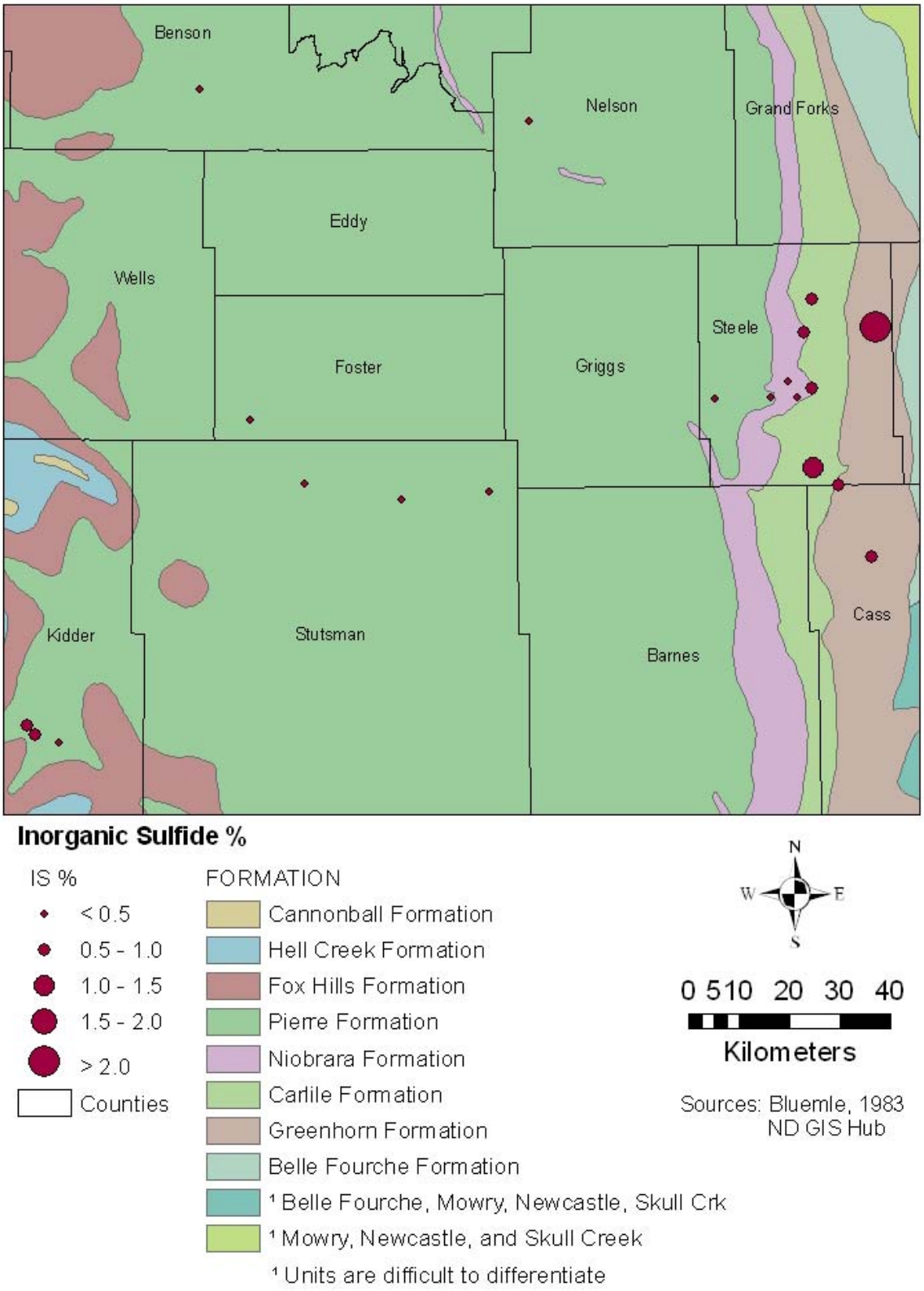

Figure 7: Distribution of inorganic sulfide within the study area.

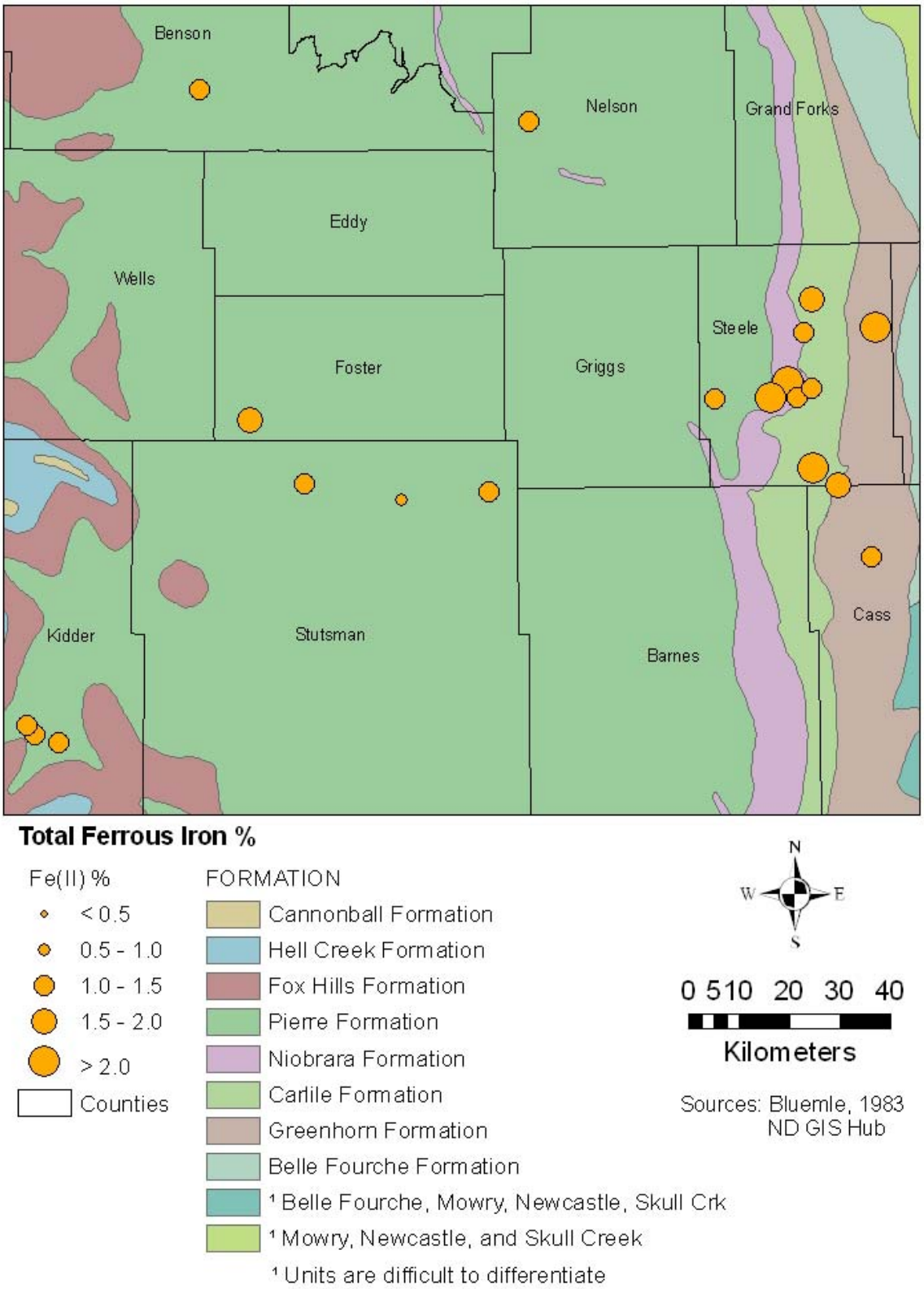

Figure 8: Distribution of total ferrous iron within the study area.

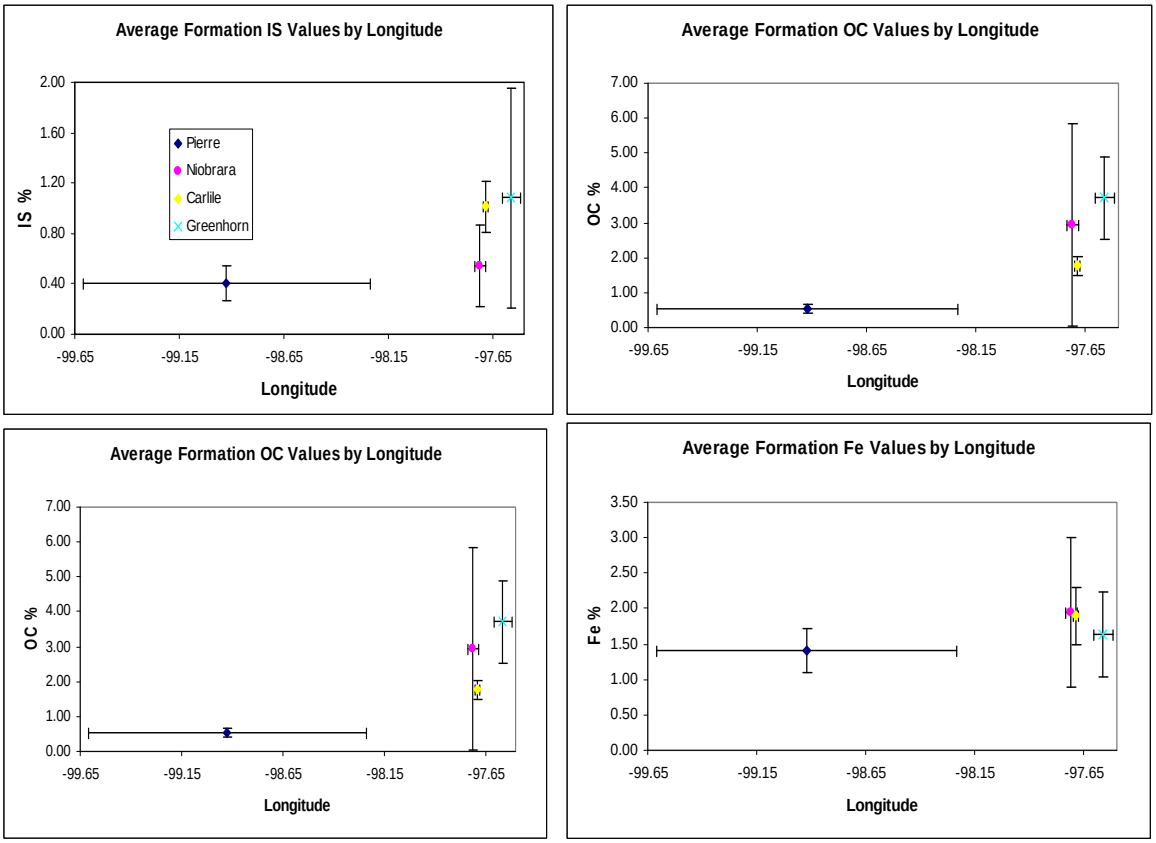

Figure 9: Average values by formation for each donor. The bars represent ± 1 standard deviation, both in concentration and spatial range.

carbonate by weight (S. Klapperich, 2008). The subcrop of these formations represents a geographically small area that is also approximately the easternmost extent of deposition. As a result a sharp facies change could explain the variability observed. As noted earlier, two distinct members have been described in the Niobrara and these may be evident in the results. The Pierre Formation, which has the greatest exposure, also has the least variability. This occurs despite the samples likely representing the Degrey, Gregory, and possibly Pembina Members.

In a broader perspective, the e^- distribution observed in underlying bedrock is not unlike that observed in the local aquifer systems. The dominant e^- donors in the Niobrara, Carlile, and Greenhorn Formations are organic carbon and inorganic sulfide. Aquifers east of the Pembina Escarpment and thus within the vicinity of these formations also tend to be enriched in OC and

pyrite (e.g. the EVA). In aquifers to the west, iron tends to the dominant e^- donor, just as iron is the predominant donor in the Pierre (Tesfay, 2006).

According to Clayton et al. (1980) the general direction of glacial movements in eastern North Dakota was south to southwest. As a result, several aquifers were deposited in close proximity to Niobrara, Carlile, and Greenhorn Formations and likely contain significant amounts of these units within their sediments. Figure 10 illustrates these aquifers, which like the EVA, are likely to be rich in e^- donors. This list may not be exclusive, as other aquifers, such as the southern portion of the Spiritwood system may also contain sediments from the formations studied. There is also no distinction between the coarseness of aquifers or other factors that may influence their donor concentration or reactivity. However, the number of aquifers whose electron donor capacity remains unexplored and yet share similar depositional characteristics to the EVA illustrates how widespread similar reactive aquifers may be in eastern North Dakota.

These geologic phenomena are decidedly not unique to North Dakota. These Late Cretaceous units were deposited by the Western Interior Seaway, which at its maximum extent covered the entire central North American continent from the Arctic Sea to the present day Gulf of Mexico. As a result, these formations are widespread and recognized across most of the Great Plains states. Certainly, large variations would be expected owing to the large geographic extent of these units. For example, the Niobrara and Greenhorn Formations are recognized as limestones in Nebraska and Kansas (Shurr, 1984; MacDonald and Byers, 1988). However, just as certain areas may be less likely to contain e^- donors, they may be concentrated elsewhere.

We suggest that most shale formations have the potential for significant quantities of e^- donors, particularly if they are known to contain pyrite or higher concentrations of organic material (> 1%) or both. Furthermore, wherever these formations exist in glaciated terrains the

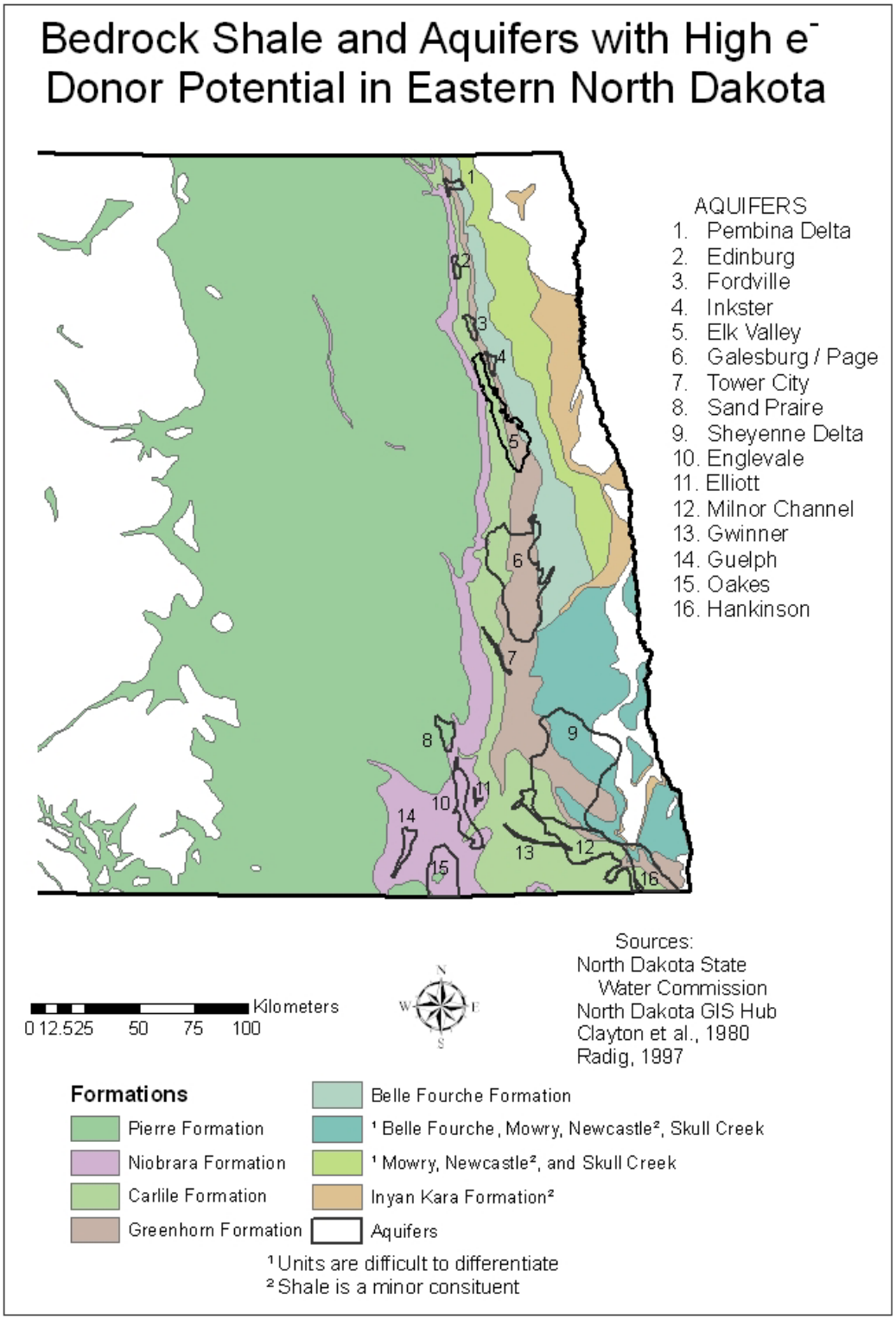

Figure 10: Map of eastern North Dakota aquifers with high electron donor potential based on local bedrock formations.

potential for aquifers composed of shale parent materials, such as the Elk Valley Aquifer, is very good. Certainly some of these aquifers will contain significant quantities of e^- donors as well, principally those associated with the most recent glacial events.

Figure 11 shows gray and black shales of the upper Midwest as well as the extent of the most recent, glaciation (Wisconsinan) and the major associated ice movements. Notice that King and Beikman (1974) classify the shale units in eastern North Dakota as "gray shales". There may be other gray shale units in the upper Midwest that also have relatively high concentrations of e^- donors. Furthermore, any aquifers derived of the black shale units of Michigan, Indiana, or Ohio are very good candidates for e^- donors.

These associations are not only limited to their effect on denitrification. Wherever large supplies of e^- donors exist the redox conditions of an aquifer will be affected. As stated by McMahon and Chapelle (2008, pg. 259) "Reduction/oxidation (redox) processes affect the chemical quality of ground water in all aquifer systems. Redox processes can alternately mobilize or immobilize potentially toxic metals associated with naturally occurring aquifer materials . . . contribute to the degradation or preservation of anthropogenic contaminants . . . and generate undesirable byproducts such as dissolved ferrous iron (Fe^{2+}), hydrogen sulfide (H_2S), and methane (CH_4) . . ." The associations of shale, glacial activity, and subsequent aquifer deposition may be a controlling factor of water quality in the United States and perhaps even on a global scale.

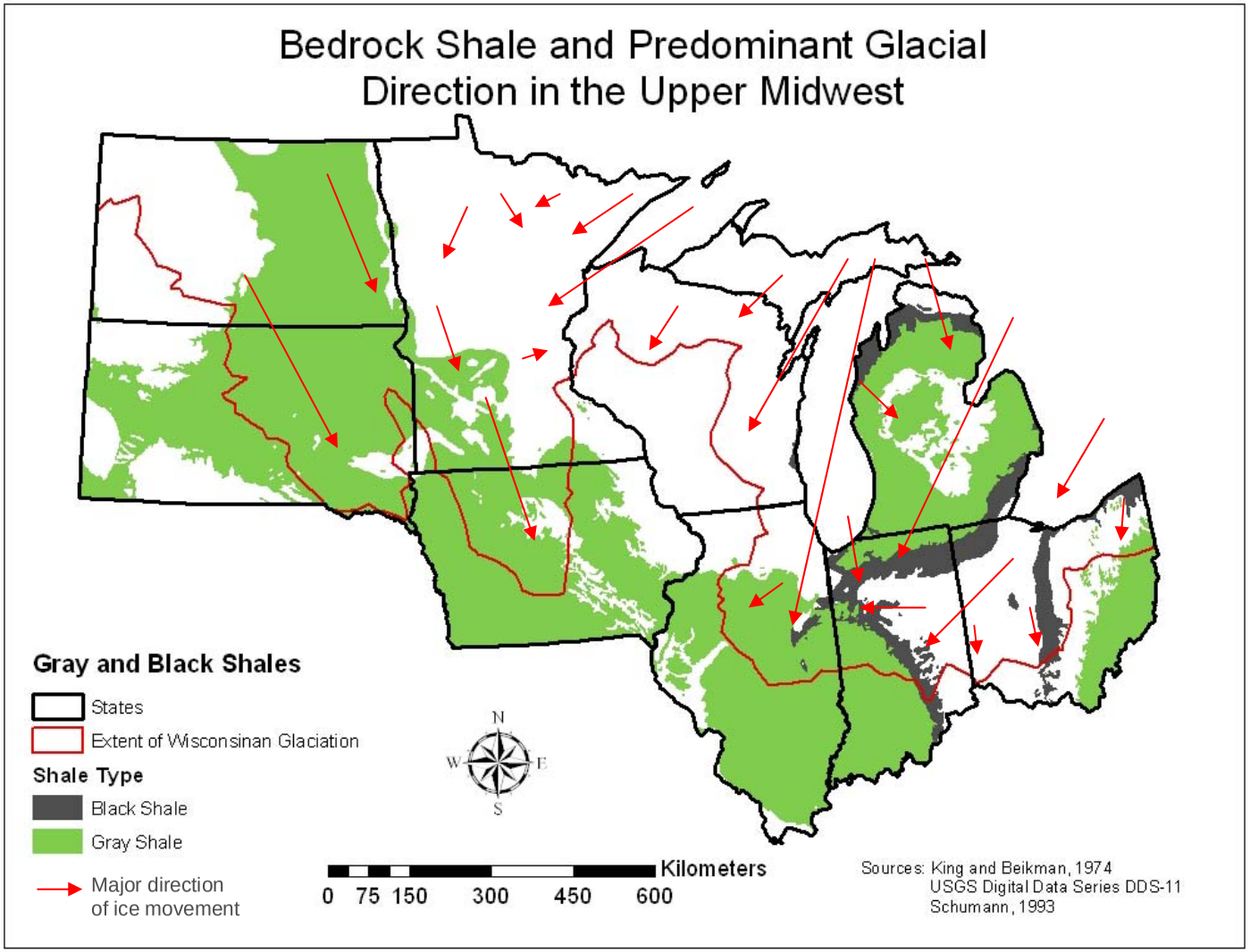

Figure 11: Map of shale formations in the Upper Midwest and the extent of the most recent glaciation. Any glacially derived aquifers that exist in this region have the potential to be rich in electron donors.

CONCLUSIONS

An exploratory study of four eastern North Dakota shale formations has been conducted and showed significant differences in their e^- donor capacity. Dominant minerals of the formations, as identified by XRD, are quartz, calcite, clay minerals (smectite, illite), with lesser amounts of muscovite, feldspar, and pyrite. The western Pierre Formation has the lowest average donor contents while the eastern Greenhorn Formation has the highest average values. The Pierre also showed the least variation of the formations tested, while the Niobrara showed the greatest. The variation in the Niobrara is likely the expression of two distinct members, a calcareous shale unit and a chalky shale unit.

Organic carbon, inorganic sulfide, and ferrous iron are all important e^- donors, while organic sulfide was present, but only relatively high at a few sites. Organic carbon concentrations in the Pierre range from 0.3% to 0.7% and are comparatively low, while concentrations in the Niobrara range from 0.4% to 5.5% and in the Greenhorn range from 2.5% to 4.8%, a significantly higher amount. Pyrite (as inorganic S) concentrations in the Pierre range from 0.01% to 0.5%, while the Niobrara (0.2% – 0.9%) and Greenhorn (0.5 – 2.1%) again have significantly greater amounts. Ferrous iron was generally present in concentrations of 1.0% to 2.0% over the entire study area with some higher concentrations measured in Greenhorn (2.2%) and Niobrara (3.5%) boreholes. Organic sulfide was generally insignificant, but was present in measurable amounts (0.1% to 0.8%) in samples that were also rich in organic carbon.

Significant correlations exist for the various e^- donors, showing a general increase in donor content from west to east. The donors are also correlated with each other indicating that if high concentrations of one donor are found, high concentrations of the other donors are also likely to be found. Thus, within eastern North Dakota, aquifers composed of sediments from the

older and more eastern bedrock formations have a greater probability of having high concentrations of e^- donors in their sediments.

The association of e^- donor-rich bedrock shale, glacially driven deposition, and correspondingly e^- donor-rich aquifers is not a phenomenon unique to North Dakota. The conditions exist across the northern United States and perhaps many areas of the world for similar development of aquifers rich in e^- donors. It is suggested that future research projects in North Dakota and elsewhere take careful consideration of the bedrock or other potential parent materials when assessing the redox potential of regional aquifer systems.

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