



# **Preliminary Hydrogeochemical Investigation of Alberta's Groundwater Database to Locate Areas with Diamond Potential**

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D.R. Eccles<sup>1</sup> and J. Sciarra<sup>2</sup>

<sup>1</sup>Energy Resources Conservation Board  
Alberta Geological Survey

<sup>2</sup>Formerly of Alberta Geological Survey

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Energy Resources Conservation Board  
Alberta Geological Survey  
4<sup>th</sup> Floor, Twin Atria Building  
4999 – 98<sup>th</sup> Avenue  
Edmonton, Alberta  
T6B 2X3  
Canada

Tel: (780) 422-1927  
Fax: (780) 422-1918  
E-mail: EUB.AGS-Infosales@gov.ab.ca  
Website: www.ags.gov.ab.ca

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## **Acknowledgments**

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## **Abstract**

The compilation of Alberta-based groundwater chemical data from various government sources resulted in a database with 236 809 records. In contrast to poor-density kimberlite-indicator mineral data, these groundwater data provide regional coverage through most of Alberta. Hence, the objective of this preliminary study is to investigate hydrogeochemical relationships between groundwater and known kimberlite/ultramafic fields in Alberta, and to identify anomalies in other parts of Alberta that may have formed by contact with the unusual mineral assemblages associated with an undiscovered field of ultramafic rocks. This innovative approach does not yield any ubiquitous relationships between provincially scaled hydrogeochemical signatures and known ultramafic bodies in Alberta, but does highlight nickel, chromium and potassium anomalies that cannot be explained by any known geological features and may entice interest for future exploration in these areas.

# 1 Theory and Approach

The hydrogeochemical survey technique has been used to locate various buried commodities, including gold, base metals, uranium and other ore deposits (e.g., Leybourne, 1998; Gilliss et al., 2004; Pirlo and Giblin, 2004; de Caritat et al., 2005; Leybourne and Cameron, 2006). While the hydrogeochemical technique has historically been used to search for these commodities, it is not as common a tool for kimberlite exploration. The only known references for hydrogeochemical surveys in kimberlite exploration are Kosolapova and Kosolapov (1962) and Sadler et al. (2003). Orientation studies by these authors over known ultramafic bodies have shown that groundwater interaction with kimberlite produces characteristic aqueous geochemical anomalies, and that identification of these anomalies may aid in the location of undiscovered kimberlite.

In Alberta, a database of water well and oil and gas well groundwater chemical data has been compiled from various government sources (225 441 records) and from the Alberta Geological Survey data holdings (11 368 records), resulting in 236 809 records (Shauer and Lemay, 2006). The data have been flagged for quality assessment using the culling criteria adopted from Hitchon and Brulotte (1994).

Kimberlites are rich both in elements of ultramafic affinity (magnesium, cobalt, nickel, chromium) and in incompatible elements (e.g., light rare-earth elements, niobium), which gives these rocks their characteristic geochemical signature. Thus, it seems viable that a first-pass, hydrogeochemical investigation of the groundwater database might detect areas with kimberlite/diamond potential in Alberta. This innovative approach has merit, particularly because of the size and density of the groundwater database versus other databases common to diamond exploration, which is really in its infancy stage because economic concentrations of diamonds were only discovered in Canada in 1991. For example, the Alberta kimberlite-indicator mineral database, which summarizes electron microprobe data from a variety of surficial samples (e.g., bedrock, stream sediment, till), is a significantly smaller database (sample density of 1 site/440 km<sup>2</sup>; Eccles et al., 2001) in comparison to the groundwater database (sample density of 1 site/3 km<sup>2</sup> albeit with fewer wells in northern Alberta; Appendix 1).

One caveat to this approach is complications associated with chemical transfers between shallow, intermediate and deep-flow systems. While we acknowledge the groundwater database includes readings from water wells that sampled deeper parts of the Western Canada Sedimentary Basin (WCSB), which reaches thicknesses of over 5000 m in western Alberta, kimberlites are derived from depths of >150 km in the Earth's surface and occur in fields of up to about 200 individual kimberlite bodies (e.g., Ekati and Diavik properties, Lac de Gras, Northwest Territories). This means a kimberlite field's chemical properties could become part of the regional fingerprint in a sedimentary basin regardless of depth.

We make no attempt, therefore, to assign a groundwater depth cut-off to this study, but do discuss the depth of some of the anomalies because deep-flow systems are innately enriched in most elements relative to shallower water samples (T. Lemay, personal communication, 2007). Nevertheless, with the depth of the groundwater samples in mind, a positive feature of the database is that Shauer and Lemay (2006) showed there are approximately 114 000 culled wells that sampled regional Cretaceous to Paleocene hydrostratigraphic zones (as defined by Bachu, 1999; Table 1). Hence, a large portion of the groundwater samples were taken at the same stratigraphic levels as the sedimentary rocks that host the approximately 88 Ma to 60 Ma northern Alberta kimberlite province (Eccles et al., in press) and the approximately 104 Ma to 95 Ma Fort à la Corne, Saskatchewan, kimberlite field (Heaman et al., 2004).

**Table 1. Distribution of Cretaceous to Quaternary Alberta water wells using the regional hydrostratigraphic zones of Bachu (1999). Brackets on right side highlight the radiogenic kimberlite emplacement ages of the approximately 88 Ma to 60 Ma northern Alberta kimberlite province (Eccles et al., in press) and the ~104 to 95 Ma Fort à la Corne, Saskatchewan, kimberlite field (Heaman et al., 2004).**

<b>Regional Hydrostratigraphy</b>	<b>Stratigraphic Age</b>	<b>Number of Water Wells</b>	
Quaternary/Drift	Pleistocene	41072	
Paskapoo-Scollard	Maastrichtian-Paleocene	31010	Coniacian to Paleocene northern Alberta kimberlite province
Battle-Horseshoe Canyon	Middle Campanian-Maastrichtian	20876	
Bearpaw	Middle Campanian	3340	
Belly River	Early Campanian	15068	
Lea Park	Santonian-Early Campanian	451	
Milk River	Santonian	644	
Colorado	Turonian-Coniacian	1201	Fort à la Corne kimberlite field
Upper Mannville	Albian	130	
Lower Mannville	Barremian-Aptian	323	
<b>Total wells</b>		<b>114 115</b>	

Finally, the results of this study must only be perceived as preliminary, particularly because there hasn't been a hydrogeochemical study of groundwater associated with northern Alberta kimberlite. This type of study is required to show irrefutable evidence that hydrogeochemical surveys can be used to discover kimberlite fields in the Western Canadian Sedimentary Basin. We hope this work can initiate a study similar to one of Sader et al. (2003), in conjunction with a more thorough investigation of the groundwater database.

## 2 Database Search, Shaded Contour Map Methodology and Presentation of Data

A geochemical comparison of various sample media in an area with known kimberlites, the Buffalo Head Hills kimberlite field, shows kimberlite clearly has elevated magnesium, chromium and Ni, and lower potassium in comparison to bedrock (shale, siltstone and sandstone), soil (A and B-horizon), and till (upper and lower tills; Figure 1). In Figure 1, we suspect that the few bedrock samples that approach the chemical fields for kimberlite could contain fragments of, or are mixed with, kimberlite because they include samples from cores that tested kimberlite targets. Based on these results and those of Sadler et al. (2003), Ca, Cr, K, Mg, dissolved inorganic carbon (DIC), pH, total alkalis and Ni were isolated from the groundwater database for investigation.

To determine which shaded contour map interpolation method displayed the data with the highest degree of accuracy and consistency, several 'test surfaces' were generated using different raster interpolation methods: Inverse Distance Weighted (IDW), Kriging and Natural Neighbors. The IDW interpolation method was chosen because we felt it best suited data with variable well density.

The data are complicated by culled and non-culled records, and wells that contain multiple readings per well, so that we had to determine exactly what type of data was most important to display in this report.

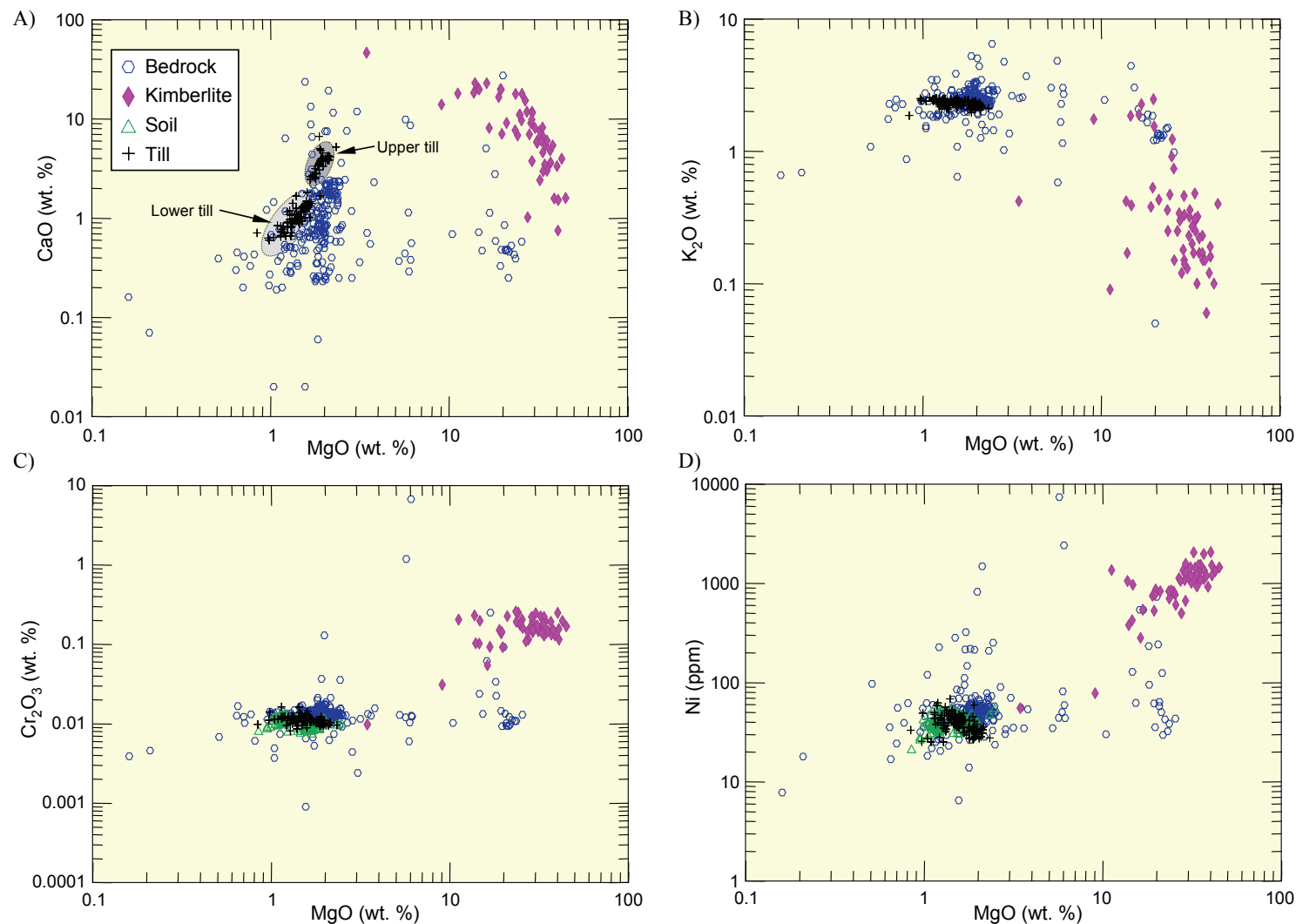


Figure 1. A comparison of selected elements for different media from the Buffalo Head Hills kimberlite field area. Bedrock (mudstone, siltstone and sandstone) data from Fenton et al. (2006a) and R. Eccles (unpublished data, 2006). Kimberlite (pyroclastic and resedimented volcanoclastic) data from Eccles (2004) and Eccles et al. (in press). Soil (B and C-horizon) data from Fenton et al. (2006b). Till (general, lower and upper tills) data from Fenton et al. (2006a). CaO and K<sub>2</sub>O were not available in the soil dataset.

Our initial interpretation considered the following five criteria for each element:

1. Well locations – water well locations for each respective element. It is imperative to consider these maps to evaluate the meaning of any anomalies generated by the elemental-shaded contour maps. For example, is the anomaly the result of a cluster of values, or is the anomaly debatable because it reflects only a single value?
2. Quality chemistry – recent: indicates culled dataset values (culling method adopted from Hitchon and Brulotte, 1994); in the case of multiple readings within a single well, the last, or most recent, values are used to create the shaded contour map.
3. Quality chemistry – average: indicates culled dataset values (culling method adopted from Hitchon and Brulotte, 1994); in the case of multiple readings within a single well, the shaded contour map shows an average of all recorded readings.
4. Total chemistry – recent: indicates culled and non-culled values; in the case of multiple readings within a single well, the last or most recent, values are used to create the shaded contour map.
5. Total chemistry – average: indicates culled and non-culled values; in the case of multiple readings within a single well, the shaded contour map shows an average of all recorded readings.

Our investigation determined that several of the criteria listed above produced similar results, and therefore, we determined that only two images are important to the current report: well location and the most recent quality chemistry. The well location maps for each element are presented in Appendix 1. With the exception of dissolved inorganic carbon and Ni, the shaded contour maps with the most recent measured quality chemistry records (i.e., image number 2 above) provided what we determined to be the most accurate display of information. The DIC and Ni data were not culled, so for these elements we used the total chemistry records using the most recent measurements (i.e., image number 4 above). Shaded contour maps generated for Mg, Ca, K, Cr, Ni, pH, total alkalinity and DIC are presented as Figures 3 to 10, respectively, and accompany the following text.

### 3 Results

Appendix 1 shows the locations of the water wells used in this study for each element. Water wells with Mg, Ca and K, and pH and alkalinity provide excellent coverage in the plains region of southern Alberta (south of latitude 55° and east of longitude 116°) and in populated northern areas, such as Grande Prairie–High Prairie (NTS 83M and 83N), Peace River (NTS 84C and 84D), High Level–Fort Vermillion (84K) and Fort McMurray (74D and 74E).

For exploration geochemistry, it is important to note that most groundwater contains only eight major (more than 1 ppm) dissolved constituents: Ca, Mg, Na, K, HCO<sub>3</sub>, SO<sub>4</sub>, Cl and SiO<sub>2</sub> (Levinson, 1974). Therefore, trace elements are not always analyzed. Wells with Ni values are less dense than Mg, Ca and K, with few data above latitude 56°. Water wells with Cr and DIC values are restricted to either southern Alberta (south of latitude 55°) or a few wells from the area surrounding the community of Peace River.

#### 3.1 Hydrogeochemical Correlations with the Geology of Alberta

Groundwater chemistry is generally a function of the original recharge composition, water-rock interaction and the time that water is in contact with geological material, such that common groundwater elements (e.g., Mg and Ca) are typically associated with shallow-flow systems and/or areas of recent



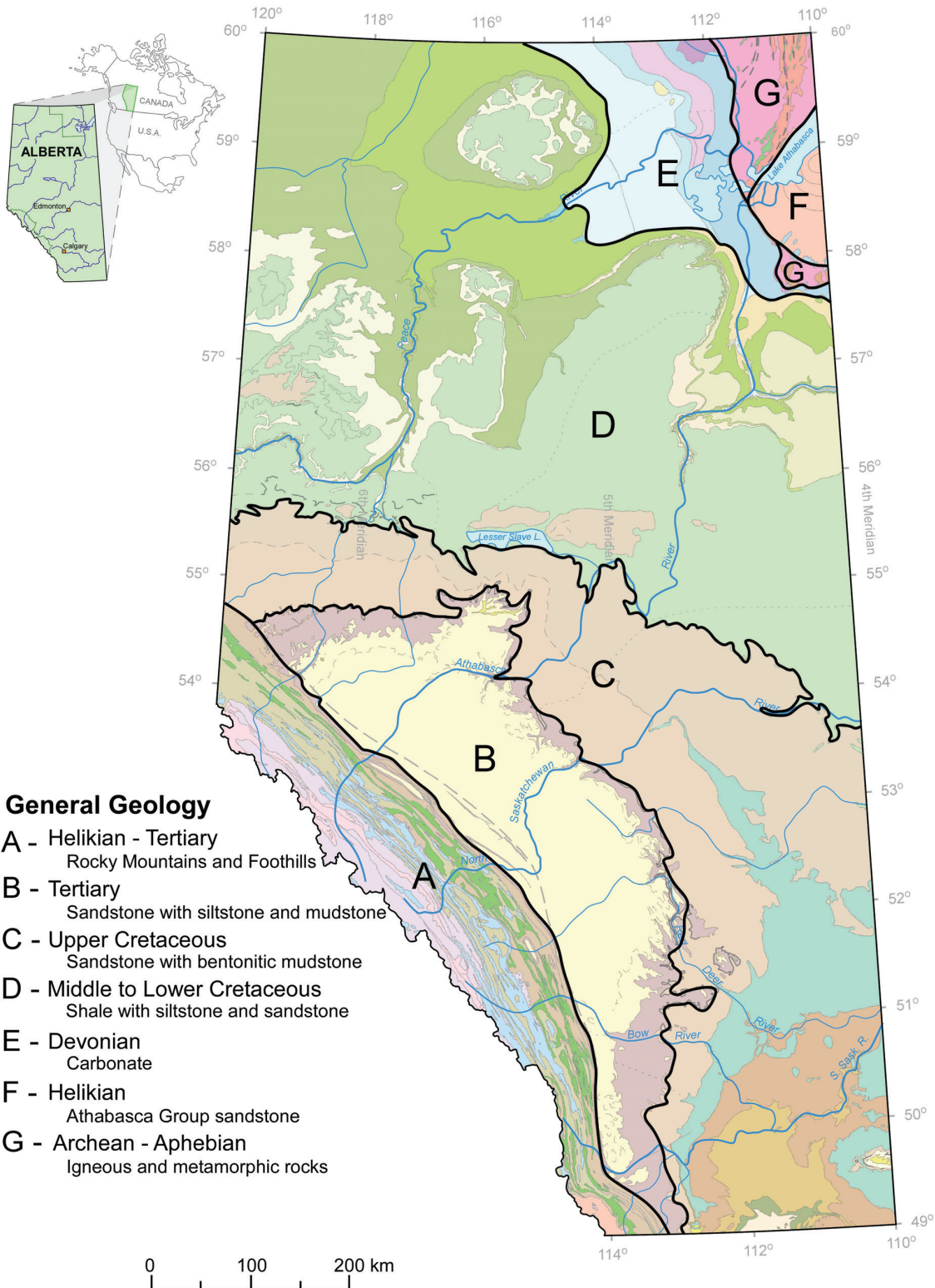


Figure 2. Generalized geology bedrock map of Alberta. Modified after Hamilton et al. (1999).

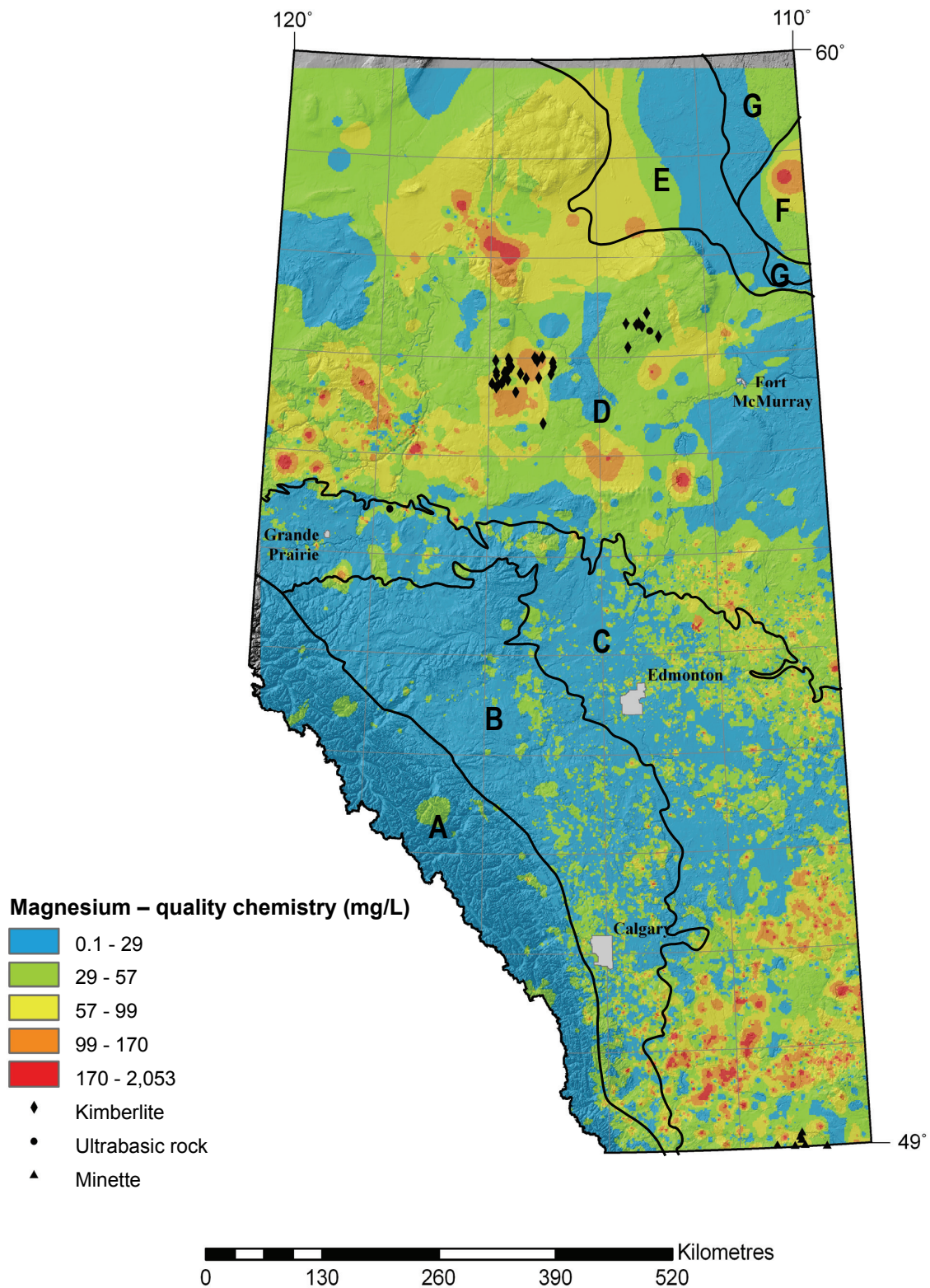


Figure 3. Groundwater magnesium-shaded contour map using the most recent well analysis from a culled dataset.



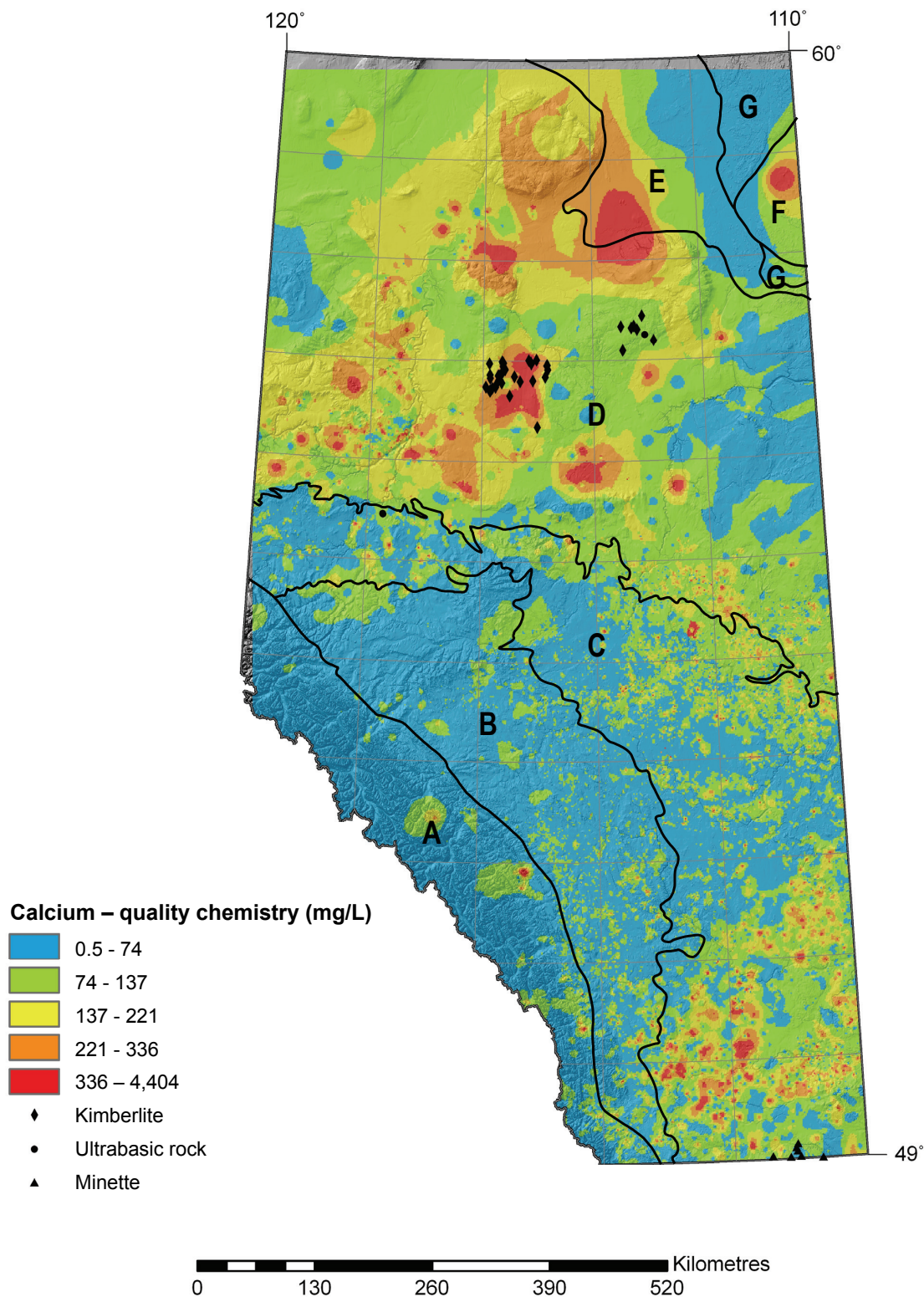


Figure 4. Groundwater calcium-shaded contour map using the most recent well analysis from a culled dataset.

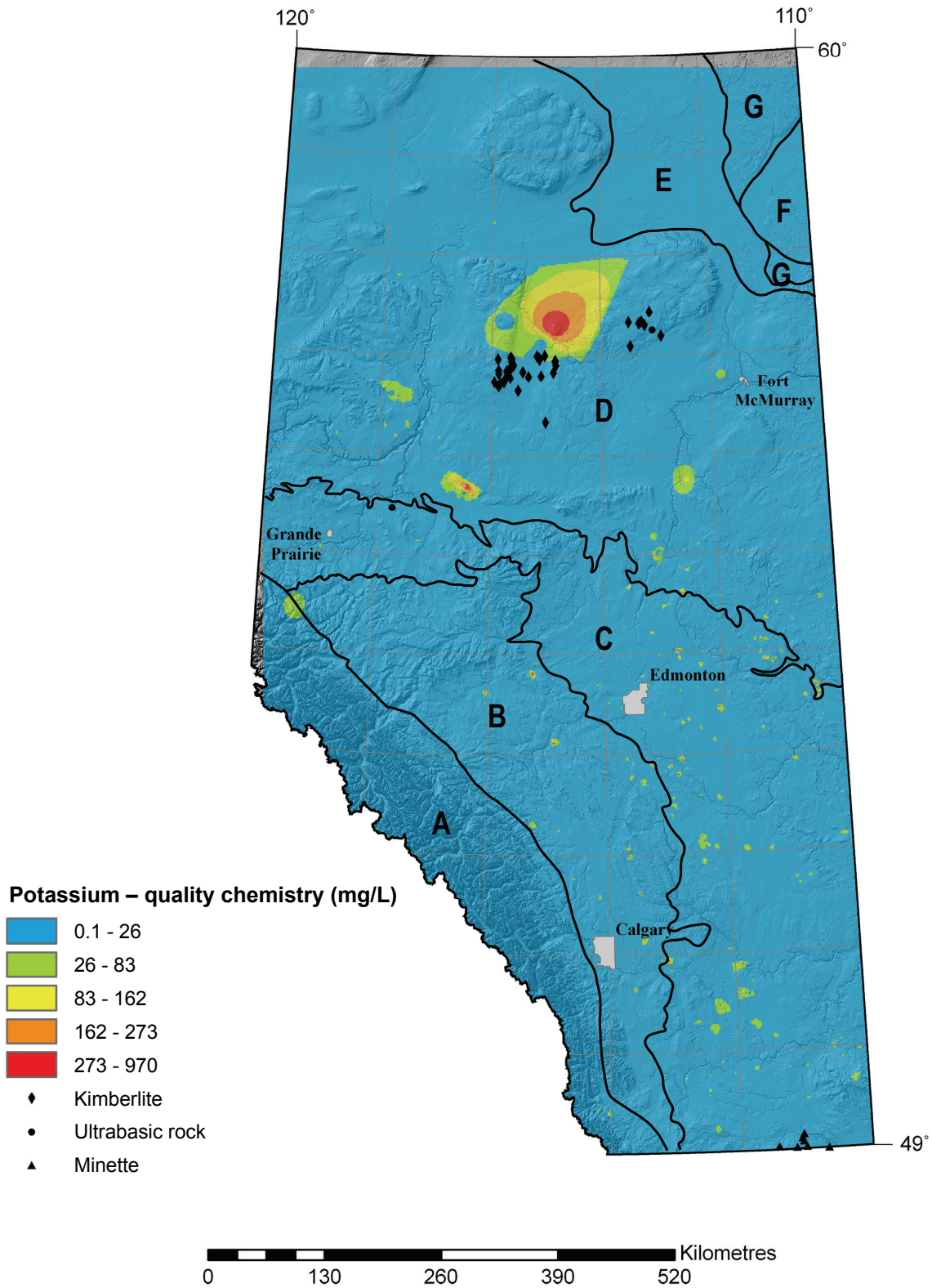


Figure 5. Groundwater potassium-shaded contour map using the most recent well analysis from a culled dataset.



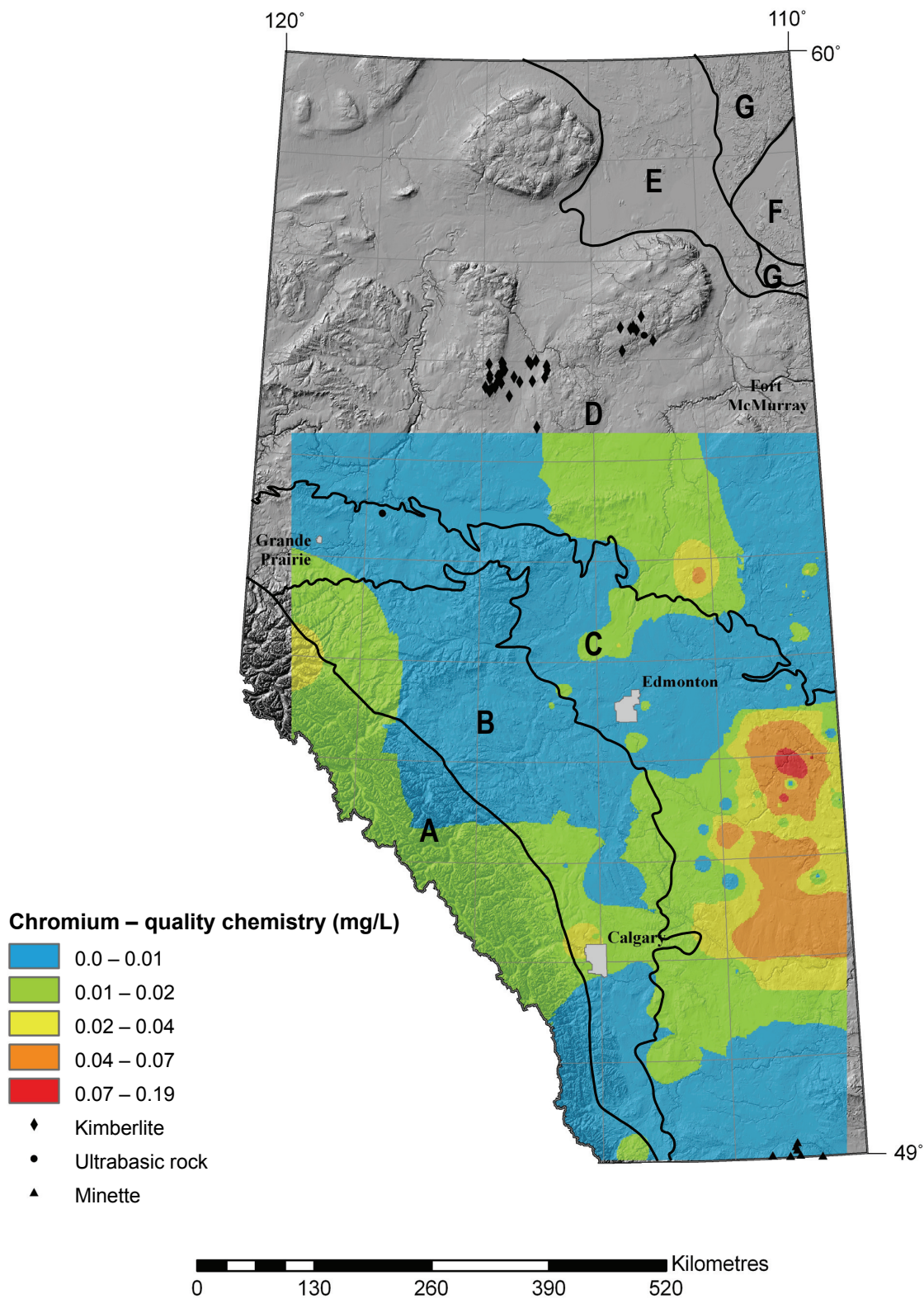


Figure 6. Groundwater chromium-shaded contour map using the most recent well analysis from a culled dataset.

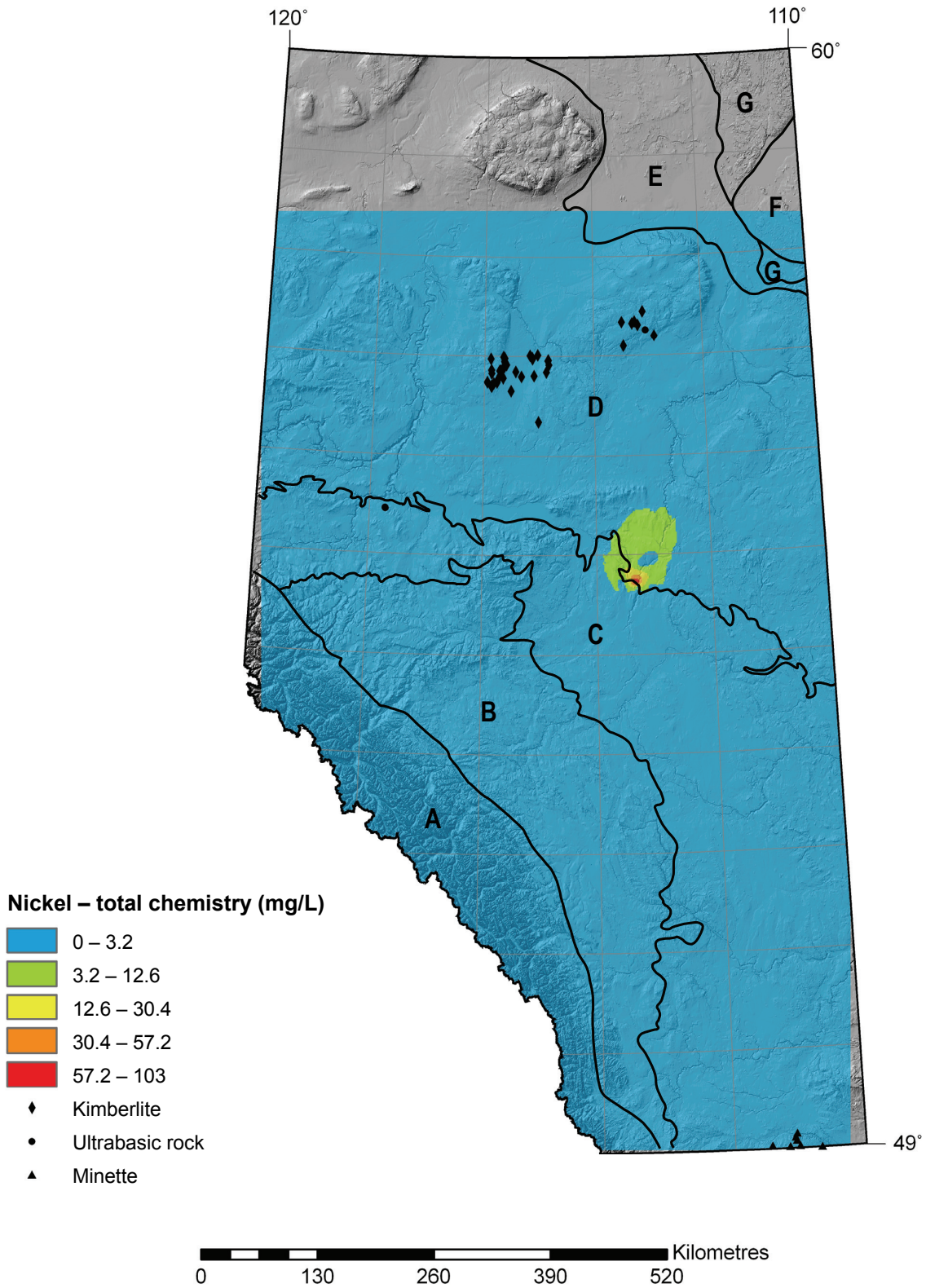


Figure 7. Groundwater nickel-shaded contour map using the most recent well analysis from culled and non-culled datasets.



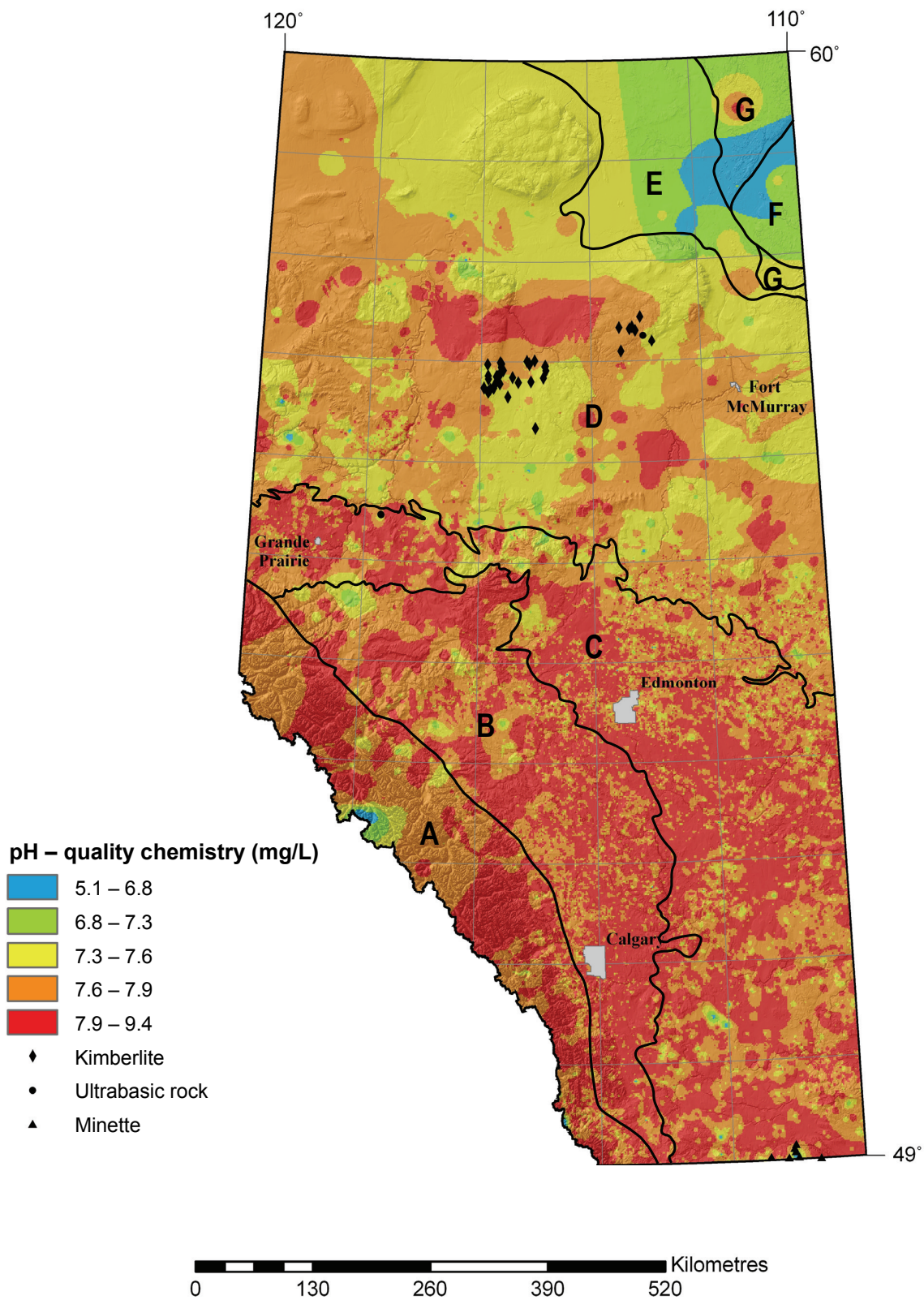


Figure 8. Groundwater pH-shaded contour map using the most recent well analysis from a culled dataset.

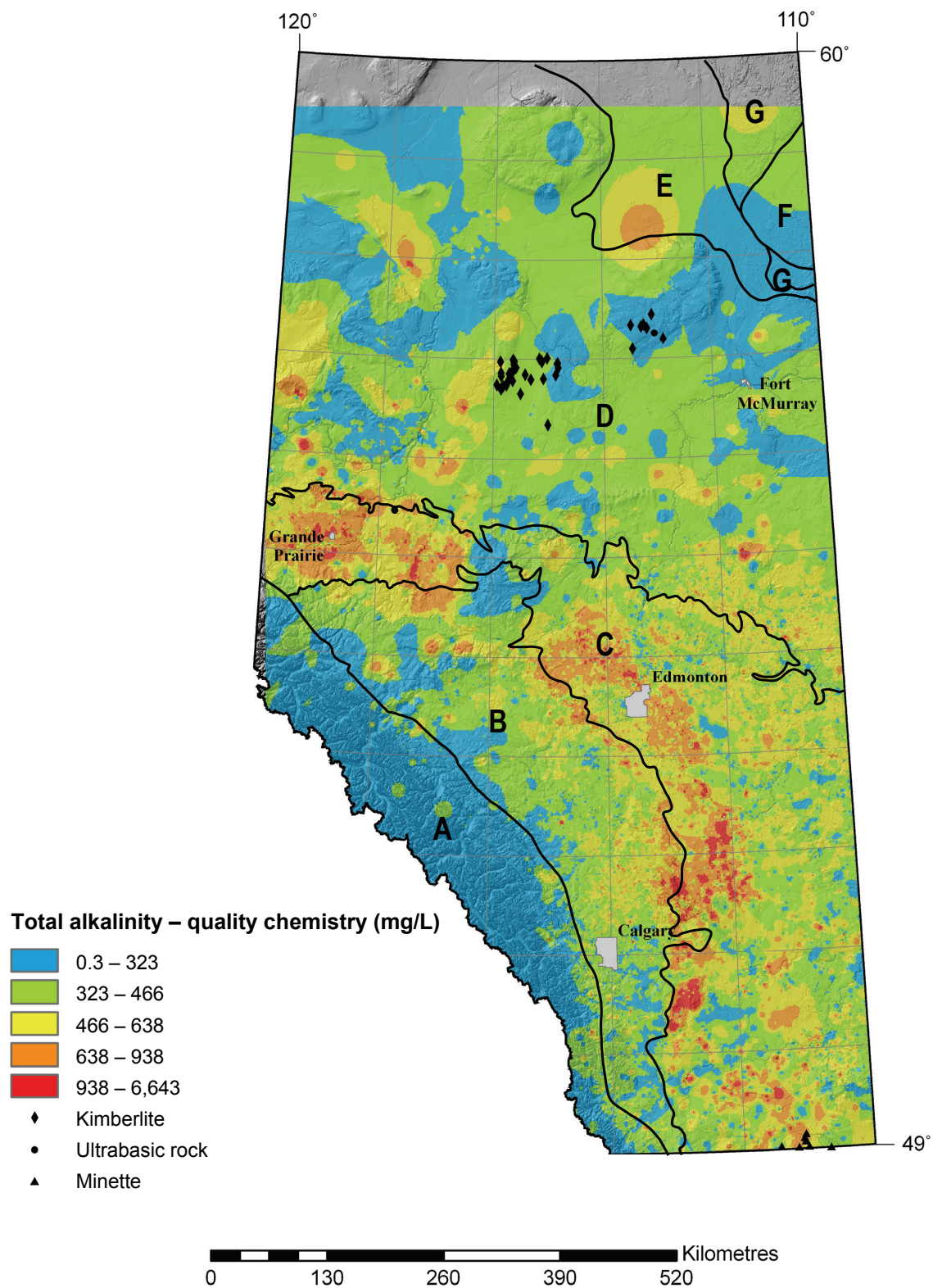


Figure 9. Groundwater total alkalinity-shaded contour map using the most recent well analysis from a culled dataset.



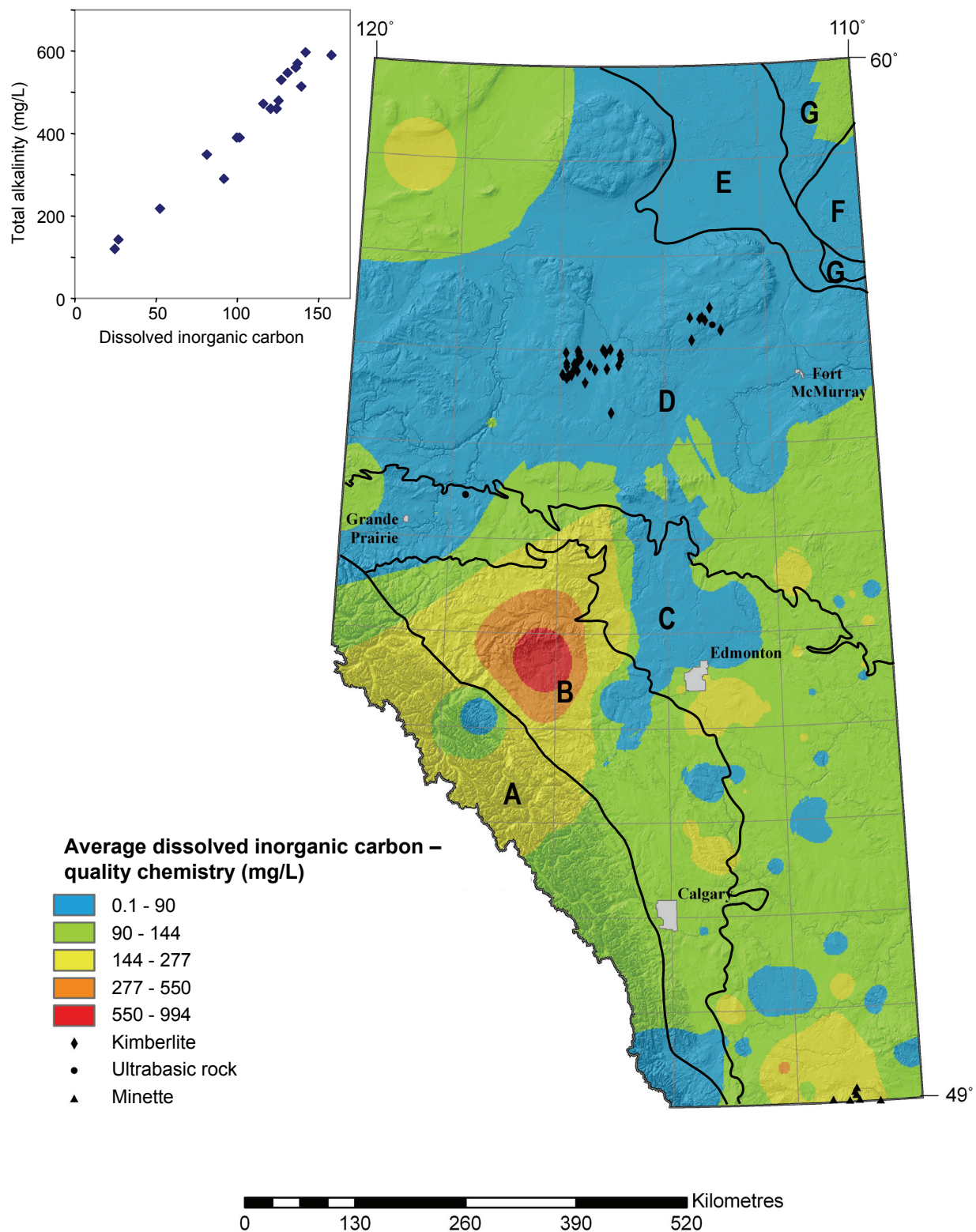


Figure 10. Groundwater-dissolved, inorganic carbon-shaded contour map using the most recent well analysis from culled and non-culled datasets. The inset map compares total alkalinity with dissolved inorganic carbon.

recharge. However, if groundwater crosses from one geological medium to another, the groundwater may become chemically active until it reaches a new chemical equilibrium. Thus, groundwater compositions may present an indicator of the geological environment in which it is hosted. To test this, we have simplified the geological map of Alberta (Figure 2) and added general geological unit polygons to the hydrogeochemically shaded contour maps.

Groundwaters with elevated Mg and Ca correlate well with Cretaceous strata (Figures 3 and 4), based on the assumption that several wells correlate with the over 114 000 Lower Mannville to surficial deposit based wells (Table 1). In northern Alberta, the middle to Late Cretaceous strata is dominated by shale and mudstone of the Smoky Group and Shaftesbury and Loon River formations. In addition, Quaternary deposits form the local landforms over virtually all of northern Alberta (e.g., Pawlowicz and Fenton, 1995). Therefore, we suspect the Mg-Ca hydrogeochemical signature is linked to interactions with some mixture of high-Mg bedrock and surficial deposits contaminated with up-ice Paleozoic carbonate rock (M. Fenton, personal communication, 2007; Figure 1) that would dissolve easily and contribute to water chemistry. Thus, it is possible that local variations in northern Alberta till such as the high-Mg and -Ca upper till unit in the Buffalo Head Hills area, which is caused by an increased abundance of Palaeozoic material in the upper till unit (Fenton et al., 2006a; Figure 1a), may result in 'false' hydrogeochemical Mg-Ca anomalies. In southern Alberta, an increase in Mg and Ca correlates with the Oldman and Foremost sandstone-dominated formations. This might be related to groundwater-bedrock interaction because the sandstone-dominated Tertiary rocks to the northwest have low Mg and Ca, relative to the Oldman and Foremost formations. These observations show that groundwater data might be an additional tool in geological mapping. Finally, we reiterate that bedrock Mg-Ca hydrogeochemical anomalies in northern and southern Alberta must take into consideration, shallow flow systems in the upland regions.

Groundwater pH measurements show that southern Alberta is generally acidic ( $\text{pH} < 7$ ; Figure 8). In contrast, northern Alberta is dominated by neutral pH ( $\text{pH}$  of 7) with localized areas of both basic ( $\text{pH} > 7$ ) and acidic groundwater (Figure 8). Less acidic areas of northern Alberta likely are buffered by  $\text{CaCO}_3$  incorporated in middle to Late Cretaceous mudstones and Quaternary sediments from Paleozoic rocks in northeastern Alberta. A comparison of pH versus Mg and Ca (Figures 8, 3 and 4, respectively) shows that acidic areas in northern Alberta (e.g., north of latitude  $57^\circ$ ) correlate well with low-Mg and Ca areas. Another plausible explanation for neutral pH groundwater in northern Alberta could be associated with a large number of samples from deeper wells. For example, wells penetrating into the carbonate platform, which underlies Cretaceous strata in Alberta, would increase the concentration of most elements, including Mg and Ca.

High groundwater alkalinity ( $> 5 \text{ mg/L}$ ) in southwestern Alberta shows a relationship with Tertiary sandstone-dominated units (Figure 9), and thus is probably related to the total acid-neutralizing capacity of the silicates. Isolated, high-alkalinity anomalies in northern Alberta may be similarly related to intermittent bedrock exposures of sandstone-dominated Pelican and Grand Rapids formations, and the Dunvegan Formation in the Late and Early Cretaceous, respectively.

Dissolved inorganic carbon is generally low ( $< 90 \text{ mg/L}$ ) for most of northern Alberta. The DIC values have a 1:1 relationship with alkalinity (Figure 10, inset) that suggests acid neutralization correlates well with carbonate ( $\text{CO}_3^{2-}$ ) and bicarbonate ( $\text{HCO}_3^-$ ).

### 3.2 Hydrogeochemical Observations in Ultramafic Field Areas

Ultramafic rocks are located in four separate areas of Alberta, including southeastern Alberta (Sweetgrass Intrusives dominated by minette rock types), northwestern Alberta (Mountain Lake ultrabasic cluster), north-central Alberta (Buffalo Head Hills kimberlite field) and northeastern Alberta (Birch Mountains

kimberlite field). The provincially scaled investigation of the Alberta groundwater database as part of this study does not depict any unequivocal relationships between hydrochemistry and ultramafic rocks discovered to date in Alberta. Chromium and nickel data, which are unfortunately not commonly analyzed for and, more or less, relegated to the southern part of the province, do not show regional correlation with the Sweetgrass Intrusives. The Buffalo Head Hills kimberlite field, which is the largest field of ultramafic rocks discovered to date in Alberta and consisting of 38 occurrences of kimberlitic rocks, has a hydrogeochemical signature characterized by high-Mg and Ca (Figures 3 and 4). These apparent correlations are not observed in other areas of the province with ultramafic rock fields. For example, the Birch Mountains kimberlite field, also in northern Alberta, has only moderate Mg and Ca. Thus, any association between Mg, Ca, K and the Buffalo Head Hills kimberlite field is tenuous because hydrogeochemical anomalies could also be related to a region known to have high-Mg and Ca upper till layers (Figure 1; Fenton et al., 2006a). The same observation is true for pH and total alkalinity (Figures 8 and 9), where regional patterns are more likely related to the flow systems, bedrock and/or deposits of surficial material.

To close, Sader et al.'s (2003) investigation of groundwater in kimberlite showed that different kimberlites and kimberlite facies can have distinct hydrogeochemical values. Thus, more detailed studies between Alberta kimberlite and groundwater are required to understand their possible relationship.

### 3.3 Hydrogeochemical Anomalies

This study shows several interesting anomalies, which should be taken with caution because of the limited number of wells with trace-element data available and because there is no way to reflect on the quality of the sampling method/measurement. Nevertheless, the most significant observation regards Ni, an element associated with olivine-rich ultramafic rocks. Unfortunately, groundwater data on Ni are only available for central and southern Alberta, but Figure 7 shows a Ni anomaly near the communities of Athabasca and Calling Lake. This apparent anomaly is predominantly caused by a single Ni groundwater value of 103 mg/L at latitude 54.723° and longitude 113.314°. While it is possible that the Ni value is unrealistically high, to the point that the units may have been reported incorrectly (e.g., mg/L vs. µg/L), it is interesting that several other anomalous values between 0.14 and 7.4 mg/L Ni were also recorded in the same area. The Ni anomaly is interesting as kimberlite exploration work has shown that the Calling Lake area has some of the highest amounts of kimberlite-indicator minerals discovered in Alberta and is one of the few areas in the province that contains subcalcic pyrope (G10) garnets (Dufresne and Eccles, 2005). Thus, the area is considered a high priority target for the discovery of a new diamondiferous kimberlite field in Alberta. The groundwater database shows that the Ni anomaly is further supported as an area of interest by a nearby elevated Cr groundwater anomaly of 3.5 mg/L Cr at latitude 54.018° and longitude 113.179° (Figure 6).

Groundwater chromium data, which are not typically analyzed for and limited to southern Alberta, show elevated chromium compositions on the eastern side of the province between latitudes 51° and 53.5° (Figure 6). The Cr anomaly occurs in the Upper Cretaceous Belly River Group and Lea Park Formation, and is not directly correlated with bedrock because the anomalies are confined to eastern Alberta, while the Belly River extends in a northwesterly direction into central Alberta. Thus, the Cr anomaly is puzzling. At first, we investigated the possibility that the Cr anomaly might be related to bentonite deposited throughout southern Alberta. If this were true, we would expect the Cr anomaly to continue through, or be more pronounced, the thick bentonite deposit regions west of the Cr anomaly (Drumheller, Dorothy-Trefoil, Rosalind and Rosebud), and/or south of the Cr anomaly (Irvine-Bullshead; Dufresne et al., 1996).

Follow-up work is recommended near the Cr anomaly, particularly because chromium might be

associated with ultramafic rocks or other types of metallic mineral deposits, and this area has received little minerals/diamond exploration work. In addition, the local geology is enticing for several reasons. The area of the Cr anomaly is underlain by a high-velocity, upper mantle anomaly (i.e., thick lithosphere) and the Hearne Province's Loverna Block, which has a tentative Archean age, a north-trending aeromagnetic anomaly that separates the Loverna Block from Eyehill Eye terranes, and a north-trending zone of approximately 45 km thick crust (Ross et al., 1994; Bouzidi et al., 2002; Clowes et al., 2002; Shragge et al., 2002). These attributes represent viable criteria for the discovery of volcanic rocks such as diamondiferous kimberlite.

Another 'bull's-eye'-type anomaly includes potassium (Figure 5). With the exception of a northeast-trending K anomaly, located directly northeast of the Buffalo Head Hills kimberlite field, groundwater K is generally <16 mg/L (Figure 5). Upon closer inspection of the data, this apparent K anomaly seems to be related to a single, near-surface well record with 800 mg/L K and may not have any relationship with the kimberlite field. We point out, however, that a K anomaly in the vicinity of kimberlite fields should not be completely discounted because Sader et al. (2003), albeit in a different environment (Late Jurassic kimberlite emplaced into Archean hostrock), showed that kimberlitic waters in the Lake Timiskaming kimberlite field have a high K to Mg ratio related to an increase in the alteration of micaceous materials (phlogopite).

Two other K anomalies in northern Alberta are north of High Prairie and north of Calling Lake in the Pelican Mountains (Figure 5). The former anomaly is shallow (620 m asl), about 89 km east-northeast of the Mountain Lake ultrabasic body at latitude 55.596° and longitude 116.711°, and coupled with a low-Mg and Ca at the southern boundary of the middle to lower Cretaceous mudstones. In contrast, a small K anomaly in the Pelican Mountains is associated with elevated Mg and Ca (Figures 3 and 4) that may be related to shallow flow systems or tills as previously discussed.

## 4 Conclusion

Discovery of an economic deposit of diamonds in Alberta may take longer than other parts of Canada because of, for example, the complex Quaternary history, thickness of overburden (surficial deposits related to glacial movement and/or erosion), and the paucity of kimberlite-indicator mineral sampling. Thus, the role of scientific exploration and using whatever datasets are available in an area become a factor.

We have shown that kimberlite has a unique geochemical signature in comparison to its host bedrock, soil and till. A ubiquitous relationship between groundwater and ultramafic rocks is unclear and more detailed studies between Alberta kimberlite and groundwater are required to understand their relationship, but the hydrogeochemical technique provides an innovative approach to explore Alberta.

Groundwater data appear to be a good indicator of the geological environment, and several distinct hydrogeochemical signatures might reflect their position within the geology of Alberta. Hydrogeochemical anomalies that do not appear to correlate with any known geological boundaries are observed, particularly for Ni and Cr, near the communities of Athabasca and Calling Lake and in southeastern Alberta. These results should be of interest to future exploration and geological studies in these areas.

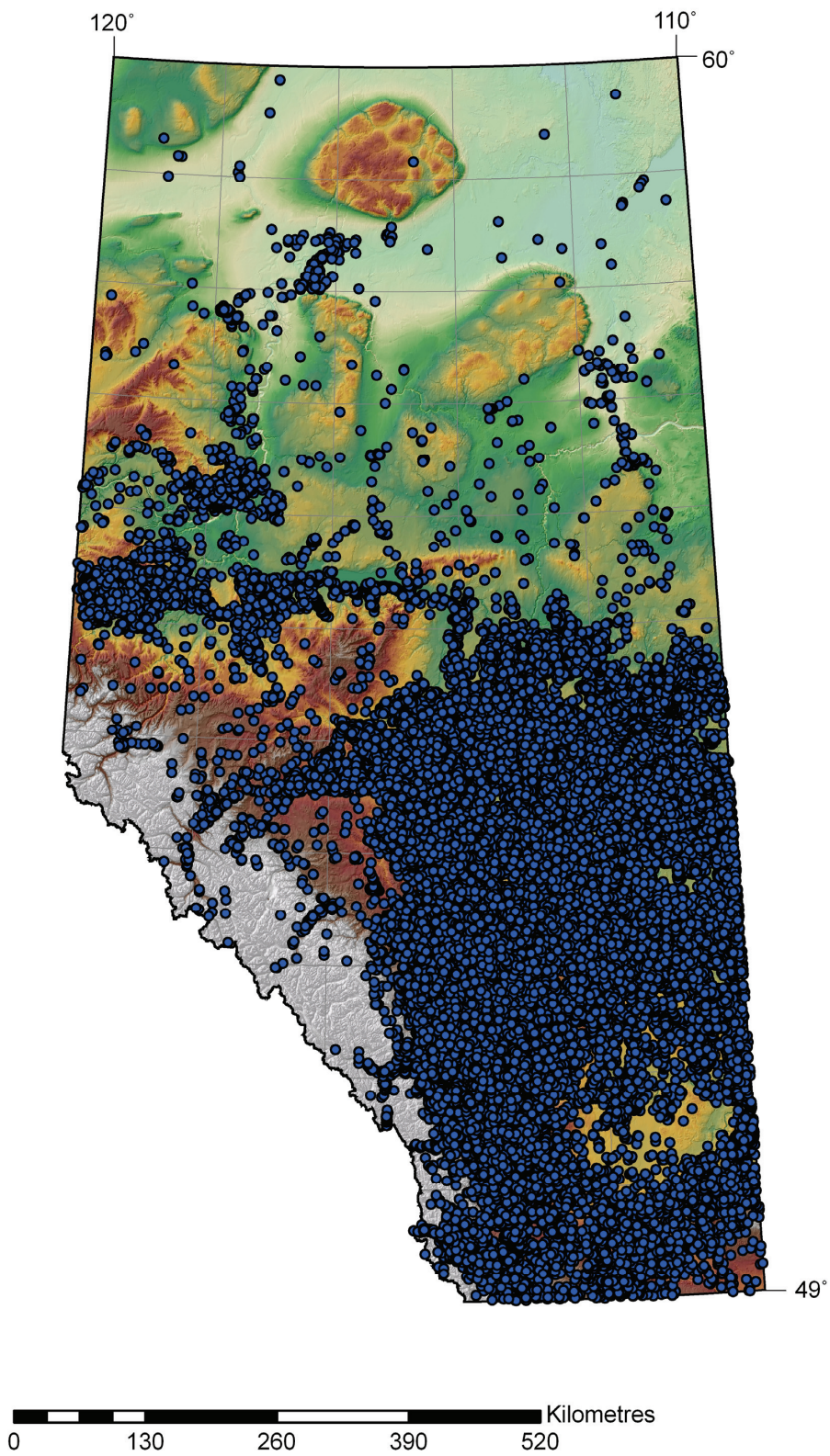


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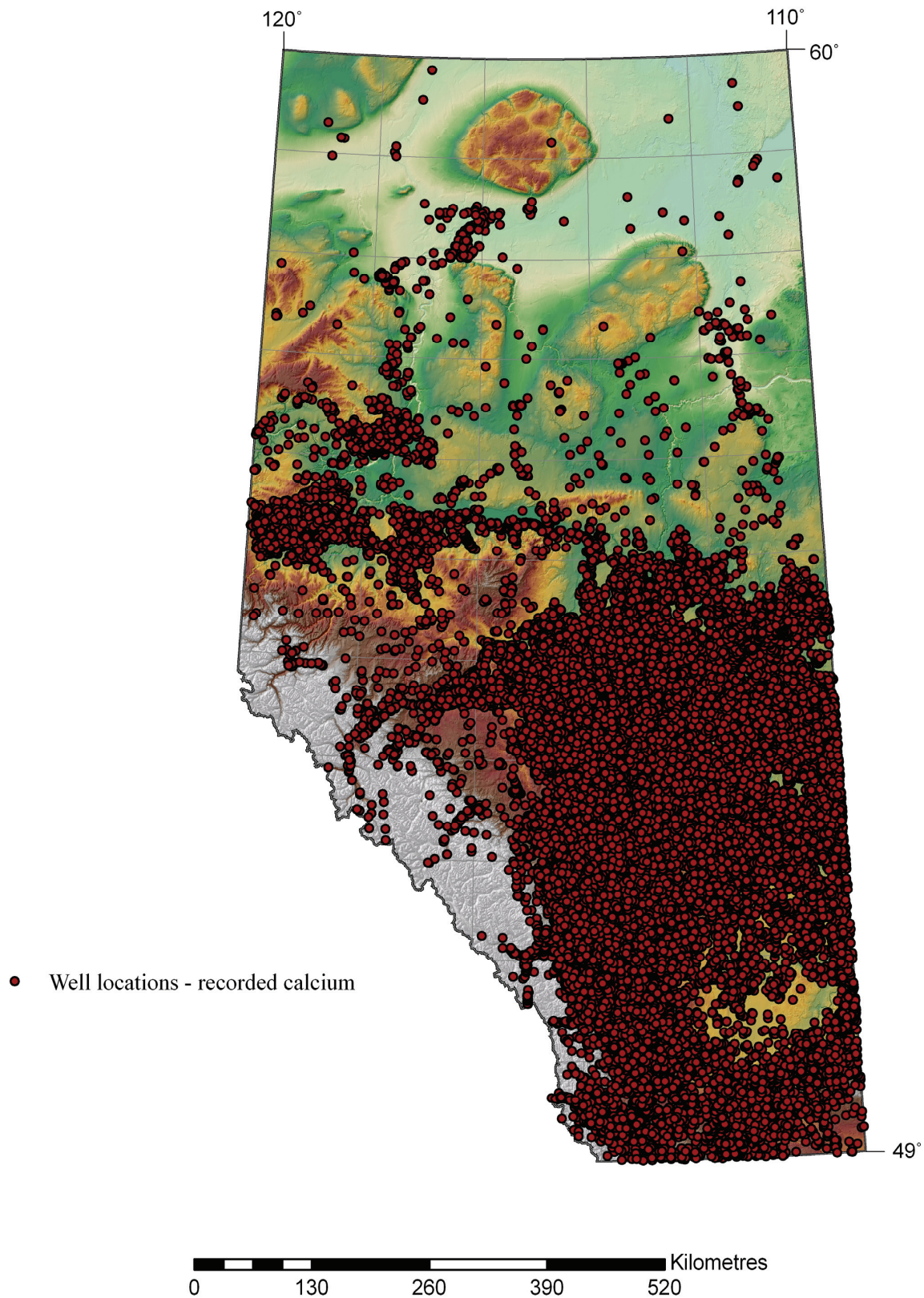
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**Appendix 1 – A Summary of Water Well Locations Used for a) Mg, b) Ca, c) K, d) Cr, e) Ni, f) pH, g) Total Alkalinity and h) Dissolved Inorganic Carbon**

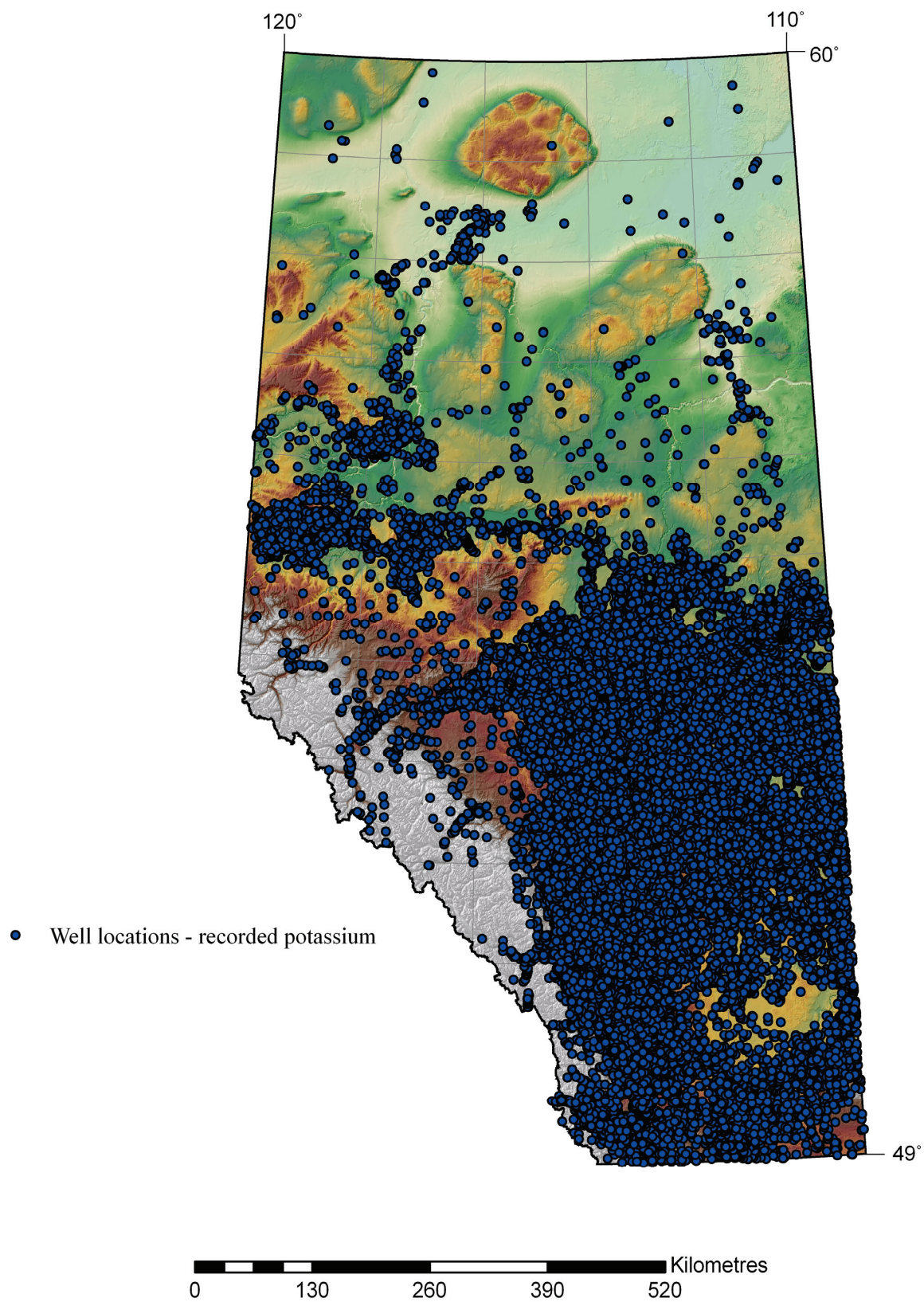


Appendix 1a. Water well locations that measured magnesium.



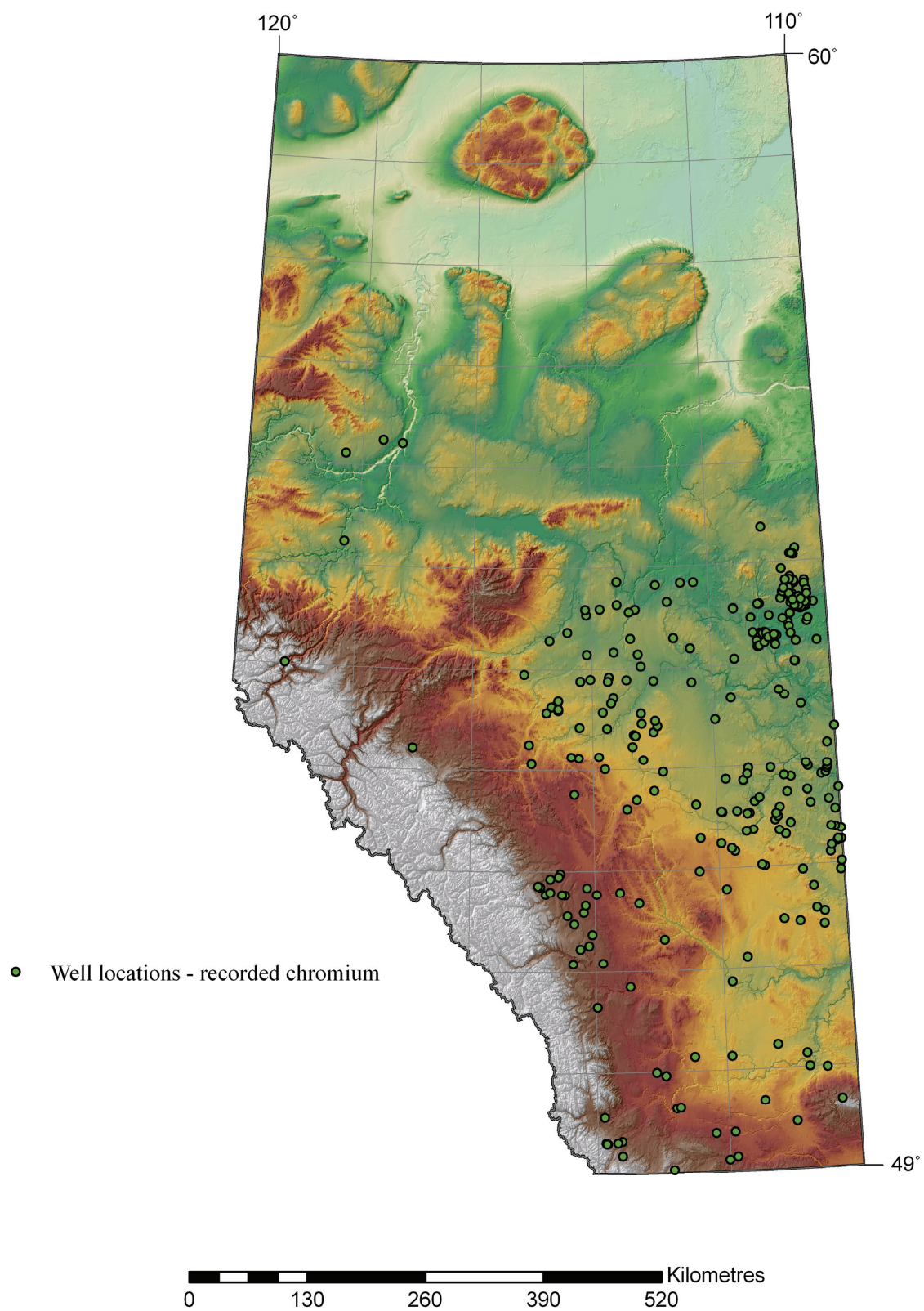


Appendix 1b. Water well locations that measured calcium.

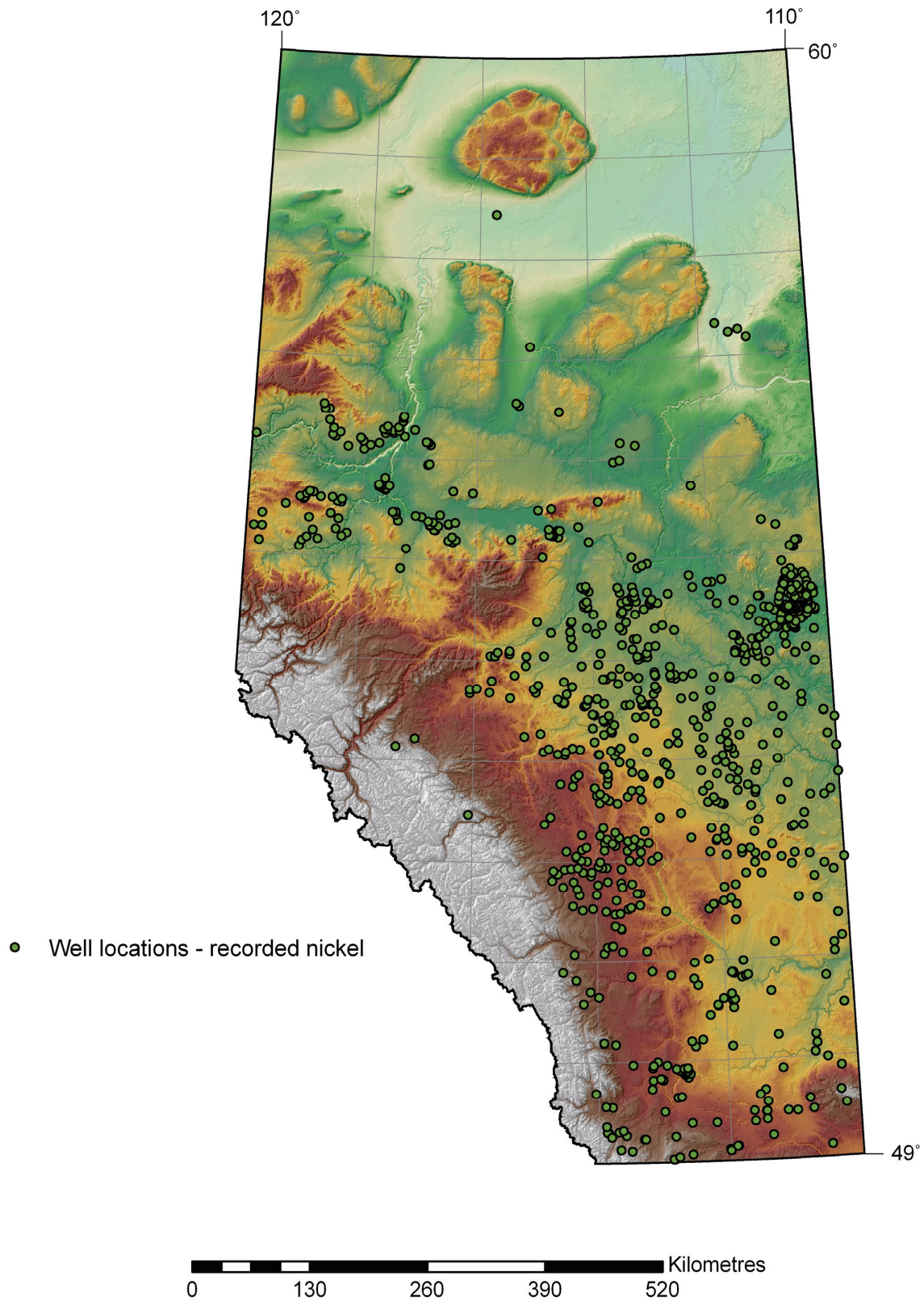


Appendix 1c. Water well locations that measured potassium.



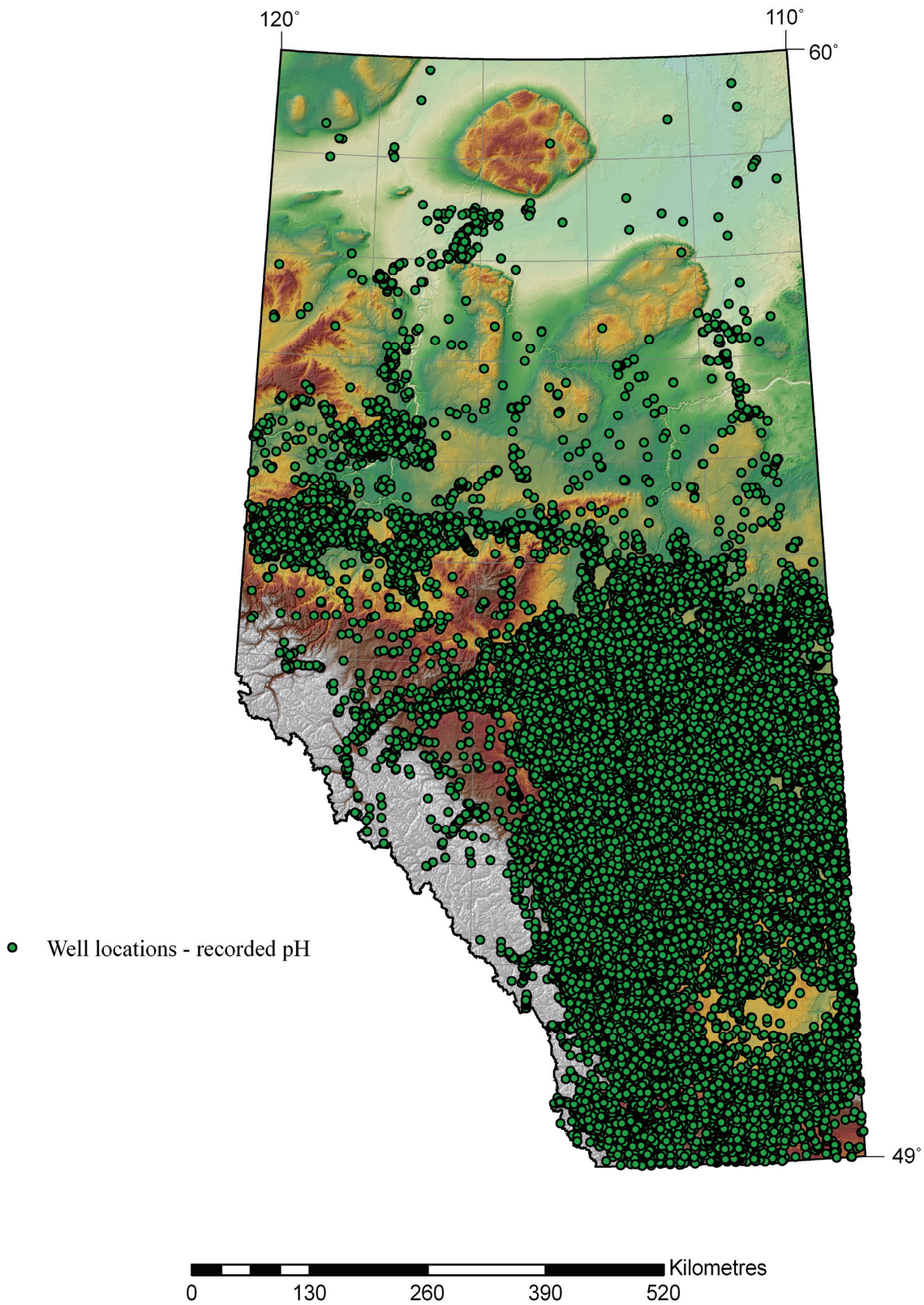


Appendix 1d. Water well locations that measured chromium.

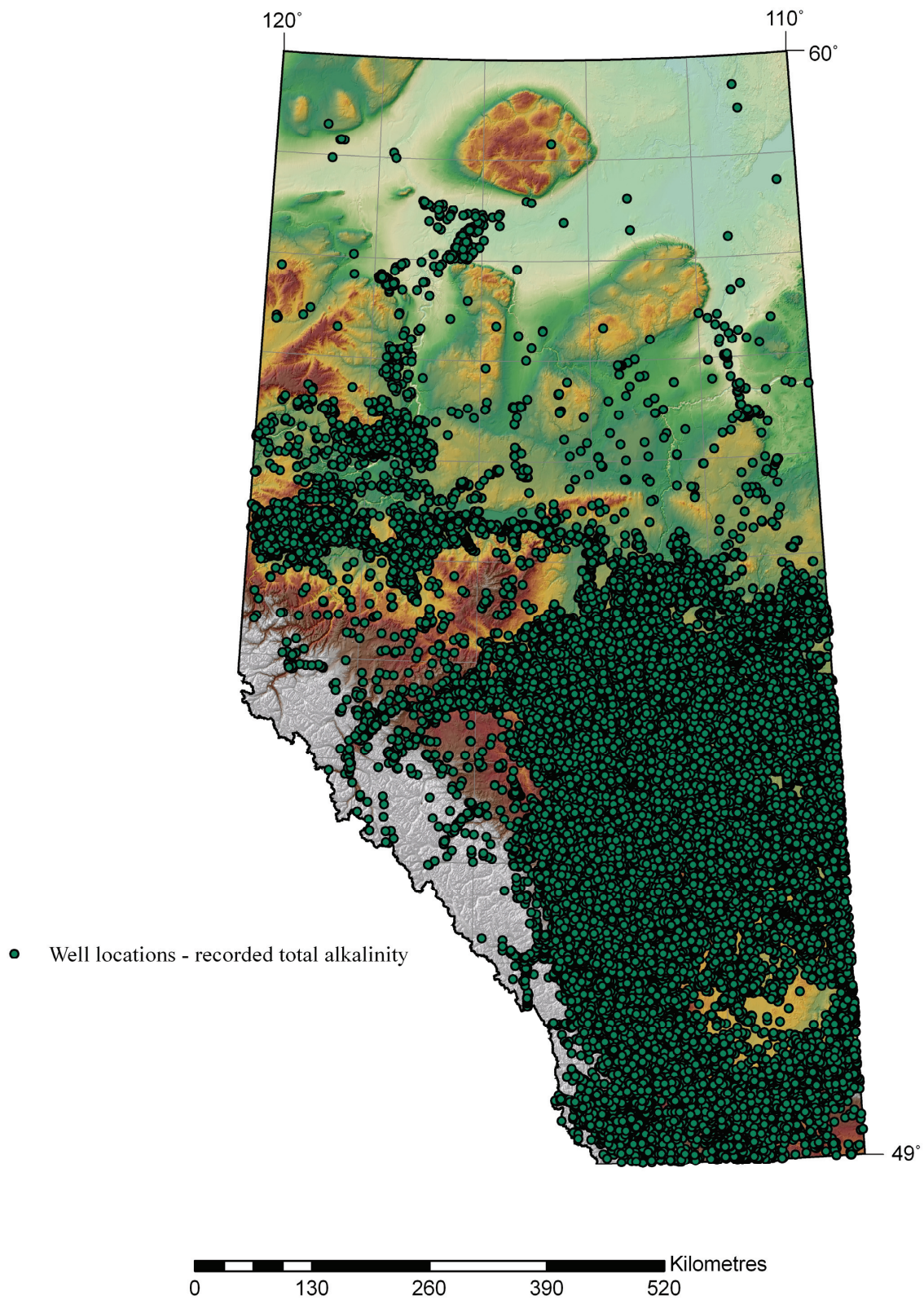


Appendix 1e. Water well locations that measured nickel.



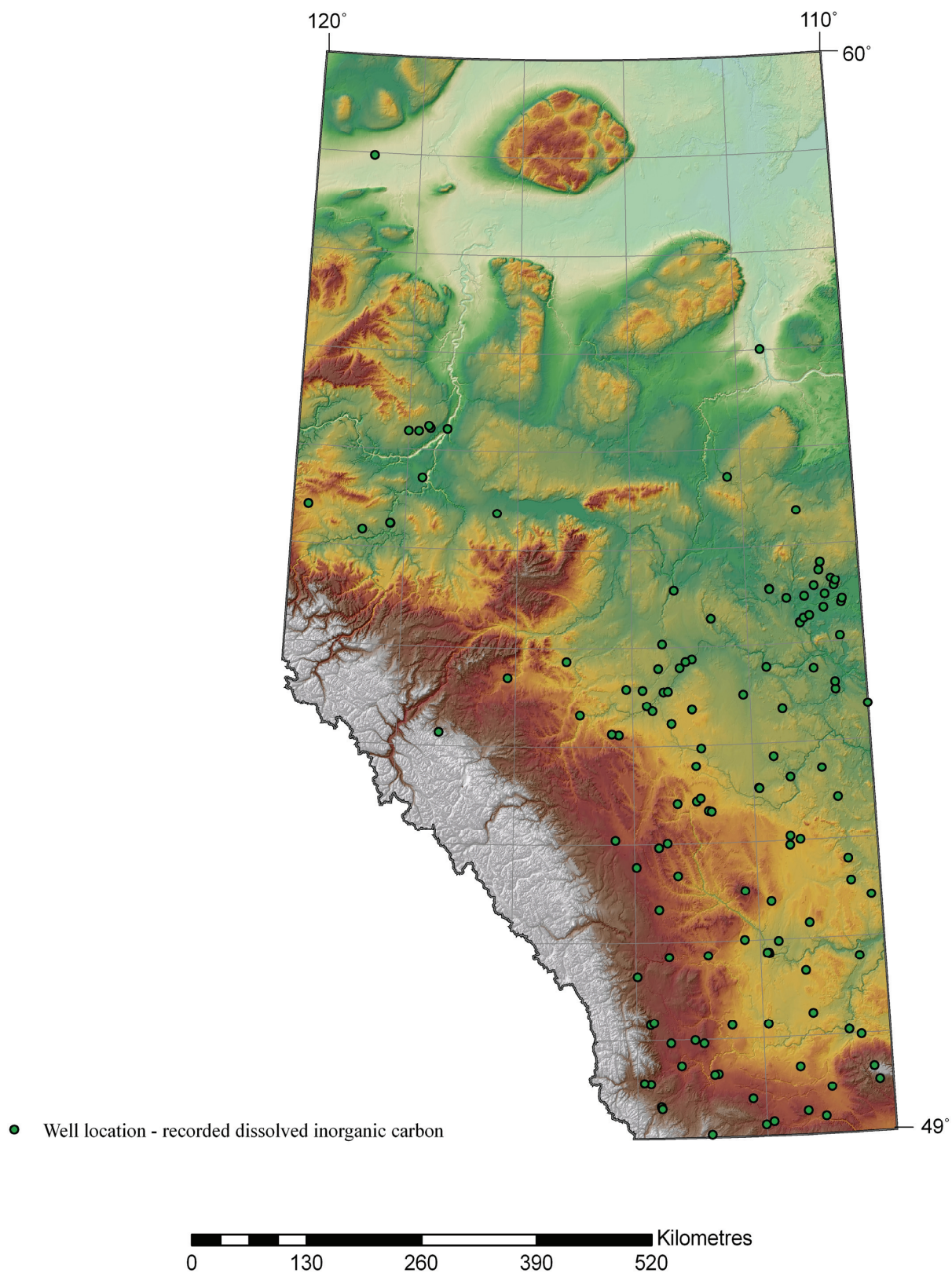


Appendix 1f. Water well locations that measured pH.



Appendix 1g. Water well locations that measured alkalinity.





Appendix 1h. Water well locations that measured dissolved inorganic carbon.