LA-UR-14-24761

Title:	Survey of Chloride Concentrations in Formation (Pore) Waters of Crystalline Rocks and Shale
Author(s):	Perry, Frank V.
Intended for:	Report
Issued:	2014-10-16 (rev.1)

Survey of Chloride Concentrations in Formation (Pore) Waters of Crystalline Rocks and Shale

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy
Used Fuel Disposition Campaign
Frank V. Perry
Los Alamos National Laboratory
June 30, 2014
FCRD-UFD-2014-000514
Los Alamos Unlimited Release LA-UR-14-24761

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ACRONYMS

Cl	Chloride (anion)
DOE	Department of Energy
DPC	Dual Purpose Canister
HLW	High-Level Waste
TDS	Total Dissolved Solids
UFDC	Used Fuel Disposition Campaign
URL	Underground Research Laboratory

USED FUEL DISPOSITION CAMPAIGN

SURVEY OF CHLORIDE CONCENTRATIONS IN FORMATION (PORE) WATERS OF CRYSTALLINE ROCKS AND SHALE

1. INTRODUCTION

The technical feasibility of direct disposal of large dual purpose canisters (DPC) is being evaluated as part of the DOE Used Fuel Disposition Campaign (UFDC). One aspect of the evaluation is analysis of criticality in the event of canister breach and flooding or changes in geometry of the canister contents (Hardin et al., 2013). Flooding of a canister by freshwater would act as a neutron moderator and increase the probability of criticality while flooding of a canister by groundwater containing dissolved ionic species could lower the probability of criticality if the ionic species include neutron absorbers. Chlorine-35 would act as a moderately effective neutron absorber because of its neutron capture cross-section and abundance in saline groundwater (Hardin et al., 2013).

The most common dissolved anion in many groundwaters is chloride (Cl^-), which combines with Na, Ca (most commonly) and other cations to form saline groundwater. Ca-Cl waters are more common with increasing depth particularly in granite due to alteration of plagioclase to albite (Gascoyne, 2004). The salinity of groundwater is synonymous with the term Total Dissolved Solids (TDS), which includes all solids dissolved in water including organic compounds, although these are generally minor. Groundwater salinity is classified in terms of TDS, from freshwater with low TDS to saline waters with high TDS.

2. Overview of Chloride and Total Dissolved Solids in Crystalline and Sedimentary Formation Waters

Chloride combines with Na, Ca, Mg and other cations to form various salts. These salts are typically the dominant constituents that make up the TDS in groundwater. Using the classification for salinity summarized in Kharaka and Hanor (2003), freshwater has TDS values of less than 1000 mg/L, brackish waters have values of 1000-10,000 mg/L, and saline waters have values of 10,000-35,000 mg/L (the upper end being equivalent to average seawater). Waters that have TDS values greater than 35,000 mg/L (more saline than seawater) are termed brines. The natural limit of TDS in groundwaters is about 350,000 mg/L due to solubility limits (DeMaio and Bates, 2013). Based on data for TDS and Cl in sedimentary basins presented by Kharaka and Hanor (2003), Cl concentrations linearly correlate with TDS and represent about 60% (± ~10%) of the TDS concentrations.

In both sedimentary and crystalline rock terranes, groundwater (i.e., formation water) typically becomes more saline with depth (Figure 1), although salinity reversals in sedimentary basins are known to occur (Kharaka and Hanor, 2003). The salinity of groundwater is due to several possible processes including mineral-rock interactions, advection or diffusion of salt from adjacent formations, or the trapping and later modification of connate seawater in the pore spaces of marine sediments (Hanor, 1994; Kharaka and Hanor, 2003; Frape et al., 2003; Gascoyne, 2004; Rebeix et al., 2014). Once present in a deep and stable geologic environment (several hundred meters or more), saline waters will tend to remain saline and stagnant because their higher density makes them resistant to mixing with more dilute waters from meteoric sources (Phillips and Castro, 2003), and, in the case of deep water in crystalline rocks, because of the low permeability of the rock and closed fractures at depth that limit connectivity and mixing with shallower meteoric waters (Frape et al., 2003). Pore waters in deep sedimentary basins are potentially more mobile because of the presence of permeable sandstones and carbonates, but pore waters in impermeable shale intervals are essentially immobile except for slow diffusion of ionic species across concentration gradients (Clark et al. 2013; Rebeix et al., 2013).

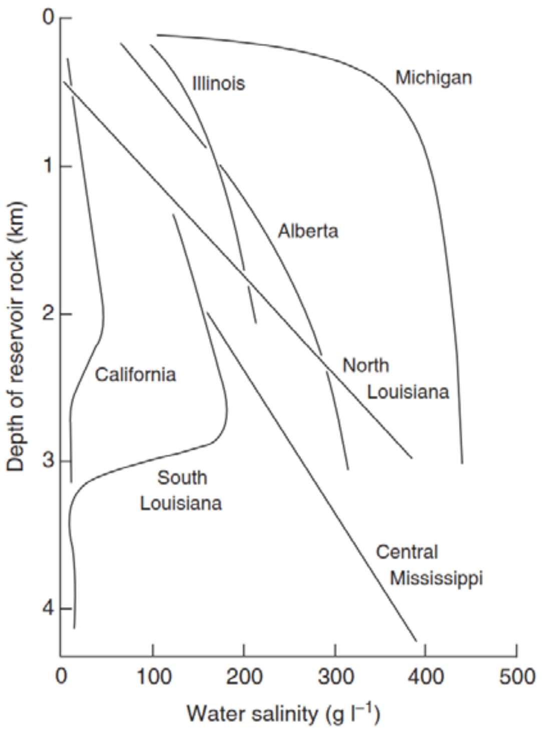

Figure 1. Salinity versus depth for sedimentary basins in North America (from Kharaka and Hanor, 2003).

3. Chloride Data for Crystalline and Shale Formation Waters

The UFDC is considering crystalline (granitic), shale and salt as potential host rocks for a HLW repository. In this section, data for chloride concentrations in granite and shale pore waters are described and compared. These data were obtained primarily for the purposes of characterizing the geologic environments for HLW disposal in Canadian or European programs. Chloride data is also available from R&D related to the oil and gas industry and carbon sequestration programs, but these data are obtained mostly from permeable rocks such as sandstones or carbonates.

Pore waters are usually sampled by isolating and sampling depth intervals in vertical boreholes, extracting the pore water from drill core in the laboratory, or from horizontal drilling in the walls underground research laboratories or mines. Sampling methods are reviewed in detail by Frape et al. (2003) and Kharaka and Hanor (2003).

Chloride concentrations reported in both shale and crystalline rock span a similar range of values, from approximately 100 mg/L or less (freshwater) to approximately 210,000 mg/L, which are near saturation levels for NaCl at temperatures of less than 100 degrees Celsius (Figures 2 and 3). Chloride concentrations versus depth in granite pore waters for different crystalline terranes are summarized in Figure 2. Also shown are reference lines for chloride concentrations for the upper limit of freshwater, representative seawater, and the chloride concentration equivalent to a 2 molal solution of NaCl (approximately 3.6 times the Cl content of seawater) The 2 molal reference line was chosen because it is the calculated value where representative DPCs would have little probability of reaching criticality if flooded by Cl-rich groundwater (Hardin et al., 2013).

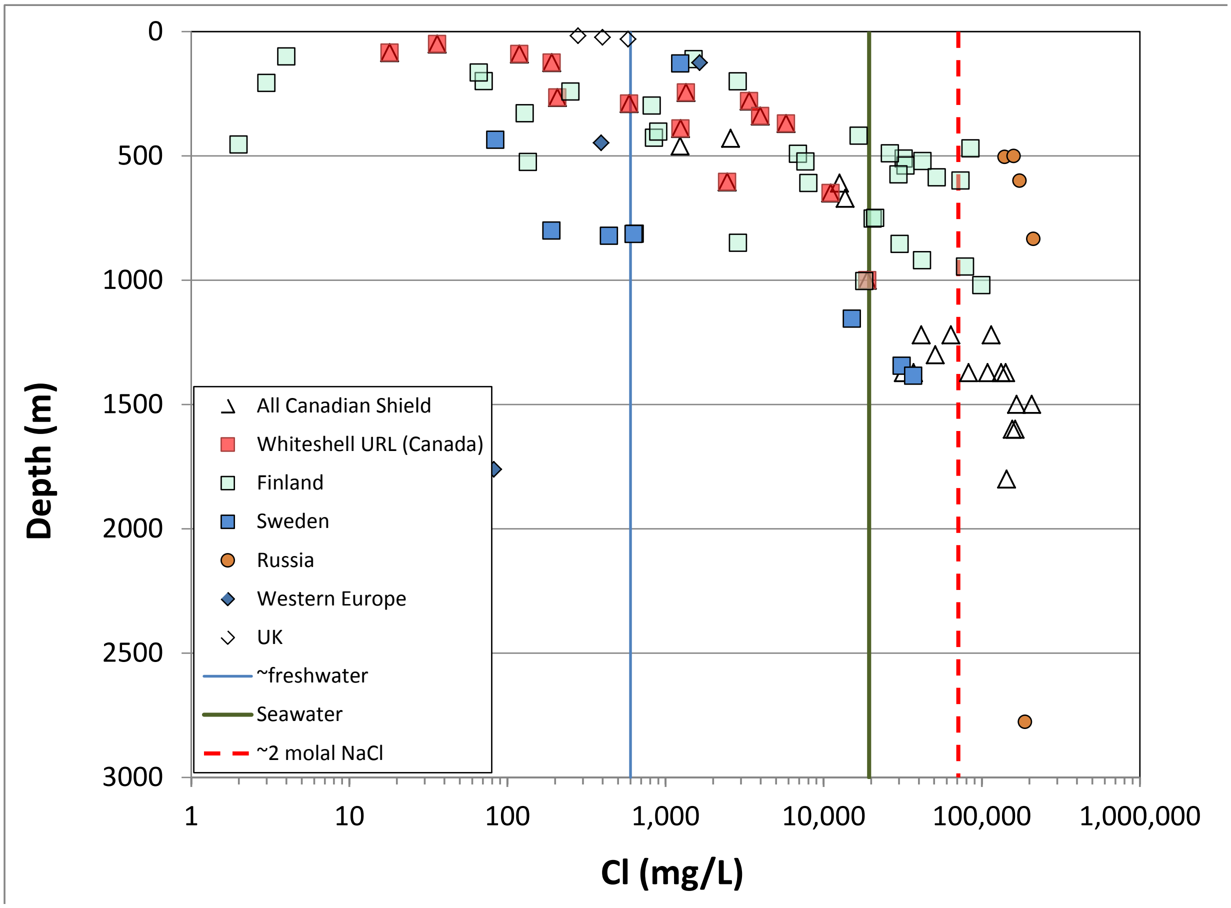

Figure 2. Cl concentration versus depth for various crystalline terranes. Data sources are documented in Frape et al. (2003). Reference lines are the upper limit for freshwater Cl concentration, average seawater Cl concentration and the Cl concentration for 2 molal NaCl.

The main trend in crystalline rocks is increasing chloride concentrations with depth (Figure 2). Nearly all freshwater samples (TDS<1000 mg/L, Cl < 600 mg/L) are restricted to depths of less than 500 meters, reflecting the domination of meteoric waters. At depths of greater than about 500 meters, pore water compositions become increasingly more saline, with Cl concentrations reaching maximum values of greater than 200,000 mg/L. A number of samples, primarily at depths greater than 1000-1500 meters exceed Cl values equivalent to a 2 molal NaCl solution (Figure 2). Samples from the Russian Siberian Platform are notably saline at relatively shallow depth (500-1000) meters (Figure 2), which has been attributed to the influence of extensive overlying evaporate deposits (Frape et al., 2003). Highly saline waters (greater than seawater or > 2 molal NaCl) are apparently common in Archean basement at depths greater than about 500 meters based on data from Canada, Finland and Russia (Figure 2). The high salinity is likely the result of a long geologic history of water-rock interactions and the emplacement of marine brines from external sources (Frape et al., 2003).

Compared to crystalline rocks, data for pore water or formation water in shale is relatively sparse (Figure 3), reflecting the difficulty in extracting pore water from shale under controlled conditions and less interest historically in determining the pore water compositions of aquitards compared to more permeable rocks that host oil and gas or use for potential CO_2 sequestration.. This situation is changing more recently with increased interest in hydraulic fracturing of shale, but this data is dominated by data from produced waters under less controlled conditions. Some of the literature sources of pore water data present the data only as graphs and those are shown in Figure 3 as fields representing the approximate range of data. Much of the better controlled data for shale pore waters comes from national programs that target shale as a potential repository host rock. As is the case with granites, pore waters reflect input from relatively fresh meteoric water at shallow depths (<500 meters) and are increasingly saline with depth. Most reported shale pore waters have Cl concentrations corresponding to salinity values that are less than that of seawater. The notable exceptions are two shale intervals that lie within the Michigan Basin. These shales (the Antrim Shale and Ordovician shales below the southern Ontario portion of the Michigan Basin) have Cl values exceeding the equivalent of 2 molal NaCl. Although the Michigan Basin has major intervals of bedded salt (both above and below these shales – see figure 4) the high Cl contents are not simply attributed to dissolution and transport of waters from nearby evaporates, but to a combination of more complex processes discussed below.

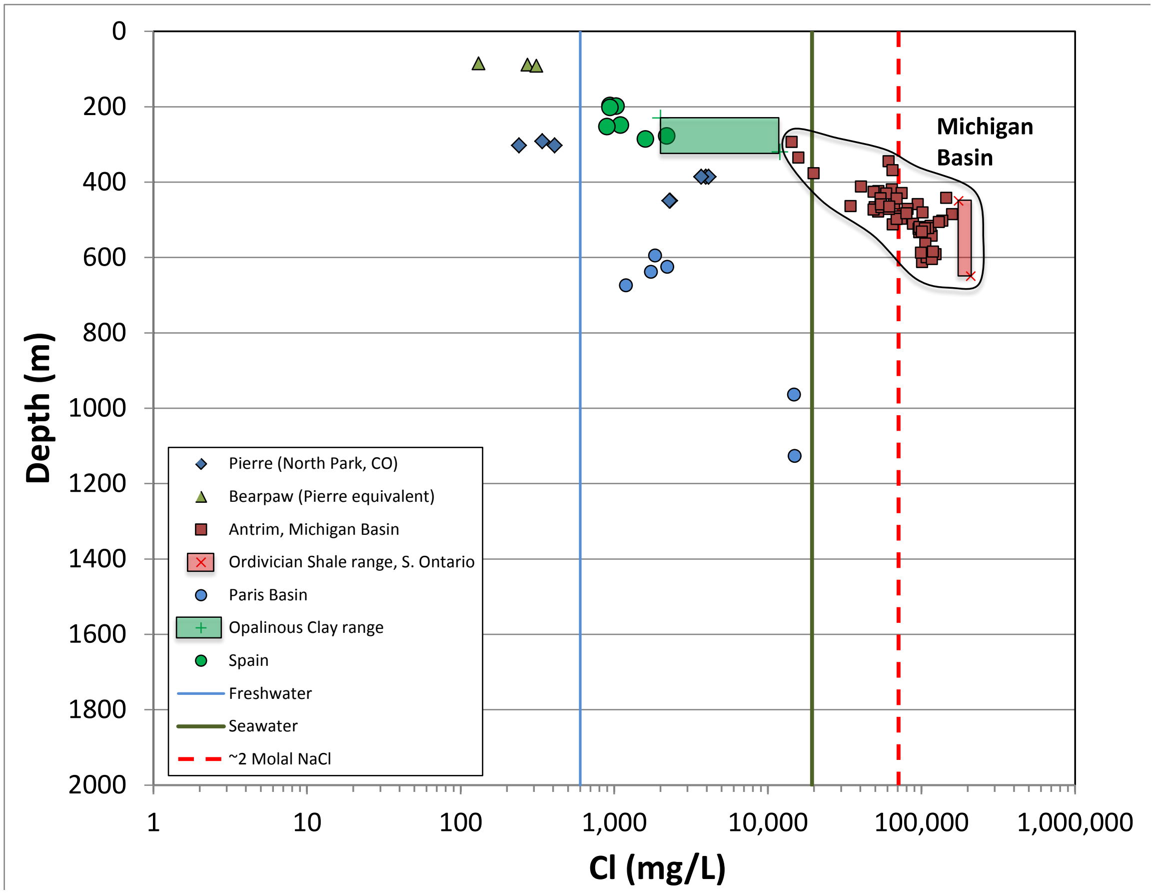

Figure 3. Depth versus Cl concentrations versus depth for selected shale formations in North America and Europe. Data sources: 1. Pierre Shale in North Park Basin, Colorado (Blondes et al., 2014); 2. Bearpaw Shale in southern Saskatchewan (Hendry et al., 2000), 3. Antrim Shale in Michigan Basin (Blondes et al. 2014), 4. Ordovician shales in southern Ontario (Clark et al., 2013), 5. Paris Basin, France (Bensenouci et al., 2013), 6, 7. Opalinous Clay, Mont Terri, Switzerland and Jurassic mudrock, Spain (Terrero et al., 2006). Reference lines are the upper limit for freshwater Cl concentration, average seawater Cl concentration and the Cl concentration for 2 molal NaCl.

4. Geologic Environments and the Origins of Saline Pore Waters

Geochemical and isotopic evidence indicate that saline pore waters can originate through several processes or combination of processes that can be described as those largely internal to the rock mass and those that involve transport of saline waters from outside the rock mass (Kharaka and Hanor, 2003; Frape et al., 2003). In granitic rocks, internal processes mainly involve water-rock reactions and alteration of minerals such as feldspars. External processes include movement of saline waters into the rock mass from basinal brines or dissolution of evaporate deposits. In shales, internal processes include incorporation of the original marine connate seawater trapped in pore spaces during sedimentation and lithification as well as subsequent modification of pore waters through water-rock interactions. External processes controlling salinity in shales include transport of basin brines, dissolution and transport of evaporate deposits and diffusion across concentration gradients (Kharaka and Hanor, 2003).

Origins of saline waters in shales of the Michigan Basin have been described in detail for the Devonian Antrim Shale and an interval of Ordovician shale in Ontario (Figure 4). For the Antrim Shale, McIntosh et al. (2004) have ascribed the origin of highly saline waters in the central part of the basin to exchange with brine originating in underlying Devonian carbonates, which have Cl/Br ratios reflecting evaporated seawater. In contrast, shale pore water near the basin margins have lower chloride concentrations, reflecting recharge by meteoric water (McIntosh et al., 2004, Figure 3B). High Cl concentrations in the Ordovician shale interval are ascribed by Clark et al. (2013) to diffusive mixing with overlying evaporative brines of the Silurian Salina Formation, which includes major intervals of bedded salt (Figure 4).

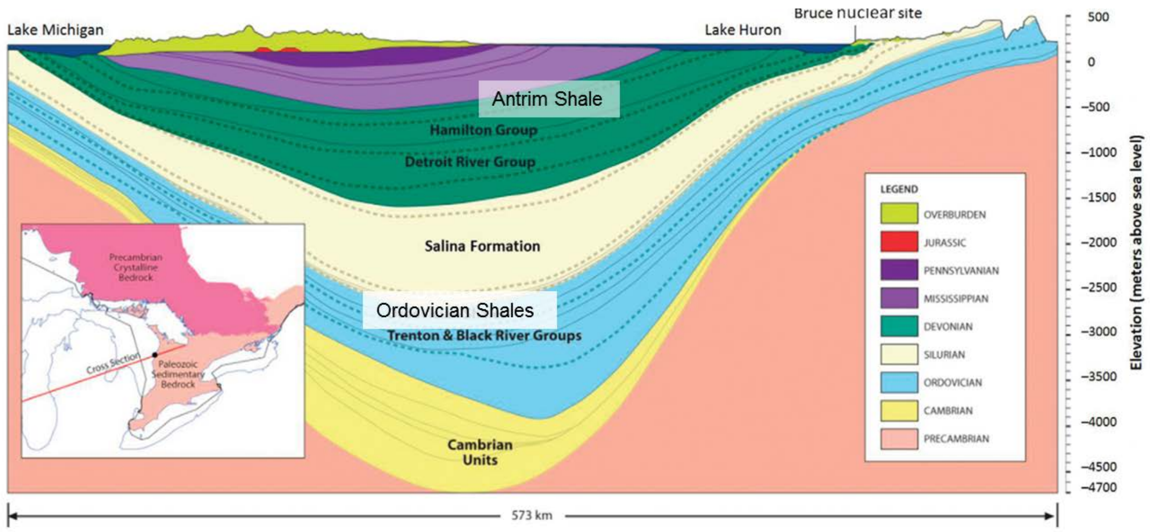

Figure 4. Stratigraphic cross-section of the Michigan Basin beneath Michigan and southern Ontario from Clark et al. (2013). Ordovician shales with high Cl concentrations are present in the upper part of the formations shown in blue. The stratigraphic position of the Devonian-age Antrim shale is also indicated. Major bedded salt units occur within the Salina Formation and the Detroit River Group.

Shales with highly saline pore waters are clearly the product of highly saline geologic environments. The major Paleozoic sedimentary basins of the US, which include the Michigan, Appalachian, Williston and Permian Basins (Figure 5), are characterized by bedded salt deposits and evaporative basinal brines that resulted from multiple marine transgressions. These environments provide the high salinity that produce high-Cl shale pore waters as connate features or products of diffusive mixing with brines in adjacent brine-bearing formations. High salinity in produced waters has been documented from the Marcellus formation in the Appalachian Basin where salinities approach 2 molal NaCl (Barbot et al., 2013). The chemistry of these waters suggests that the salinity originated primarily from seawater that evaporated and concentrated to form brines. The middle unit of the Bakken Formation in the Williston Basin is a fine-grained siltstone while the upper and lower units are black shales. The middle unit is highly saline, possibly due to ion filtration by the surrounding tight shales (Peterman et al., 2014). The salinity values for the upper and lower Bakken shale have not been reported.

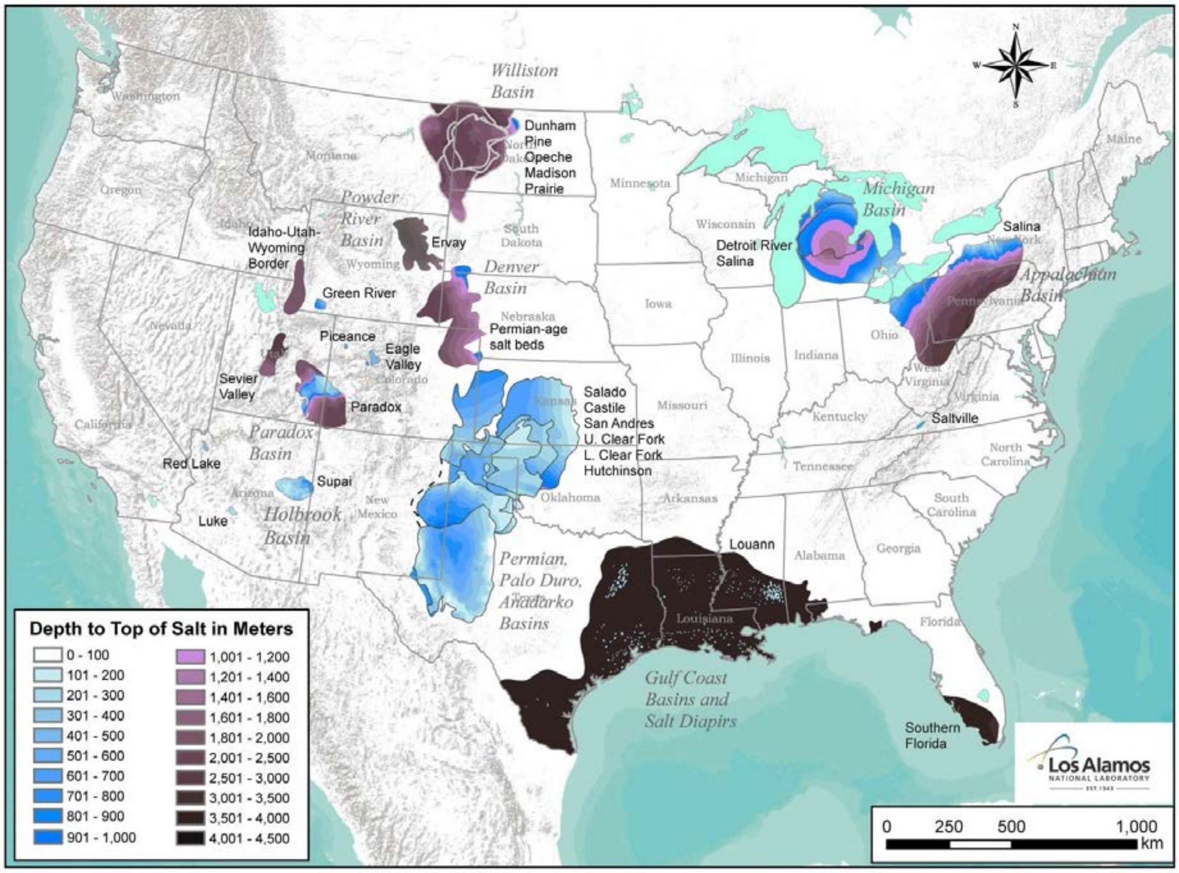

Figure 5. Distribution and Depth of salt formations in the US (from Perry et al. 2014). Basins with a long history of marine deposition, including deposition of bedded salts and marine shales, are more likely to contain shale with highly saline pore waters.

An example of the mixed origin of saline pore waters in crystalline rock is provided by a study of the Lac du Bonnet granite batholith, part of the Archean Canadian Shield (Gascoyne, 2004). The batholith hosts the Whiteshell URL in Manitoba. Pore water salinities are not as high as sampled in other areas of the Canadian Shield but lie along the Canadian Shield trend (Figure 2). Chloride concentrations increase with depth and reach that of seawater at a depth of 1000 meters (Figure 2). Gascoyne (2004) discusses several alternative origins for the salinity of water at depth in both fractures and pore fluids. The pore fluids have the highest salinity and are dominated by Ca-Cl type water, indicating prolonged (>>1 Ma) water-rock interactions involving albitization of plagioclase and a reduction of Na/Cl in the reacting fluid. These saline waters probably contributed to the salinity of the deeper fracture-filling groundwater. Although the Ca-Cl composition of the saline pore waters indicates prolonged rock-water interactions, the degree of salinity suggests that the salinity could not have originated solely within the granite mass. Low Br/Cl ratios of the deeper waters lie between those of seawater and basinal brines of the Manitoba Basin to the west, suggesting that the primary source of salinity was marine brines that infiltrated the granite during marine sedimentation in the Paleozoic. The timing also indicates that the resulting deep saline waters are old and stagnant over periods exceeding millions of years (Gascoyne, 2004).

5. Conclusions

High salinity pore waters occur at depth in both crystalline rock and shale under certain geologic conditions. Pore waters with greater than the Cl equivalent of 2 molal NaCl, sufficient to significantly reduce the probability of criticality in flooded DPCs, appear common in geologically ancient crystalline basement terranes at depths of greater than 500 meters. These saline waters primarily originated through a long history of water-rock interactions following infiltration of crystalline rocks masses by marine brines derived from overlying sedimentary rocks. The origin of highly saline waters in shale generally involves more complex processes, but shale with greater than the Cl equivalent of 2 molal NaCl are likely to be found in sedimentary basins with bedded salt deposits or histories of marine shale deposition that concentrated Cl in connate pore waters through evaporative processes and post-depositional water-rock interactions. In both crystalline and sedimentary environments, highly saline waters tend to be old and stagnant as a result of density differences and low rock permeabilities that would allow mixing with more dilute waters.

Further work is needed to determine whether data exists for chloride in geologically young granites that occur more frequently in the US (i.e. post-Archean) or for granites in tectonically active regions (potentially allowing more connectivity between shallow and deep waters). A more complete survey of the major basins in the US that contain marine sediments would help determine the overall frequency and distribution of high-chloride shales in the US and to understand and identify the specific geologic environments that contain shale with high-chloride pore waters. High-chloride shales have been documented in the Michigan Basin and likely occur in both the Appalachian and Williston Basins, although to what extent is not well documented. Based on similarity of geologic environments, high-chloride shales would be expected to occur in the Permian Basin, but no data has yet been identified to support this conclusion. It would be beneficial to include the distribution of high-Cl/high salinity shale in the Regional Geology GIS database as data is added and refined. Although data is currently limited, a number of papers have been published in 2013 and 2014 (see reference list) suggesting that new data may be emerging more frequently, particularly with the focused interest in shale as oil and gas target.

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