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The influence of water/rock − water/clay interactions and mixing in the salinization processes of groundwater

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ABSTRACT

Study region: Groundwater from the Precambrian Shield rock and Pleistocene deposit aquifers in Saguenay-Lac-Saint-Jean region (> 13 000 km^2) in the province of Quebec, Canada.

Study focus: Interpretations are based on the combination of *hierarchical cluster analysis* (HCA) results, *principal component analysis* (PCA), binary plots investigations ([Na^+, Ca^{2+}, Br^-] *vs.* Cl^-; Ca^{2+} *vs.* HCO_3^-; Ca^{2+} *vs.* Na^+) and Piper diagram investigations. The HCA and PCA was applied on 321 samples to specifically enable the identification of two very distinct salinization paths that produce the brackish groundwater in the study area.

New hydrological insights for the region: The results show that each of the two salinization paths exerts a major and different influence on the chemical signature of groundwater. Groundwater present in the crystalline bedrock naturally evolve from a recharge-type groundwater (Ca-HCO_3-dominant) to a type of brackish groundwater (Ca-(Na)-Cl-dominant) due to water/rock interactions (plagioclase weathering and mixing with deep basement fluids). Groundwater evolution in confined aquifers is dominated by water/clay interactions. The term water/clay interactions was introduced in this paper to account for a combination of processes: ion exchange and/or leaching of salt water trapped in the regional aquitard. Mixing with fossil seawater might also increase the groundwater salinity. PCA revealed that Ca^{2+}, Sr^{2+}, Ba^{2+} are highly correlated with groundwater from bedrock aquifers, while Mg^{2+}, SiO_2, K^+, $SO_4^{2-}$and HCO_3^- are more representative of the regional confining conditions.

1. Introduction

Deep groundwater in crystalline basement is typically highly mineralized, as indicated by numerous studies (Edmunds et al., 1984; Frape and Fritz, 1987; Fritz et al., 1994; Gascoyne and Kamineni, 1994; Lodemann et al., 1997; Bucher and Stober, 2010). Saline to brine waters are systematically encountered deep in the crust by 1) nuclear waste disposal programs in various countries, particularly in Canada (Gascoyne et al., 1995), Sweden (Nordstrom et al., 1989), Finland (Lahermo and Lampen, 1987), and Switzerland (Pekdeger and Balderer, 1987); in continental deep drilling programs (Russia: Kola island well; Germany: KTB); and in geothermal energy programs (France: Soultz-sous-Forêts; Switzerland: Urach; U.K.: Cornwall; USA: Los Alamos). Brackish to highly saline brines have been detected at depths down to several kilometers in many mines in crystalline rocks, particularly in the Canadian Shield (Fritz and Frape, 1982; Frape and Fritz, 1987) and in oil field sedimentary basins around the world (Fyfe et al., 1978; Kharaka

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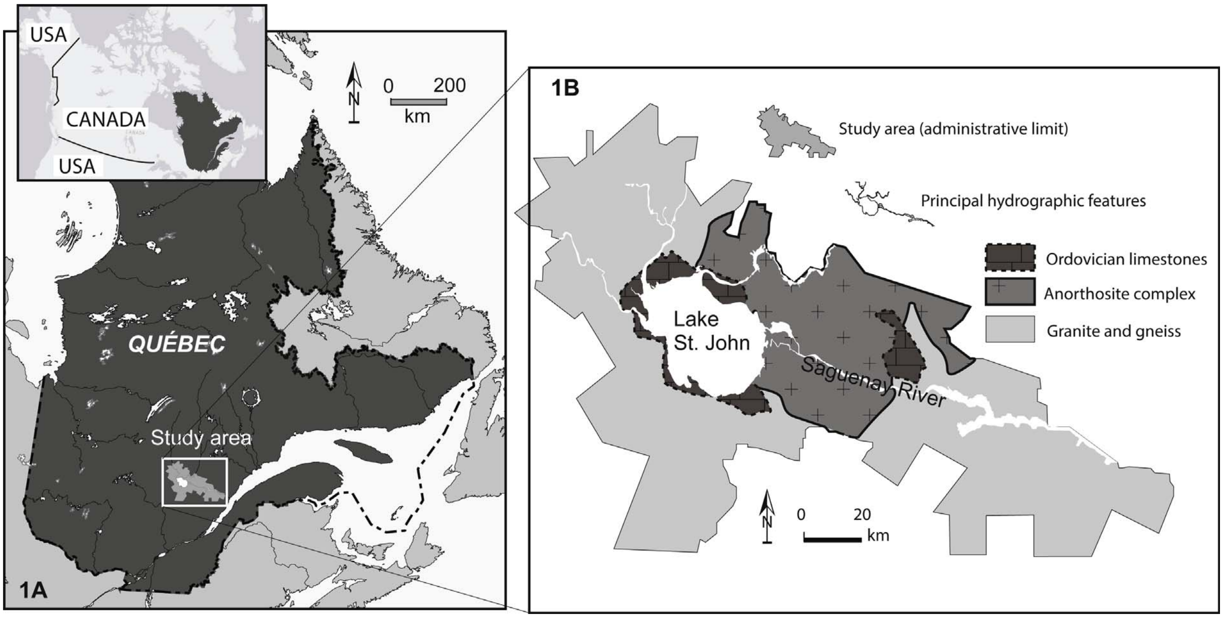

Fig. 1. A. Location of the study area and B, conceptual model of the geological features (adapted from CERM-PACES, 2013).

and Hanor, 2003). Overall, the water from basement rocks is systematically contaminated with brines at depths of less than 5 km (Pauwels et al., 1993; Bucher and Stober, 2010).

New chemical and isotopic data have yielded several hypotheses to explain the occurrence of saline groundwater deep in the crust. Total dissolved solids (TDS) generally increase with depth, and chlorides are the common salts. According to Bucher and Stober (2010), this chlorinity probably has a common global source because it is present at depth in all continental basement units worldwide. The main theories about the origins of the brines in Precambrian Shields include: 1) modified Paleozoic seawater (Bottomley et al., 1994) or basinal brines (Guha and Kanwar, 1987); 2) leaching of saline fluid inclusions in crystalline rocks (Nordstrom and Olsson, 1987); and 3) intense water/rock interactions (Frape and Fritz, 1987; Gascoyne et al., 1987; Kamineni, 1987; Bucher and Stober, 2010). More recently, studies on glaciation effects have demonstrated that glacial meltwater infiltrating bedrock aquifers has a major impact on groundwater chemistry (Lemieux et al., 2008; Aquilina et al., 2015; McIntosh et al., 2011). Clearly, a combination of several different physicochemical processes rather than a single process appears responsible for the generation of basement water (Douglas et al., 2000; Frape et al., 2003; Bucher et al., 2012). Studies of the origin and evolution of fluids in crystalline rocks are ongoing and are constantly being supplemented by new data contrasting geochemical conditions at different study sites.

Brackish groundwater have been identified at shallow depths ($<$ 100 m) in fractured rock aquifers and in Pleistocene granular aquifers in the Saguenay-Lac-Saint-Jean region (SLSJ) in the province of Quebec, Canada (Fig. 1) by Dessureault (1975) and Walter (2010). In the study area, bedrock mainly consists of a variety of igneous and metamorphic Precambrian Shield rocks and some Ordovician remnants of several units of sedimentary rocks (shale, limestone and siltstone). The rocks of the basement are cut by a Phanerozoic faulted graben that defines the limits between the highlands and lowlands. Based on the specific morphology of the graben in the SLSJ region, a discharging regional gravity-driven flow system according to the Tóth model (Tóth, 1999) would explain the natural contamination by salt of lower fresh groundwater systems in the lowlands (Walter, 2010). The lowlands are covered by highly heterogeneous surficial Pleistocene deposits that include a semi-continuous regional aquitard of marine origin left behind by the retreat of seawater approximately 10,000 years ago (Lasalle and Tremblay,1978). The leaching of trapped salt in the regional marine clay confining layer would explain the presence of brackish groundwater in some confined Pleistocene aquifers in the SLSJ region (Dessureault, 1975).

Groundwater quality has major implications for drinking water and other groundwater uses, such as agriculture and manufacturing. The SLSJ region is a perfect laboratory field for testing the hypotheses of groundwater salinization for the following reasons: 1) a large hydrogeological database, including hydrogeochemical data, covering the entire region is available; 2) the graben topography implies that all surficial waters are drained toward the lowlands, thus defining a single watershed; 3) various aquifer types are known.

This study is based on a regional-scale dataset of 321 samples. The initial purpose of the sampling was to characterize the groundwater quality and the possible exposition of the local population to natural and/or anthropic contaminants (CERM-PACES, 2013). Therefore, sampling was conducted on existing private wells, usually used for drinking water supply. The physical characteristics of the sampling wells (location of the well screen, geology of the aquifer, casing depth) are poorly documented. Based on this regional database, this paper is a first attempt to statistically characterize groundwater chemistry in the SLSJ region with the goal of deciphering the possible geochemical evolution of groundwater controlled by the process of salinization. Another objective is to