Time scales of regional circulation of saline fluids in continental crystalline rock aquifers (Armorican massif, Western France)

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ABSTRACT

In recent decades, saline fluids have been sampled worldwide at great depths in continental basements. Although some of them have been attributed to marine transgressions the mechanisms allowing their circulation is not understood. In this paper, we describe the horizontal and vertical distribution of moderately saline fluids (60 to 1400mg/l) sampled at depths ranging from 41m to 200m in crystalline rock aquifers at the regional scale of the Armorican Massif (northwestern France). The horizontal and vertical distributions of high chloride concentrations are in good agreement with both the altitudinal and vertical limits and succession of the three major transgressions between the Mio-Pliocene and Pleistocene ages. The mean chloride concentration for each transgression area is exponentially related to the time spanned until present. It defines the potential laws of leaching (displacement) of marine waters by fresh meteoric waters. The results of the Armorican aquifers provide the first observed constraints for the time scales of seawater circulation in the continental crystalline basement and the subsequent leaching by fresh meteoric waters. The general trend of increasing chloride concentration with depth and the time frame for the flushing process provide useful information to develop conceptual models of the paleo-functionning of Armorican aquifers.

Keywords: Saline fluids, crystalline basement, groundwaters, paleohydrogeology, geologic time scale, climatic events.

Highlights:

- **The Armorican massif presents clear evidences of a marine origin of the saline component in the fluids at the regional scale.**
- **High chloride concentrations are attributed to three past marine transgressions.**
- **Saline fluids provide constraints for the time scales of fluid circulation.**
- **The general trend of increasing chloride concentration with depth supports the seawater introduction by gravity-driven flow at depth in the basement.**
- **The time frame for the flushing process is useful information to develop conceptual models of the paleo-functioning of Armorican aquifers.**

1. INTRODUCTION

In recent decades, saline fluids have been sampled at great depths (0.5 - 5 km) in continental basements (Bucher and Stober, 2010; Frape et al., 2003). In several places, these fluids have been considered as old seawater introduced in aquifers during marine transgressions (Aquilina and Dreuzy, 2011; Beaucaire et al., 1999; Bottomley et al., 1994, 1999; Douglas et al., 2000; Greene et al., 2008; Louvat et al., 1999; Négrel and Casanova, 2005). Two alternative origins related either to glacial recharge of brines due to cryogenic mechanisms (Starinsky and Katz, 2003), or to anthropogenic sources (Kelly et al., 2008; Mullaney et al., 2009; Panno et al., 2006; Perera et al., 2013) have also been proposed. These three hypotheses have led to extremely different estimates of the saline fluid residence time (Devonian or Pleistocene for the Canadian brines, for example) and thus of the paleohydrogeology of the continental aquifers. Although thorough investigations have been carried out in several places, the origin and fate of the salinity are still issues. We have almost no field observations identifying the potential mechanisms leading to marine fluid introduction and conservation in hard rock aquifers, as well as the influence of glacial recharge at various depths in these aquifers remain. Furthermore, the time-scales of these mechanisms are unknown.

In this study, we investigated the effects of marine transgressions in the spatial (both horizontal and vertical) distribution of chloride concentrations at a regional scale. Since the transgression characteristics differ from one event to another, we expect to find higher concentrations in the areas flooded by the later. The decrease of chloride concentrations with time potentially provides constraints for fluid circulation time-scales in the basement. This concept is based on the fact that during transgression, a large amount of chlorides was introduced in flooded areas. Secondly, the chloride concentration of the submerged area decreases under the influence of dilution/leaching by meteoric waters. Thus, the decline in chloride concentration since the time of the last transgression is characteristic of the dilution/leaching efficiency. This makes it important to identify the last transgression that has flooded the considered area.

The study focuses on the Armorican basement (western France), where several authors have reported evidence of saline fluids (Ayraud et al., 2008; Pauwels et al., 2010). Three main transgressions were recorded during Mio-Pliocene to Pleistocene times, the latest being the highest. This is a particularly favorable context since a large part of the area flooded by the oldest and highest transgression remains unaffected by later transgression events.

2. GEOLOGICAL BACKGROUND

The Armorican basement extends over an area of 68,500 km² in the northwestern part of France. The Armorican massif is a crystalline basement localized between the English Channel and the Bay of Biscay. The northern part corresponds to the Cadomian orogenic belt (Chantraine et al., 2001). The central and southern zones belong to the European Variscan belt (Le Corre et al., 1991). The Armorican massif is a basement made of Upper Proterozoic to Paleozoic formations mainly composed of low and high metamorphic rocks (schists, sandstones and gneisses…), plutonic (granite) and volcanic (basalt) rocks deformed during the two orogenies (Cadomian and Variscan) (Fig. 1). These orogenies have initially developed the main tectonic structures of the Armorican massif: the North and the South Armorican Shear Zones (NASZ and SASZ, respectively), and the Quessoy/Nort-sur-Erdre Fault (Bonnet et al., 2000) (Fig. 1). These structures have been reactivated during Mesozoic and Cenozoic periods. Tertiary and quaternary geodynamic evolution of the Armorican massif are related to the collision between Europe and Africa (Brault, 2002; Gros and Limasset, 1984; Ziegler, 1990). This evolution mainly consists in three major steps (Thomas, 1999): (1) From the end of Cretaceous to the upper Eocene, the Armorican massif is subjected to a lithospheric buckling due to the Pyrenean compression. (2) From the upper Eocene to Oligocene the buckling decreases and the geodynamic evolution is driven by a generalized extension. (3) From the Mio-Pliocene to present days, the Armorican massif is uplifted due to a lithospheric buckling in relation with the Alpine compression. This compression is still active as observed through the Armorican massif seismic activity (Lenôtre et al., 1999; Nicolas et al., 1990). Local topography is controlled by rock lithologies and, on a larger scale, by tectonic faults (Northern and southern shear zones (Dugué, 2007; Gumiaux et al., 2004)). It is relatively moderate with three domains of higher elevation above 200m and a maximum elevation of 416m in the east (Fig. 2).

3. HYDROGEOLOGICAL SETTING

The main groundwater flow in crystalline rock aquifers is considered to be localized in superficial formations resulting mainly from rock weathering, and below in fracture and major geologic discontinuities networks (Larsson, 1987; Stober and Bucher, 2007; Wyns et al., 2004). The compartmentalized structure includes various reservoir scales and characteristic physical parameters (permeability, porosity…) varying over several orders of magnitude (Clauser, 1992). At the scale of the Armorican massif a weathered layer 20 to 30m thick is present in many places, and likely ubiquitously (Brault, 2002; Dewandel et al., 2006). Roques (2013) has studied the influence of fault zones for sites characterized by high groundwater yields at the scale of the Armorican massif. At this scale, groundwater resources in the shallower part (<20m) are widespread but limited in term of productivity. Conversely, high groundwater productivities are associated to fault zones below the weathered zone. Indeed, groundwater resources at significant depth have been found in the Armorican bedrock (Le Borgne et al., 2006; Leray et al., 2013; Roques et al., 2014) and it can be considered that the fractured system constitutes a water reservoir in the continental basement. Free groundwater circulation in crystalline environments has been reported from several studies

(Banks et al., 1996; Larsson, 1987). Several studies have shown that basement is generally characterized by an interconnected fracture system at several km depth (Aquilina and Dreuzy, 2011; Edmunds and Savage, 1991; Stober et al., 2002). Hydrodynamic properties of crystalline rock aquifers of the Armorican basement have been intensively investigated in several research sites (Ploemeur and St-Brice-en-Cogles sites, Fig. 2) (Le Borgne et al., 2004, 2006; Dorn et al., 2012; Leray et al., 2013; Roques, 2013; Roques et al., 2014; Touchard, 1999) (Fig. 2). Moreover, previous studies in the Armorican basement have identified a compartmentalization of these crystalline rock aquifers from hydrological, geochemical, geological and geophysical data (Ayraud et al., 2008; Roques, 2013; Roques et al., 2014), and from regional-scale numerical modeling (Goderniaux et al., 2013). Geochemical studies also showed specific chemical compositions of the water in the deep fractured aquifer, potentially including saline groundwaters (Aquilina et al., 2013; Ayraud et al., 2008; Pauwels et al., 2013).

4. CHLORIDE DATABASE

The quantity supplied and the quality of the main groundwater resources in the Armorican massif are monitored through a public well network (ADES: “banque nationale d’Accès aux Données sur les Eaux Souterraines”, National database for groundwater resources, http://www.ades.eaufrance.fr/). For most of these wells hydrogeological informations (geographical location, altitude, depth, drilling log, borehole parameters, water inflow points, etc…) are available through a second public database of drillings (BSS: “Base de données du Sous-Sol”, http://infoterre.brgm.fr/). The precise location of water inflows is not described for each well, and it has been considered that the water inflow corresponds to the base of the well. This assumption is valid taking into account the drilling goal which is to stop the well drilling when a sufficient water inflow is found.

The network of wells investigated covers the whole Armorican basement and includes more than 1800 drillings with an average depth of approximately 40m. Chemical records, such as chloride or nitrate concentrations, are available for each drilling. We first preprocessed the database of 1874 chloride measurements and removed wells that are potentially not representative of natural chloride concentrations. We removed wells close to a potential anthropic pollution source (industrial estate, garbage dump, mill pond…), and wells with a large variability through time (large standard deviation of chloride concentration higher than 30%). We also did not consider the wells at a distance less than one kilometer from the current coastline, whose concentration may be directly influenced by current saltwater intrusion. 716 of the 1874 wells have been excluded from the database, i.e. 38% of the total. The vertical distribution of the chloride concentrations for the remaining values was analyzed by intervals of 10m from an altitude of 350m above sea level to -125m. The average chloride concentration and the 90th percentile were calculated for each 10m interval.

5. MARINE TRANSGRESSION CHARACTERISTICS

Chlorides of marine origin that are not brought by rainfall (i.e. concentrations higher than 40 mg.l^{-1}) are likely related to marine transgressions that flooded the Armorican massif from times to times. The likely scenario is that a fairly large amount of chlorides is injected during each transgression in submerged regions, and that the salt concentration decreases from the end of the transgression event due to dilution or leaching by meteoric waters. If the leaching/dilution is efficient enough, for instance if the time lag between two successive transgressions is larger than the leaching time, the system is fully reset by the last event (i.e. the amount of chloride injected during the last event is much larger than the residual of formers). The objective of this part is to characterize the last transgressions that have flooded the Armorican massif.

According to stratigraphic record studies in the Armorican Massif and, to the eustatic sea-level fluctuations (Hardenbol et al., 1998), three main transgressions can be identified since the Mio-Pliocene. The oldest of Messinian age has been identified in several places (Néraudeau et al., 2003; Van Vliet-Lanoe et al., 1998), and dated between 6 and 4.6 Myr by several methods (ESR: Electron Spin Resonance Spectroscopy on quartz, $^{87}Sr/^{86}Sr$ on shells and bones in "Redonian" shelly sands or "Faluns" (Mercier et al., 2000; Néraudeau et al., 2002). These sediments would attest of the maximum transgression of the late Neogene in northwestern France (Néraudeau et al., 2010). This transgression corresponds to a high sea level of +90m according to Hardenbol et al., (1998). The second transgression is mostly characterized by the deposition of clays, which contains few bioclastic constituents (Morzadec-Kerfourn, 1997, 1977). The so-called Redon clays formation are dated as Pliocene: Piacenzian (Reuverian, ~2.7+/-0.3 Myr) from a pollen analysis (Morzadec-Kerfourn, 1982, 1997). The corresponding sea level is around +60m according to the chart (Hardenbol et al., 1998). The last known transgression in the area is characterized by clay deposits that cover the Redon clays (Morzadec-Kerfourn, 1997). According to pollen analysis of the Lanrinou clay at Landerneau (Morzadec-Kerfourn, 1982, 1997), these sediments can be correlated with the lower Pleistocene around 1.6-2 Myr (Gelasian/Calabrian). The corresponding event coincide with the high sea-level stand of +30m (Hardenbol et al., 1998).

Thus, at least three marine transgressions, with three different paleocoastlines, must be considered for the Armorican massif: the oldest, which is also the highest, is Mio-Pliocene: Messinian (~5.3+/-0.8 Myr) with sea level +90m asl, the second is Pliocene: Reuverian (~2.7+/-0.3 Myr) with sea level +60m asl; and the most recent is Pleistocene: Gelasian/Calabrian (~1.8+/-0.2 Myr) with sea level +30m asl.

Using local studies on the large-scale relief development and the paleotopographic evolution of the Armorican basement (Bonnet et al., 1998, 2000; Brault et al., 2004; Guillocheau et al.,

2003; Lague et al., 2000; Lenôtre et al., 1999; Morzadec-Kerfourn, 1997; Van Vliet-Lanoe et al., 1998), a paleotopography was reconstructed for the whole area.
Globally, the topography evolution is the result of tectonic movements, climate and eustatic variations since the Mio-Pliocene. The modern topography is characterized by incised valleys with an incision average depth of 60-100m and significant topographic variations. The onset of the current incised and dense hydrological network is probably not older than 1Myr (Bonnet et al., 1998, 2000; Lefebvre et al., 1994). This topography contrasts with the smooth planation surface of the Mio-Pliocene (Brault et al., 2004). The development of the Pleistocene topography of the Armorican massif is explained by vertical movements due to the N160 compression generated by the Alpine collision (Bonnet et al., 1998; Müller et al., 1992; Nicolas et al., 1990). This differential tectonic uplift has been estimated from geomorphological studies (Bonnet et al., 1998, 2000; Lague et al., 2000). Incision is measured using a digital elevation model analysis. A distributed field of incised quantities is produced for each individual drainage basin (Jost, 2005). Moreover, relief induced by fluvial incision partly reflects continental movements and can be used to estimate uplift. Indeed, considering that the drainage networks adjust to sea level, the induced incision has the same magnitude in different basins. Thus the difference of incision is used to estimate the relative amounts of differential uplift between basins. The estimation of differential uplift for each basin has been grouped by zone due to the regional organization. A differential tectonic uplift has been observed for the western part compared to the eastern part, along the Quessoy/Nort-sur-Erdre fault (Brault et al., 2004; Jost, 2005).

From these previous work, to reconstruct the paleotopography of the whole area, we first used a digital elevation model (DEM, 100m resolution) given by the Institut Géographique National (IGN) to generate several surfaces providing an estimation of the Pleistocene topography prior to erosion and valley incision (Bonnet et al., 1998, 2000). Within a rectangular 20 km large sliding window, either the highest point or the Q90 quantile was recorded. This process allows for the creation of a surface above the present-time topography connecting the highest points and filling the valleys. The use of the Q90 quantile provides a smoother result than the maximum which may be too influenced by isolated peaks. The generated surface does not include the unknown amount of erosion of peaks and crests and thus should be considered as a minimum. Then, the uplift (Jost, 2005) was subtracted from the preprocessed topography. Last the paleocoastlines were reconstructed for the three transgressions by comparing the reconstructed topography with the expected sea level derived from Hardenbol et al., (1998). The Messinian and Reuverian transgressions had covered a large part of the Armorican massif, except the highest elevations; the last Gelasian/Calabrian transgression had flooded areas along the current coastline, and the lowest inland parts (Fig. 3).

6. RESULTS

6.1. Origin of chlorides

Within the framework of this study, 12 sites (monitoring sites in Fig. 2) presenting moderately saline fluids (relative to the high chloride concentration) were subjected to further geochemical and isotopic analysis (only Br concentrations are presented here, see Aquilina et al., 2014). Salinities ranging from 60 to 1400mg/l were recovered at depths ranging from 41m to 200m, except for the Cinergy drilling project where water was collected at a depth below 450m in fractured schist, with a chloride concentration of 1240mg/l.

The chloride to bromide relationships is presented in Fig. 4 for the 12 sites investigated geochemically. The chloride concentration is linearly correlated with bromide along the rainfall-seawater mixing line (Fig. 4). This strongly suggests that the saline fluids in the Armorican basement are of marine origin and correspond to paleoseawater diluted by meteoric waters (Bottomley et al., 1994; Casanova et al., 2001; Frape et al., 1984; Fritz, 1997; Gascoyne and Kamineni, 1994; Nordstrom et al., 1989).

Chloride has three potential sources: (1) (paleo)seawater, (2) rainfall potentially concentrated by evapotranspiration processes, and (3) anthropogenic sources (agricultural fertilizers such as KCl, pig slurry and cattle manure). If we exclude a 1-km band across the coastline, the meteoric waters in Brittany have a maximum mean chloride concentration of 10-18mg.l^{-1} with a relatively low variation range (Ayraud et al., 2008; Martin et al., 2004). Evapotranspiration in Brittany represents about 50-60% of the total precipitation, and cannot provide chloride concentrations in recharge water higher than 40 mg.l^{-1} (Ayraud et al., 2008). Agricultural pollutions may increase the concentrations to 50mg.l^{-1} in the most intensively farmed areas (Martin et al., 2004). Thus these two processes cannot explain the very high concentrations observed. Furthermore a negative correlation between nitrate and altitude has been observed. Above 100m, the nitrate concentration is almost constant and below 100m the nitrate concentration decreases with depth. This negative correlation between nitrate and altitude clearly as well as gas groundwater dating (Ayraud et al., 2008) indicates that below this depth the anthropogenic influence decreases. These results underline that the anthropogenic sources are more related to shallow aquifers, contrary to deep saline fluids. Many other sources of chloride exist (as evaporitic deposits of geological formation…). But the relationships between chloride and bromide will be completely different for evaporated brines or evaporite leaching.

Thus, chloride concentrations are clearly out of the potential range of modern waters even including anthropogenic sources. The correlation between bromide and chloride (Fig. 4) supports a marine origin for these groundwater (Bottomley et al., 1994; Carpenter, 1978; Freeman, 2007). The simplest mechanism which explains the high chloride concentration observed is a marine component related to the last transgressions.

6.2. Spatial and vertical distributions of chloride

The chloride distribution presented in Fig. 5 shows the altitudinal limits of the last three major transgressions between the Mio-Pliocene and the Pleistocene (Messinian ~5.3 Myr, Piacenzian ~2.7 Myr and Gelasian-Calabrian ~1.8 Myr). These limits correspond to 90, 60 and 30m, respectively. This map shows relatively high chloride concentrations (60 to 1400mg/L) around the current coastline and in a few large domains whose current topography is clearly above sea level. Only three zones present chloride concentrations below 40mg/L. These zones correspond to the three domains of higher elevation above 200m and to the area above the higher Messinian paleocoastline altitude of +90m asl. Fig. 6 shows the vertical distribution of chloride concentrations according to the altitude of the base of the well. Above 100m, the chloride concentration is almost constant, increasing only slightly with depth, the values ranging from 10 to 40mg/l. Below 100m, some drastic changes in the chloride-depth trends are observed. The main one is apparent at approximately 70m, with chloride concentrations up to 200 $mg.l^{-1}$ observed below this depth. The chloride concentrations below 70m increase strongly with depth (approximately $0.5mg.l^{-1}.m^{-1}$ for the average and more than $1mg.l^{-1}.m^{-1}$ for the 90^{th} percentile). This trend contrasts with the almost constant chloride concentrations in the areas not affected by past marine transgressions.

The distribution of chloride concentrations is in good agreement with the paleocoastlines (Fig. 5). The increase of chloride concentration with depth (Fig. 6) also supports this correlation. The vertical distribution of chloride concentrations likely indicates that, during each of the last transgressions, seawater was introduced by gravity-driven flow at great depth in the basement, and has only partially been flushed by meteoric waters.

6.3. The chloride releasing rate

The three paleocoastlines of past marine transgressions can be used to define four spatially distinct domains in the Armorican massif: three of them correspond to places where either the

Messinian, Reuverian and Gelasian/Calabrian transgressions is the last marine event that covered them; the fourth is the domain that was not flooded Fig. 5. The average chloride concentration for each area has been calculated and attributed to the age of the latest marine transgression. Fig. 7 shows that the average chloride concentration for each area is inversely related to the time elapsed since the last corresponding marine transgression.

This relationship shown in Fig. 7 can be fitted by a simple exponential function of the general form:

$$\boldsymbol{c} = \boldsymbol{c_{in}}\,\mathbf{exp} - \frac{t_e}{\boldsymbol{\tau}} + \boldsymbol{c_o}, \qquad (1)$$

where *c* is the current chloride concentration, $\boldsymbol{t_e}$ is the age of the last transgression event, $\boldsymbol{\tau}$ a characteristic time scale, $\boldsymbol{c_o}$ a background concentration, and $\boldsymbol{c_{in}}$ an additional concentration injected at the time *t*. Equation (1) is the solution of the differential equation:

$$\frac{\mathbf{d}\boldsymbol{c}}{\mathbf{d}\boldsymbol{t}} = -\frac{(c - c_o)}{\boldsymbol{\tau}} + \boldsymbol{c_{in}}\boldsymbol{\delta}(\mathbf{t_e}), \qquad (2)$$

$\delta(t)$, the delta function, simulates quasi-instantaneous injection of chlorides at transgression times. The background chloride concentration $\boldsymbol{c_o}$ can be measured in places not influenced by past marine transgression; it is estimated to $21.5 \pm 0.3\mathrm{mg.l^{-1}}$. The regression fit leads to a time constant τ of 2.3 ± 0.1 Myr, and an injected concentration of $100 \pm 14\ \mathrm{mg.l^{-1}}$. The range errors for τ and c_{in} are calculated from the two regression fits generated from the errors on the dating methods used for each characteristic sediments and from the standard deviations of the current chloride concentration of each area. The envelope provided by the two regression fits shows the sensitivity of the parameters according to the standard errors. This residence-time order of magnitude is consistent with the residence time of several million years suggested by (Thury et al., 1994) for deep water as well as several studies supporting long residence times required by "fossil" seawater (Stober and Bucher, 1999). It can be noticed that these studies of fluids containing a paleoseawater end-member have chloride concentrations with an order of magnitude similar to those presented here.

7. DISCUSSION

7.1. General trend of increasing salinities with depth

The main results of this paper present clear evidences on the origin and the age of saline fluids in the continental crust at the scale of the Armorican massif. We report the vertical distribution of chloride concentration which presents a concentration increase with depth at the Armorican massif scale. Such a trend has already been observed in several places throughout the world in continental crust.

Highly saline brines have been found in various geological environments in the Canadian Shield (Frape et al., 1984; Fritz and Frape, 1982; Gascoyne and Kamineni, 1994), in the crystalline basement of Europe (Black Forest in Germany, Soultz-sous-forêt in France) (Aquilina et al., 1997; Pauwels et al., 1993; Stober and Bucher, 1999), in the Fennoscandian shield (Fritz, 1997; Nordstrom et al., 1989) and in the England Carnmenellis Granite (Edmunds et al., 1985). Saline fluids sampled in these sites report a wide range of chloride concentrations. At the surface, chloride concentration ranges from around ten to hundred mg/L, at much greater depth around 500m concentration values are between one hundred to thousands mg/L and below 1km depth concentrations range from hundreds to tens of thousands mg/L.

For all these sites chloride concentration have been analyzed by intervals of depth where the average chloride concentration is calculated in order to define the concentration gradient until approximately 1km of depth (Fig. 8). The Armorican data are also plotted on this graph (Fig. 8). All the studies show a general increase of salinity with depth. In the first three hundred meters a high gradient of salinity is observed and between 350 and about 700m, another gradient is observed. Below this depth, a stabilization seems to be observed although there are relatively few data (Fig. 8). However the main difference between all studies relies in chloride concentrations of groundwater samples at shallow depths. In fact, chloride concentration can vary by one order of magnitude, with concentrations around ten to hundred mg/L, as for the Armorican basement and the Canadian Shields, respectively (Fig. 8).

Previous studies (Aquilina et al., 1997; Edmunds et al., 1985; Frape et al., 1984; Fritz and Frape, 1982; Fritz, 1997; Gascoyne and Kamineni, 1994; Nordstrom et al., 1989; Pauwels et al., 1993; Stober and Bucher, 1999) have been realized in the framework of nuclear repository, geothermal or scientific programs with the aim to investigate the deep continental crust at depths ranging from several hundred meters to several kilometers. In this study we made a synthesis of a large number of wells in a much shallower part of the crystalline basement (41 to 200m). Despite the different purposes, we report similarities, specifically the distribution of chloride with depth which suggests common hydrogeological mechanisms. The salinity gradient from surface to greater depth and the smoothing of the evolution below a certain depth suggest two hydrodynamic behaviors. Such information can be useful to develop conceptual models of basement aquifers functioning. In addition, in this study we provide a time frame constraint of these processes in order to contribute to a better understanding.

7.2. Chloride releasing rate

Fig. 7 shows that the relationship between concentration and transgression age can be fitted by a decreasing exponential function, whose parameters give three different characteristics: the background concentration $\boldsymbol{c_o}$ which can be independently evaluated in places that have not been flooded by marine transgressions, $\boldsymbol{c_{in}}$ the additional concentration injected in the system during a transgression, and $\boldsymbol{\tau}$ the “dilution” time scale. Note that even if the choice of the exponential function is rather arbitrary considering the small number of constraints, both $\boldsymbol{c_{in}}$, the curve extrapolation for an event of age 0, and $\boldsymbol{\tau}$, the time to achieve a significant decrease, are rather well determined. However, it is also important to note that situation where three areas have been submerged successively by marine transgressions is exceptional. Even if, the three field-base data points makes for a weak fit, the contribution provides on the saline fluids residence time is clearly better than all previous studies and consequently constitutes a strong constraint. According to the fitting values, the average chloride concentration likely increased by about 100mg.l^{-1} after each transgression. This is a rather low value compared to the seawater concentration of ~19 g.l^{-1}, which indicates that the original seawater has replaced only part of the freshwater initially present. During transgression, mechanism drives the displacement of former fresh groundwater by seawater, but this process enables the saline fluid circulation at great depth in fractured aquifers through the most permeable structures. Nevertheless, all scales of porosity containing former fresh water are not directly influenced. The presence of saline fluid in all scales of porosity requires the diffusion of saline fluid on long term. Thus, the former fresh water already presents has a great contribution on the injected concentration value and has a strong tendency to decrease the value. Then, the C_{in} value estimated in our study is related to the entire volume of the aquifer which tends to reduce the value. And, note that this value corresponds to the increase of the average chloride concentration in the sampling zone that is mostly below 100 m of the current topography. If there is a systematic increase of chloride concentration with depth, as observed in the upper section, the average will increase as well. A deeper sampling could then give higher $\boldsymbol{c_{in}}$ values. The fit also indicates that chloride flushing from the aquifers is a process requiring approximately 2.3 Myr to return to initial conditions. The leaching process time constraints the long-term hydrodynamics of Armorican aquifers but incorporates many environmental conditions specific to the Armorican massif. Indeed, the efficiency of the leaching process is influenced by numerous physical parameters and paleohydrologic conditions. One of the most important parameter is the topographic gradient controlling gravitational flow and consequently fluid migration. However, meteoric fluid migration into deeper parts of aquifer depends on the hydrostratigraphic configuration of the region. The intensity of topography driven flows is mainly controlled by geographic and climatic conditions. Changes in topographic elevation due to tectonic and erosion processes also impact the behavior of flow systems. In crystalline rock aquifers, as the Armorican basement, tectonic structures (faults and fractures) play a major role through the formation of preferential pathways. Moreover, sea level fluctuations can greatly influence topography driven fluid flow. In the case of an important sea level modification, meteoric fluids may circulate deeper and induce mixing. Thus, the characteristic residence time estimated in our study includes specific physical parameters relating to the Armorican aquifers (geometry of the geological formations, geomorphological features…) and all the changes caused by paleohydrologic conditions since the seawater introduction (tectonic, erosion, sea-level fluctuations, climate changes…). While taking account of the specified points and despite uncertainties on paleocoastlines and the exponential function arbitrarily chosen, the essential point is the clear evidence of past marine transgression during the last millions years and thus leaching processes being active during a similar duration. We use these characteristic time of hydrodynamic processes to constraint the conceptualization of basement aquifers functioning in the two next sections.

7.3. Conceptualization of Armorican aquifers paleohydrogeology

The Armorican massif presents clear evidences of a marine origin of the saline component in the fluids at the massif scale. During marine transgression, seawater was introduced into the basement by density-driven flow. This mechanism induced the displacement of former fresh groundwater by seawater. Then due to diffusion process taking place on million year (according to the time since transgression) the diffusion length scale (few hundred meters) leads to a perfect mixing between marine waters and freshwaters already present in the whole rock porosity. Third, following transgression, the marine signature contained in the system is flushed out by groundwater circulations fed by meteoric waters. The preservation of marine signature throughout the Armorican basement and the clear increase with depth support the seawater introduction by gravity-driven flow at depth in the basement followed by a flushing phase with limited downward fresh groundwater circulation loops. The flushing process leads to the displacement of marine waters in the upper part of Armorican aquifers. The limited depth of groundwater circulations is explained by the dense hydrological network, the high sea-level and the low topography relief within the Armorican massif. Moreover, the chloride releasing rate provides a time frame for the flushing process which has been estimated in the order (of magnitude) of a few million years.

Such information can be used to develop conceptual models of the paleo-functioning of Armorican aquifers. The objective of this section is thus to propose conceptual models that may account for the chloride increase with depth on one hand and for the chloride concentration increase fit with time presented above.

The crystalline basement of the Armorican massif presents aquifers with a high transmissivity associated to fault zones (Roques et al., 2014). Considering the current topography of the Armorican massif including three domains of higher elevation above 200m, the groundwater flow system is driven gravitationally which leads to both local and regional circulation loops (Toth, 1963). Considering the modern situation and constraints provided by the distribution of chloride discussed previously, two main possibilities may explain the distribution of saline fluids in Armorican aquifers.

7.3.1. First conceptual model: Perfectly mixed aquifer

First, the crystalline rock aquifers are considered as a perfectly mixed reactor where the time constant of millions of years is also the residence time of chlorides in the system. The chloride contained in the system is slowly flushed out by freshwater under the influence of topography-driven groundwater flow (Toth, 1963). This model requires that chlorides are located in a compartment of the groundwater system whose recharge is far lower than the current recharge rate (around 200 $mm.yr^{-1}$) at the top boundary of the system (see Appendix A). This does not necessarily means that this conceptual model is not consistent with data. On the contrary, it seems consistent with the flow partitioning between local and regional flow systems initially presented (Toth, 1963) and precised more recently (Cardenas, 2007; Goderniaux et al., 2013). The characteristics of the partitioning between shallow aquifers and deep aquifers have been studied using the topography of Brittany and assuming a constant permeability with depth (Goderniaux et al., 2013). This study shows four interesting results about the partitioning between shallow (short circulations related to first-order basins) and deep (more regional circulations) aquifers: i) the "deep" compartment can be quite shallow depending on local topography characteristics; ii) the residence time of particles is well fitted by an exponential function, which means that the concentration flushing should behave similarly; iii) the partitioning depends on the total recharge; (iv) the recharge flow in the deep aquifer is 2-5 times smaller than the total recharge. These recharge values are not small enough to explain the 2.3 Myr residence time observed for chlorides, which could mean either that the first model is inconsistent with data, or that the assumption of Goderniaux et al., (2013) is unrealistic. A permeability decrease with depth, may observed in the continental crust with a likely factor of 100 within the first kilometer (Ingebritsen and Manning, 1999; Saar and Manga, 2004; Stober and Bucher, 2007). Such decrease could account for a much smaller recharge of the deep groundwater system and thereby a flushing process less efficient. Through modeling is ongoing to further test this hypothesis.

7.3.2. Second conceptual model: Deep reservoir

In the second case, the presumption is that chlorides could be localized in a deep reservoir i.e. in the deeper part of the aquifer. Then chlorides would be leached out from the aquifer system after diffusion from the deep reservoir towards the active part of the crystalline rock aquifers where leaching is efficient. Calculations for this conceptual model (see Appendix A), lead to a "salt" layer thickness of 40m that does not seem unrealistic as regards the chloride evolution with depth observed. However this conceptual model would predict very high concentrations at depth that are not yet observed in the Armorican basement in the absence of very deep drillings. But, this could be in agreement with highly saline fluids sampled in various geological environments at great depths worldwide (Fig. 8). As in the crystalline basement of the Black Forest where Stober and Bucher (1999) suggest that the deep salt water discharges is related to the upwelling of deep water which may bring up chloride from a deep reservoir. However, it can certainly be affirmed that the salt contained in the deepest part is not solid due to the chloride to bromide relationships which excludes this possibility.

The next step of this study will be to test these two functioning hypothesis with numerical modeling in order to provide more realistic models. The objective is to provide some constraints on the saline fluid circulation at the regional scale as well as to understand if the heterogeneity and hydrodynamic conditions may induce a wide range of leaching rates which could explain the large range of chloride concentrations observed.

8. CONCLUSION

Chloride concentrations in groundwater were investigated in the Armorican basement at shallow depth (from +350 to -150masl). The high concentrations observed in some places (from 60 to 1400mg/L) are shown to originate from marine transgressions. The distributions of high chloride concentrations are in good agreement with both the altitudinal and vertical limits and succession of the three major transgressions between the Mio-Pliocene and Pleistocene ages. During each of the last transgressions, seawater was introduced by gravity-driven flow at great depth in the basement. This seawater end-member has only partially been flushed by meteoric waters (over 1 to 2 million years) between successive marine transgressions, and since the last one. Considering the paleocoastlines, three zones have been affected by the transgressions. The average chloride concentration calculated for each area is inversely related to the time elapsed since last marine transgression. This relationship between concentration and transgression age can be fitted by a decreasing exponential function which indicates that chloride flushing from the aquifers is a process requiring approximately 2 Myr. The fate of chloride is conceptualized using two main models: a dilution or leaching of a deep reservoir. Both models provide information on the history of the saline fluids in fractured aquifers. The first model requires a drastic partitioning between shallow and deep aquifers. In the second model, chlorides are supposed to be released by diffusion from a deep reservoir, leached by fresh groundwater flow and bringing up to the shallower aquifer. The model supposes a deep reservoir, which has not yet been identified in the Armorican massif, but could exist. This study thus provides important constraints on the seawater circulation in hardrock aquifers at a continental-scale area.

APPENDIX A

The objective of this section is to develop simple calculations that aim at figuring out the meaning of the data and fit presented before. We first assume that the average of chloride concentrations measured is related to the average chloride concentration in the aquifer used in the model. Because of the increase of chloride concentration with depth and because of the limited sampling depth, it is unreasonable to pretend that the average of the measurements equals the chloride average concentration in the entire aquifer. Thus, we just guess that the chloride average in the entire aquifer evolves with a similar time scale to the measured averages, which occur for instance if the depth dependency function is similar in different places. Regardless of the model, the general evolution of the chloride concentration is given by a mass balance equation of the type:

$$\frac{\mathbf{d}(\boldsymbol{V}\bar{\boldsymbol{c}})}{\mathbf{d}\boldsymbol{t}} = -\boldsymbol{Q_c} + \boldsymbol{Q_{in}} \quad (3)$$

where $\boldsymbol{V}$ is the system volume, $\bar{\boldsymbol{c}}$ the average chloride concentration in the system, Q_c the total flow at the system discharge boundary, and $\boldsymbol{Q_{in}}$ the total flow at the system recharge boundary. The "system" can be the entire aquifer or any part of it. $\boldsymbol{Q_{in}}$ represents a potential chloride inflow from the recharge boundary. If we assume a background concentration $\boldsymbol{c_o}$, $\boldsymbol{Q_{in}}$ can be written as:

$$\boldsymbol{Q_{in}} = \iint_{\boldsymbol{S_r}} \boldsymbol{r}(\boldsymbol{s}).\boldsymbol{c_o}\mathbf{d}\boldsymbol{s} = \boldsymbol{c_o}.\boldsymbol{A_r}.\bar{\boldsymbol{r}} \quad (4)$$

where $\boldsymbol{S_r}$ is the system recharge boundary, $\boldsymbol{r}(\boldsymbol{s})$ the recharge at any point *s* of the boundary, $\boldsymbol{A_r}$ the recharge boundary surface, and $\bar{\boldsymbol{r}}$ the average recharge flow.

We then define two end-member models that may explain the chloride evolution in basement aquifers.

The perfectly mixed aquifer

In the first model, the chloride contained in the deeper part of the aquifer is slowly flushed out from the system along the discharge at a rate $\boldsymbol{Q_c}$ such as:

$$\boldsymbol{Q_c} = \iint_{\boldsymbol{S_d}} \boldsymbol{q(s).c(s).\mathrm{d}s} \tag{5}$$

where $\boldsymbol{S_d}$ is the system discharge boundary, $\boldsymbol{q(s)}$ the flow discharge at any point *s* of the boundary, and $\boldsymbol{c(s)}$ the chloride concentration. In a perfectly-mixed reactor, the total concentration at the boundary is equal to the concentrations average. Even if this approximation is certainly unlikely in highly heterogeneous aquifers, we assume that the $\boldsymbol{Q_c}$ integral can be estimated from the averages of concentrations and discharge $\boldsymbol{Q_c}$ defined as:

$$\boldsymbol{Q_c = O.A_d.\bar{q}.\bar{c}} \tag{6}$$

where $\boldsymbol{\bar{q}}$ and $\boldsymbol{\bar{c}}$ are the discharge and concentration averages, respectively, and $\boldsymbol{A_d}$ is the total surface of the system discharge boundary. $\boldsymbol{O}(1)$ is a constant equal to 1 in the perfectly-mixed approximation, and whose order of magnitude is about 1 if the approximation is not rigorously exact. The water mass-balance requires that the total discharge equals the total recharge: $\boldsymbol{A_d\bar{q} = A_r\bar{r}}$. If we assume that the aquifer system is a rectangular box fed from above with a recharge $\boldsymbol{r}$, using a thickness $\boldsymbol{h = \frac{V}{A_r}}$, equation ((3) writes as a first-order kinetic equation :

$$\boldsymbol{\frac{\mathrm{d}\bar{c}}{\mathrm{d}t} = \frac{(c_o - O(1).\bar{c})}{\tau}} \tag{7}$$

with the time constant $\boldsymbol{\tau}$ equal to $\boldsymbol{\frac{h}{r}}$.

If we consider that $\boldsymbol{r}$ is of the same order as it is now in Brittany (about 200mm.yr^{-1}), given the time constant $\boldsymbol{\tau}$ of 2.3 Myr, we predict an unrealistic aquifer depth $\boldsymbol{h}$ of about 500km. Although the actual depth is not known, it is likely less than a few km and more likely about 1 km. This means that the dilution model is valid only if the recharge is at least 2 to 3 orders of magnitude less than the current rainfall.

The deep reservoir diffusion model

In the second model, we assume that chlorides are leached out from the aquifer system by diffusion from a deep layer of thickness $\boldsymbol{h'}$ without any advection. $\boldsymbol{Q_c}$ is a bit different from equation (7) because diffusion occurs i) on all the system boundaries, and ii) at a rate equal to $\boldsymbol{q(s) = D \frac{\partial c(s)}{\partial n}}$, where $\boldsymbol{n}$ is the direction perpendicular to the system boundary. It is not easy to estimate simply $\boldsymbol{q(s)}$. We assume that the concentration gradient establishes in a length scale of the order of the smallest aquifer dimension $\boldsymbol{h'}$, which is a reasonable assumption if the aquifer thickness is small compared to its horizontal extent $\boldsymbol{Q_c}$is defined as :

$$\boldsymbol{Q_c = O'.A.D.\frac{(\bar{c} - c_o)}{h'}} \tag{8}$$

with $\boldsymbol{O'}$ an “order-of-magnitude” constant similar to $\boldsymbol{O}$. The influx $\boldsymbol{Q_{in}}$ is now nil and the general equation writes as:

$$\boldsymbol{\frac{d\bar{c}}{dt} = \frac{(c_o - \bar{c})}{\tau'}} \tag{9}$$

with $\boldsymbol{\tau' = O'^{-1}.\frac{h'^2}{D}}$.

The molecular diffusion $\boldsymbol{D_m}$ of chloride in water is of the order of 2.10^{-9} $m^2.s^{-1}$ (Li and Gregory, 1974; Wang et al., 1953). Considering a porosity of 1%, the diffusion $\boldsymbol{D}$ of chloride is of the order of 2.10^{-11} $m^2.s^{-1}$. A time constant of 2.3 Myr is thus consistent with a salt layer thickness of about 40 m.

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FIGURE CAPTIONS

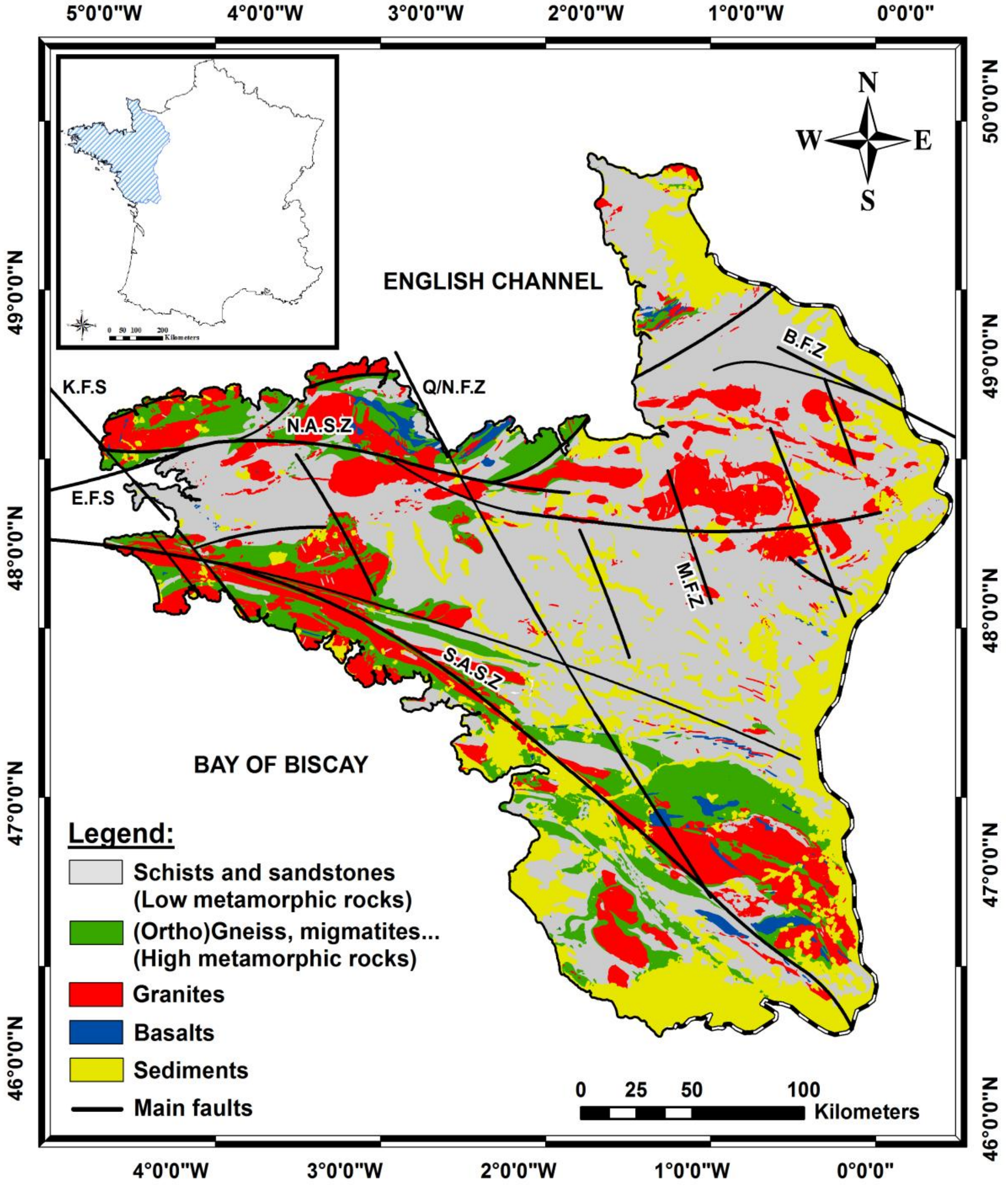

Fig. 1. Simplified geological map of the main lithological units and main geological structures of the Armorican Massif: NASZ: North Amorican Shear Zone; SASZ: South Armorican Shear Zone; Q/NFZ: Quesssoy/Nort-sur-Erdre Fault Zone; MFS: Mayenne fault System; KFS: Kerforne Fault System and EFS: Elorne Fault system (according to Bonnet et al. 2000).

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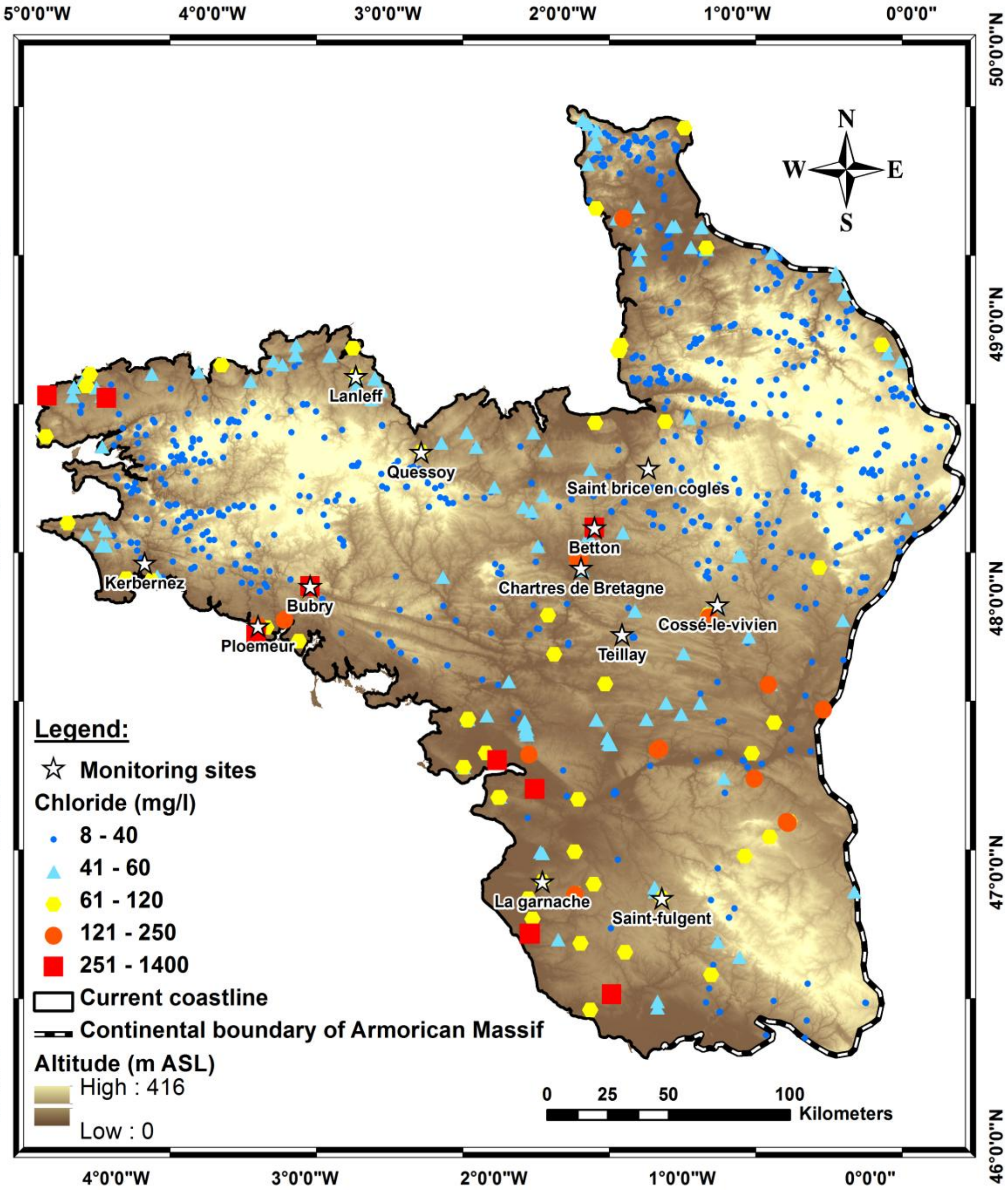

822 **Fig. 2. Map of the Armorican Massif including the distribution of chloride concentration for the whole area (from**
823 **preprocessed chloride database) and the location of the 12 sites investigated.**

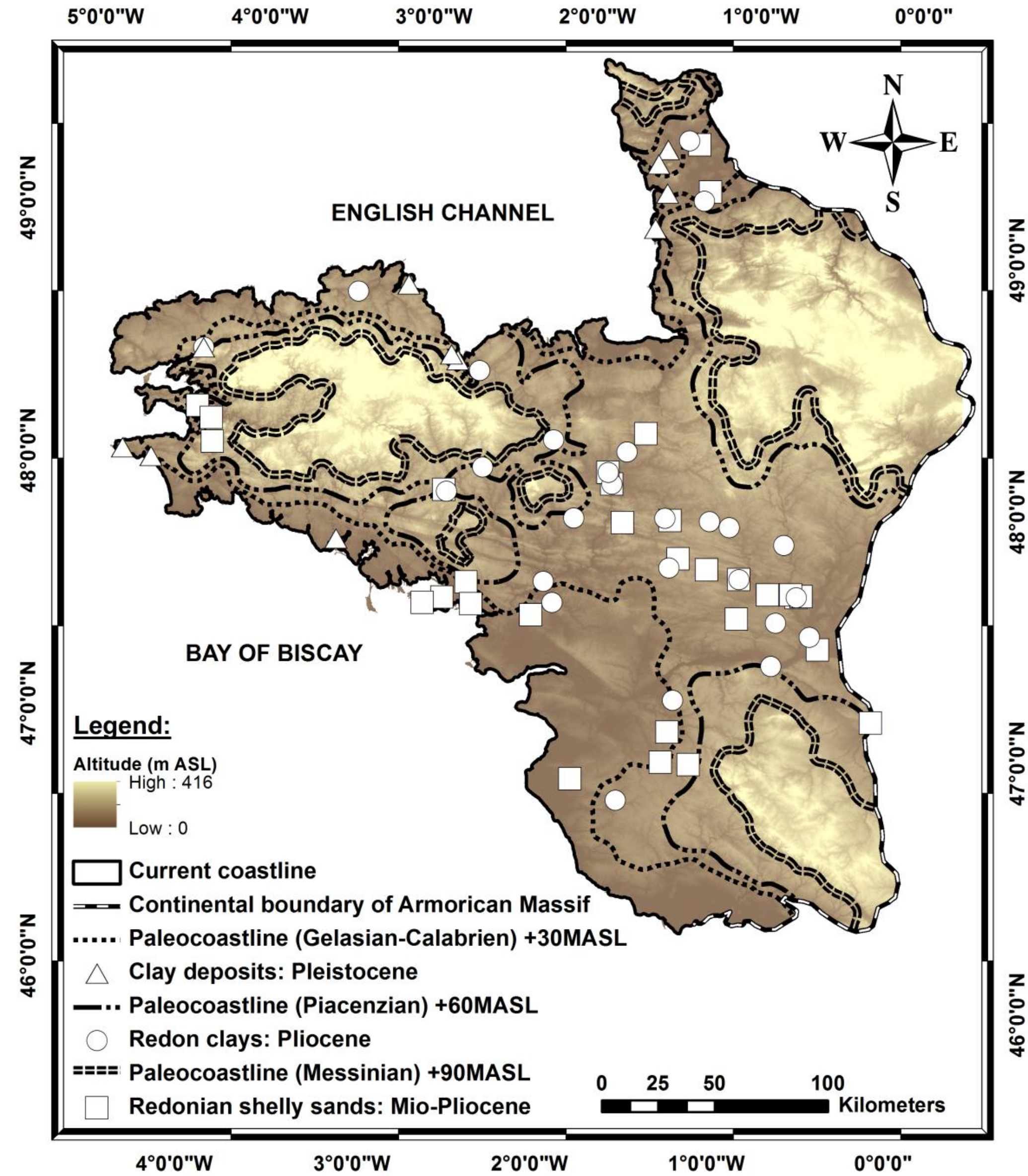

Fig. 3. Localization of paleocoastlines on the current topography for past marine transgressions since the Mio-Pliocene time and characteristic sediments associated for each flooding period.

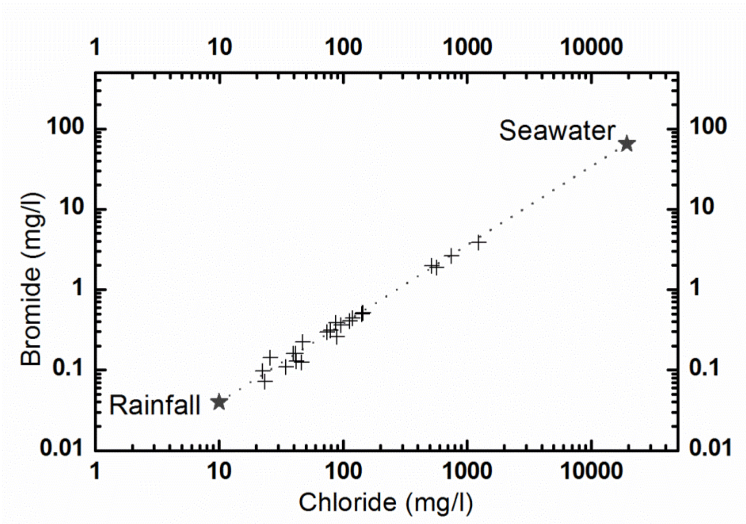

Fig. 4. Br versus Cl concentrations of groundwater in the 12 sites investigated.

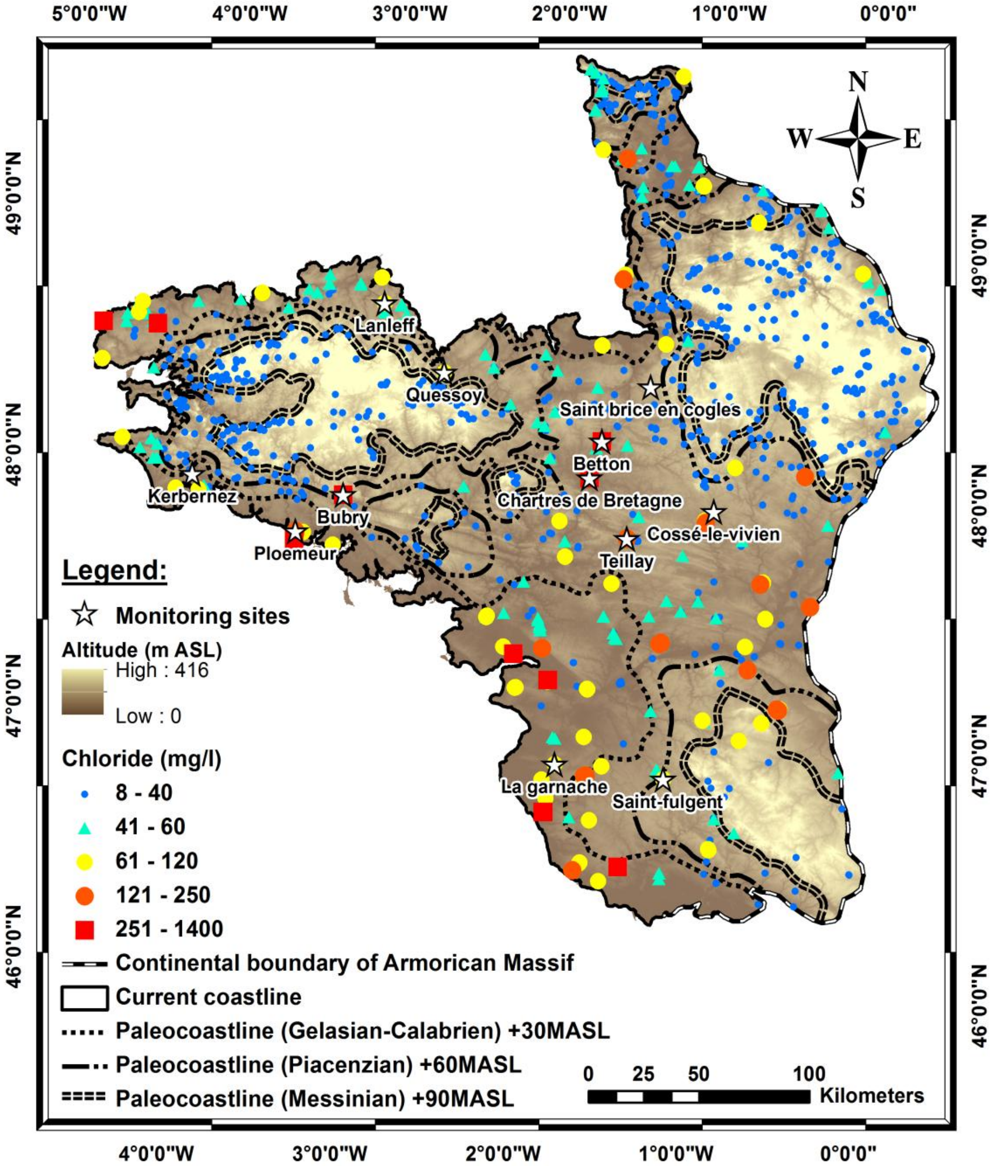

Fig. 5. Distribution of paleocoastlines on the current topography for the three transgressions.

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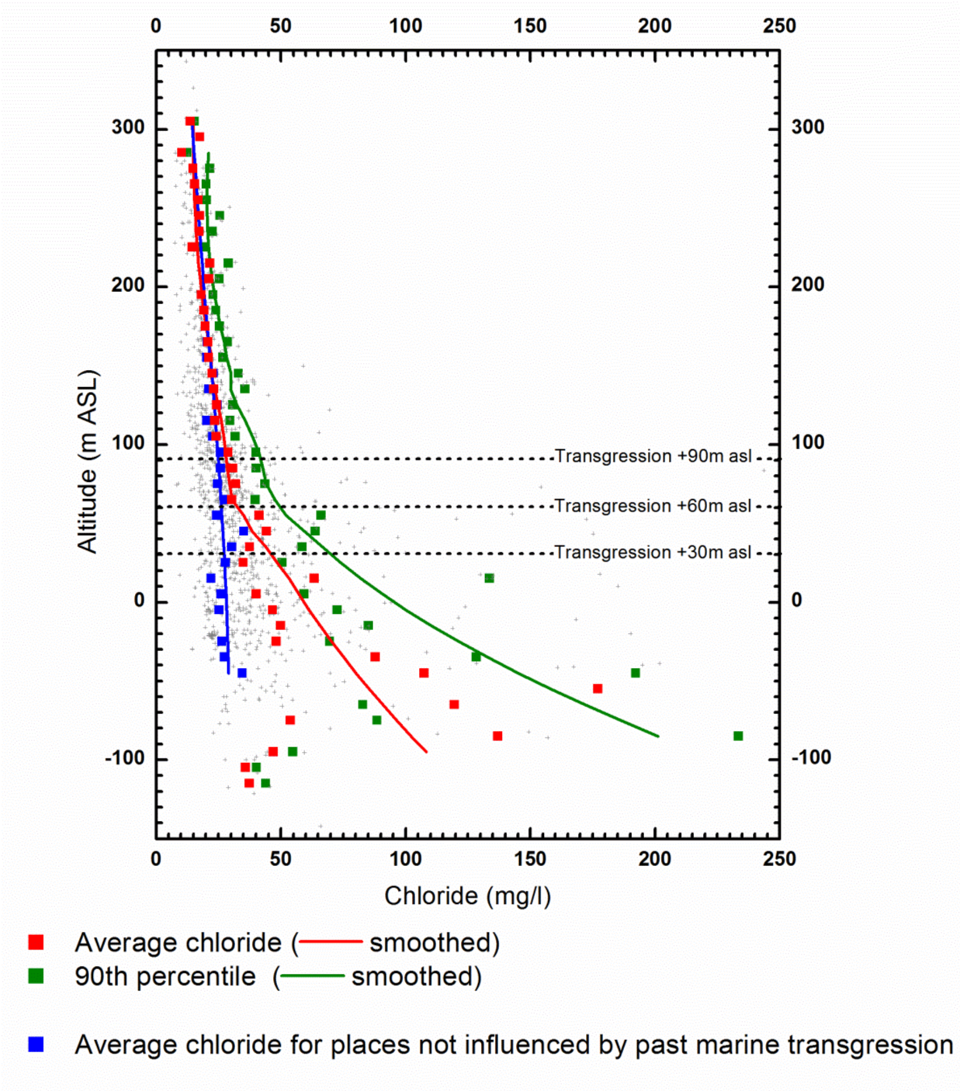

833 **Fig. 6. Chloride concentrations versus altitude of well base.**

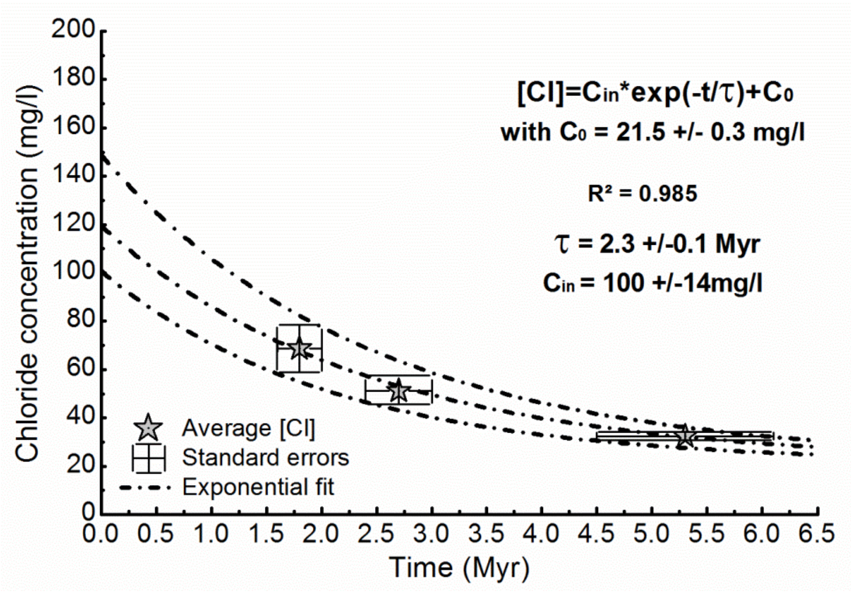

Fig. 7. Average chloride concentration for each transgression zone versus the elapsed time since the transgression.

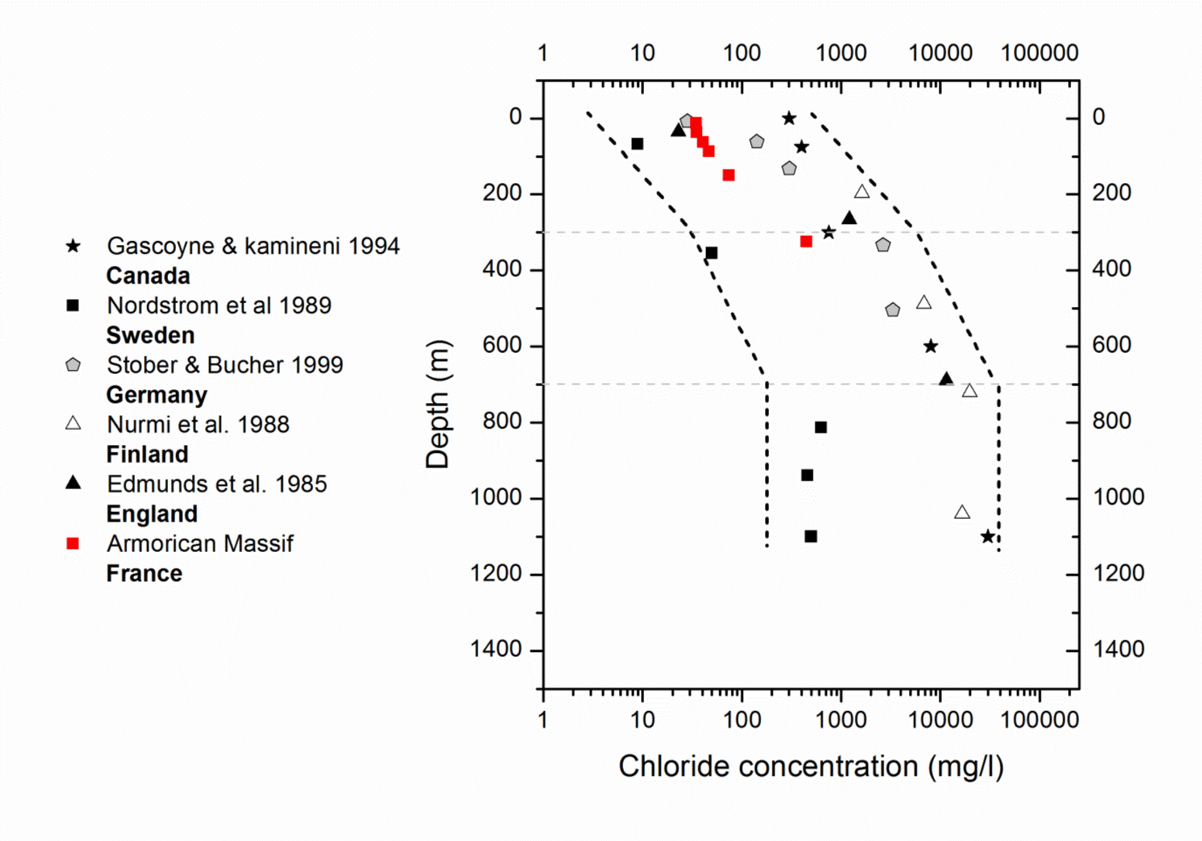

Fig. 8. Chloride concentration (mg/l) versus depth (m) recorded in continental basement around the world compared with the data of the current study.