Fluid chemistry of the low temperature hyperalkaline hydrothermal system of the Prony Bay (New Caledonia)

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Abstract

The terrestrial hyperalkaline springs of the Prony Bay (southern lagoon, New Caledonia) have been known since the XIXth century, but a recent high resolution bathymetric survey of the seafloor has revealed the existence of numerous submarine structures similar to the well-known Aiguille de Prony, which are also the location of high pH fluid discharge into the lagoon. During the HYDROPRONY cruise (October 28th to November 13th, 2011) samples of waters, gases and concretions were collected by scuba divers at underwater vents. Four of these sampling sites are located in the Prony Bay at depths up to 50 m. One (Bain des Japonais spring) is also in the Prony Bay but uncovered at low tide and another (Rivière des Kaoris spring) is on land slightly above the seawater level at high tide. We report the chemical composition (Na, K, Ca, Mg, Cl, SO_4, Dissolved Inorganic Carbon, SiO_2(aq)) of 45 water samples collected at 6 sites of high pH water discharge, as well as the composition of gases. Temperatures reach 37°C at the Bain des Japonais and 32°C at the spring of the Kaoris. Gas bubbling was observed only at these two springs. The emitted gases contain between 12 and 30 % of hydrogen in volume of dry gas, 6 to 14 % of methane, and 56 to 72 % of nitrogen, with trace amounts of carbon dioxide, ethane and propane.

pH values and salinities of all the 45 collected water samples range from the seawater values (8.2 and 35 g/L) to hyperalkaline freshwaters of the Ca-OH type (pH 11 and salinities as low as 0.3 g/L) showing that the collected samples are always a mixture of a hyperalkaline fluid of meteoric origin and ambient seawater. Cl-normalized concentrations of dissolved major elements first show that the Bain des Japonais is distinct from the other sites. Waters collected at this site are three component mixtures involving the high pH fluid, the lagoon seawater and the river water from the nearby Rivière du Carénage. The chemical compositions of the hyperalkaline end members (at pH 11) are not significantly different from one site to the other although the sites are several km away from each other and are located on different ultramafic substrata. The very low salinity of the hyperalkaline end members shows that seawater does not percolate through the ultramafic formation.

Mixing of the hyperalkaline hydrothermal end member with local seawater produces large ranges and very sharp gradients of pH, salinity and dissolved element concentrations. There is a major change in the composition of the water samples at a pH around 10, which delimitates the marine environment from the hyperalkaline environment. The redox potential evolves toward negative values at high pH indicative of the reducing conditions due to

bubbling of the H_2-rich gas. The calculation of the mineral saturation states carried out for the Na-K-Ca-Mg-Cl-SO_4-DIC-SiO_2-H2O system shows that this change is due to the onset of brucite formation. While the saturation state of the Ca-carbonates over the whole pH range is typical of that found in a normal marine environment, Mg- and Mg-Ca-carbonates (magnesite, hydromagnesite, huntite, dolomite) exhibit very large supersaturations with maximum values at pH around 10, very well marked for the Bain des Japonais, emphasizing the role of water mixing in mineral formation.

The discharge of high pH waters of meteoric origin into the lagoon marine environment makes the hydrothermal system of the Prony Bay unique compared to other low temperature serpentinizing environments such as Oman (fully continental) or Lost City (fully marine).

I. Introduction

In 2000, the discovery of the submerged Lost City hydrothermal field (LCHF) along the Mid-Atlantic ridge has focused attention on the role of ultramafic rock alteration (i.e. serpentinization) in the global geochemical cycles of carbon and hydrogen as well as in producing favorable environmental conditions for the synthesis of prebiotic molecules (Fruh-Green et al., 2003; Kelley et al., 2001; Kelley et al., 2005). At Lost City, the fluids produced by the serpentinization process are characterized by high pH (9 – 11) and moderate temperatures (40-90°C) and are enriched in calcium, methane and hydrogen compared to background seawater (Kelley et al., 2005). The highly-reducing conditions of the serpentinizing environment allows the development of abiotic organic compounds (Lang et al., 2010) and hosts a large and specific community of microorganisms (Brazelton et al., 2010; Brazelton et al., 2006b). Such hyperalkaline hydrothermal systems may have been numerous on the early Earth, as well as on the Martian surface (Szponar et al., 2012) and may have also been the locus of the emergence of earliest forms of life (Muntener, 2010; Russell, 2007; Russell et al., 2010).

Although the Lost City site focused the attention of the scientific community, low temperature high pH hydrothermal systems have been previously reported on-land in ophiolites at several locations over the world, such as in Oman (Barnes and O'Neil, 1969; Chavagnac et al., 2013b; Neal and Stanger, 1984b; Stanger, 1985), in Bosnia (Barnes et al., 1978) , in Northern Italy (Ligurian Alps, (Chavagnac et al., 2013b; Cipolli et al., 2004), in New Caledonia (Launay and Fontes, 1985), and more recently in Ontario (Sader et al., 2007), in Newfoundland (Szponar et al., 2012) and in California (Morrill et al., 2013). In ophiolites, hyperalkaline fluids derived from freshwater have low salinity and can mix with close-to-neutral continental runoff waters. In the marine environment, besides the Lost City site, high pH fluids are found at the mud volcanoes of the Mariana forearc where they ascend from the serpentinites of the subducting plate (Mottl, 2009; Mottl et al., 2004). Lost City and Mariana forearc hyperalkaline fluids have salinities close to that of seawater and mix with deep seawater at the vents. Such hyperalkaline systems can therefore be characterized by the type of environment in which these peculiar high pH fluids discharge and the type of local waters with which they can mix (Table 1).

The Prony hydrothermal field (PHF) appears quite unique as low salinity, high pH waters discharge into a coastal marine environment, the New Caledonia southern lagoon. The terrestrial alkaline springs of the Prony Bay have been known since the XIXth century (Garnier, 1871). A recent high resolution bathymetric survey of the seafloor has revealed the existence of numerous submarine structures similar to the well-known “Aiguilles de Prony”, which are also the location of high pH fluid discharge into the lagoon (Pelletier et al., 2006).

During the HYDROPRONY cruise (October 28th to November 13th, 2011) samples of waters, gases and concretions forming at the high pH fluid outlets were collected by the scientific team with the help of scuba divers. We here report the chemical composition of 45 water samples collected at 6 sites of high pH water discharge. Four of these sampling sites are located offshore in the Prony Bay at water depths up to 50 m (ST07, ST09, ST11 and ST12), one (Bain des Japonais, noted below as BdJ spring) is also in the Prony Bay but uncovered at low tide and one, set up as a spa by the local touristic administration (Rivière des Kaoris, shortened below as Kaoris spring), is on land slightly above the seawater level at high tide. Furthermore, we present the chemical composition of gases emitted at these last two sites. No such gas bubbling has been observed at the deeper offshore sites (namely ST07, ST09, site ST11 and ST12). These data show that mixing of the alkaline hydrothermal end member with local seawater produces large ranges and very sharp gradients of pH, salinity and dissolved element concentrations. We then calculated the mineral saturation indices to investigate the conditions of the formation of brucite and Mg-Ca-carbonates in this peculiar environment.

II. Geological setting of the Prony hydrothermal field

The New Caledonia islands group is located on the eastern margin of the Australian plate on the western side of the Vanuatu subduction zone. The NW-SE elongated main island represents the emerged portion of the New Caledonia ridge and includes a large allochtonous sheet of oceanic lithosphere thrusted over continental basement at the Late Eocene (Avias, 1967; Cluzel et al., 2001; Pirard et al., 2013). The 3.5 km thick ophiolite nappe covers an area of 7000 km^2 distributed throughout the island, the main part covering the southern end of the main island. It is composed of harzburgite in which numerous intercalations of dunites and pyroxenites are capped by gabbroic rocks (Guillon, 1975; Pirard et al., 2013). The lithological evolution from dunites to gabbros is marked by an enrichment in aluminum, calcium and alkali (Guillon, 1975). Seismic reflexion and bathymetry show that the topography of the terminations and the borders of the island are controlled by major normal faults (Chardon et al., 2008; Chardon and Chevillotte, 2006; Collot et al., 1982; Flamand, 2006). The association of large low angle detachment faults and high angle conjugate normal faults leads to a general thinning of the ultramafic nappe during its post-obduction evolution (Chardon and Chevillotte, 2006; Lagabrielle and Chauvet, 2008; Lagabrielle et al., 2005). In their recent petrological study of the Massif du Sud, (Pirard et al., 2013) indicate that the ophiolite reaches a thickness between 1000 and 4000 m. The intensity of tectonic deformation allows fluid transfer from the surface down to the ultramafic nappe, as evidenced by a thick (1-300 m) zone of sheared serpentinite (Guillon, 1975) as well as cm-thick silica infills bearing vertical striae along the faults zone (Lagabrielle and Chauvet, 2008). Fluid circulation within the mantle peridotite induces the formation of hyperalkaline hydrothermal fluids produced by serpentinisation reactions (Pelletier et al., 2006).

These obducted ultramafic rocks are exposed to an intense weathering under a tropical climate. A large part of New Caledonia's main island ("Grande Terre", nicknamed "Le caillou") is covered by a thick lateritic alteration layer with an enrichment at its base in nickel and cobalt that are mined and treated by local metallurgical plants (Bonvallot et al., 2012; Quesnel et al., 2013).

Hydrothermal springs were observed at the mouth of the Rivière des Kaoris and at the Baie du Carénage (this latter one also named “Bain des Japonais”) as early as the end of XIXth century (Garnier, 1871). Also in the middle of the Prony Bay, a high carbonated pinnacle towering 35 m above the seafloor up to 2m below the water surface, called “Roc Aiguille” or "Aiguille de Prony", has been known for a long time as a navigation hazard. It is the location of springs well known to scuba divers (Launay and Fontes, 1985; Magnier, 1979). During scientific cruises on the *R/V Alis* in 2004 and 2005, multi-beam bathymetric map and scuba dives revealed that the bottom of the Prony Bay is the location of several two to ten meter high domes and pinnacles, besides the “Aiguille de Prony”, at water depths between 30 and 50 m, sometimes located on 200 m-wide and few meters deep circular depressions, with hydrothermal chimneys at their centers (Pelletier and Chevillon, 2006; Pelletier et al., 2006). These formations, that looked anomalous in regard of the general topography of the lagoon floor, are generally composed of a main whitish chimney towering several meters above the seafloor surrounded by additional peripheral smaller chimneys or pinnacles.

III. Sampling locations, procedures and analytical methods

III.1. Sampling locations

During the HYDROPRONY cruise, which took place on the *R/V Alis* from October 28th till November 13th 2011, fluid samples and chimney sections were collected on land and at sea by divers at the underwater sites. The sampling locations of the HYDROPRONY cruise are of three types: one single site on land: the Kaoris spring, one site uncovered at low tide: the BdJ spring, and 4 underwater sites named “deep sites” (ST07, ST09, ST011 and ST12) (Fig. 1). The geological map (Fig. 1; (Maurizot and Vendé-Leclerc, 2009)) indicates that the eastern side of the Prony Bay is composed of gabbros and peridotites (with no indication of their degree of serpentinization) and the western side of serpentinites, so that there must be a transition between the two types of rocks under water in the Prony Bay. The sites ST09 and ST11, as well as the BdJ spring, seem to be located on a serpentinized substratum, while the sites ST07 and ST12 are closer to the serpentinites. The Kaoris spring is located at the transition between the peridotites and the serpentinites. To date, it is nevertheless impossible to have a better idea of the nature of the substratum at the HYDROPRONY sampling sites.

The Kaoris spring is situated above the sea level at the eastern end of Baie du Carénage (Fig. 1). It has been channeled by the Caledonian touristic administration into a small pool (about 2 m by 3 m, 1.5 m deep), the water discharge being located on one side at the bottom of this pool.

The Bain des Japonais spring is located in the western branch of the Baie du Carénage close to the mouth of a small creek (Rivière du Carénage). There, many vents discharging fluids and gas bubbles can be found on and around these platforms that are uncovered at low tide (Fig. 2). On one of them a small bath nowadays made out of bricks has been built by the convicts ("bagnards" in French) at the end of the XIXth century for the use of the administrators of the nearby Prony penitentiary. It has been later named Bain des Japonais (bath of the Japanese) due to its use by the Japanese workers in the neighbouring mining camps. This bath is usually filled by a hose plugged into one of the vents, but it was empty in November 2011 and no water was flowing out of this hose, despite many active vents around the platform. It has been observed that water flows out of this hose at high tide. The tidal range in the Prony Bay is about 1m. It is sufficient to build up the pressure and make the water flow out of the hose at high tide. A series of samples has been taken at one of the underwater vents located about 10 cm below the surface at low tide on the side of the main platform, the first sample by inserting the plastic syringe directly into the vent, and the following samples at increasing distances from the vent in order to collect fluids in the whole dilution range from the high pH end member to the normal seawater of the Baie du Carénage. The flow rate is so small that at 30 cm away from the vent orifice, pH and temperature have the values of the lagoon seawater, free of any discharge. This small plume is nevertheless large enough to allow measurements (such as the *in situ* pH-redox potential, see below) and sampling to be carried out over the whole pH range.

Before the cruises on the *R/V Alis* in 2005 (Pelletier and Chevillon, 2006; Pelletier et al., 2006), the only known submarine edifice was the pinnacle located in the middle of the Prony Bay ("Aiguille de Prony", Site ST07). It was previously described as a coral formation before its hydrothermal origin was established (Launay and Fontes, 1985; Magnier, 1979). Scuba divers commonly describe the discharge of shimmering fluids and gas bubbles all around the pinnacle, that can be virtually "lit up as candlelight" but this activity changes over the years. During the dives of the HYDROPRONY cruise, the activity was apparently at a minimum, with very limited fluid discharge and no gas bubbles. Four of the underwater structures revealed by the high resolution bathymetric survey of the Prony Bay during the 2005 *R/V Alis* cruise (Pelletier et al., 2006) were selected as fluid sampling sites (Fig. 1). These sites (ST07, ST09, ST011 and ST12) are the location of active springs and hydrothermal concretions at depths between 20 and 50 m below sea level.

III.2. Sampling procedures, *in situ* measurements and analytical methods

The fluids were collected either with gas-tight 200 ml titanium bottles (http://wwz.ifremer.fr/deep/Instrumentation/Outils-de-mesure-grand-fond) or with sterile 60 ml polypropylene syringes equipped with a ~15 cm hose that was introduced into the vents). pH was measured directly at the vents when accessible or immediately after recovery when the fluids were collected at depth. Fluids were filtered using a mixed-esters of cellulose membrane (Millex-HA), which removes microorganisms, particles, precipitates, and suspended material larger than 0.45µm, before storage in low-density polyethylene bottles for chemical analyses on shore at the Laboratoire Géosciences Environnement Toulouse (GET, France). All fluid samples were clear, free of visible particles. They have not been acidified before storage. Gas was emitted at an almost continuous flow of millimetric to centrimetric bubbles at BdJ and Kaoris springs (Figure 2). All gas samples were collected into crimp-sealed gas glass bottles by water displacement.

Major and minor element concentrations were measured on all collected samples. Si, Mg, Ca, Na, K concentrations were measured by inductively coupled plasma optical emission spectrometry (ICP-OES; *Horiba Jobin Yvon Ultima 2*). The instrument was calibrated using synthetic standards and/or IAPSO Standard Seawater (OSIL Limited, UK) and achieved a precision of 2% or better. The analytical and instrumental procedure used for the analyses of deep site fluids is described in detail by (Besson et al., in press). The full set of standards was run before and after each group of analyses to check the performance of the instrument. In addition, one standard was run as a sample before, during and after each group of analyses, to assess the instrument drift through the course of the analyses. All the concentrations reported in Table 2 are, therefore, drift and blank corrected. Anion concentrations (Cl, SO_4) were measured by ion chromatography (IC, *Dionex ICS 2000*), which was similarly calibrated using IAPSO seawater as a standard at various dilution factors. Dissolved inorganic carbon was measured using a Shimadzu TOC-VCSN instrument.

Gases from the samples collected in the 10ml glass vials were transferred into a pre-evacuated, pressure-gauged sample loop. This allows determining the total pressure of the gas samples. All gases were then analysed using a Hewlett Packard 7890A gas chromatograph fitted with HP QPlot columns and micro-catharometer (TCD) associated with a flame ionization detector (FID). Mass balance of quantified gases matches the global gas pressure of the samples.

IV. Temperatures, gas and water compositions

IV.1. Temperature

The Grand Observatoire du Pacifique Sud (GOPS) maintains a network of temperature sensors that record the temperature of the lagoon waters (http://www.observatoire-gops.org/fr/temperatures-cotieres). The yearly variation of the surface temperature is between 22°C and 28°C. The surface temperature of the lagoon water at the time of the HYDROPRONY cruise measured with a CTD probe was 24.4°C while it was 23.3°C at the lagoon floor (around 45m). The temperature of the venting fluids has been measured only at two sites: Bain des Japonais and Rivière des Kaoris (Table 2; Fig. 3). The highest temperature value at the time of the HYDROPRONY cruise was 37.6°C measured at the BdJ spring. There is a linear correlation between temperature and pH measured at the vents of the BdJ spring as a result of the dilution of the hydrothermal alkaline fluid by the lagoon seawater. Note that the temperature levels off for the highest pH values at the BdJ spring (Fig. 3).

(Garnier, 1871) measured a temperature of 33°C for the spring waters (probably those of the BdJ and the Kaoris springs) during his journey to New Caledonia at the end of the XIXth century. A few temperature values have been reported by various authors over the last few decades, such as (Cox et al., 1982) who noted 40°C at BdJ. The temperature measured at the surface of the pool at the Kaoris spring on Oct 30th, 2011 was 31°C. (Launay and Fontes, 1985) and (Cox et al., 1982) reported 32°C at this location while (Barnes et al., 1978) give 34°C (compiled in Fig. 3). The dates of the measurements are not given by these authors. During the 2012 fall, we installed temperature recorders at various alkaline vents in the Prony Bay in order to monitor the dynamics of the hydrothermal system. The first observations show a very stable temperature of the on-land Kaoris spring at 32°C, and a seasonal variation of the temperatures recorded at the BdJ spring and at the Aiguille de Prony (ST07). This seasonal variation is correlated to that of the temperature of the lagoon water to which the temperature recorders are sensitive due to their emplacement (Monnin et al., 2013).

IV.2. Gas composition

Gas bubbles were observed only at the BdJ and the Kaoris springs at the time of the HYDROPRONY cruise. We analyzed 18 samples for the BdJ spring and 11 samples for the Kaoris spring collected over a period of several months during the survey of the springs (Monnin et al., 2013). No change of the gas composition during this time interval has been detected. We here report average values of the hydrogen, methane and nitrogen contents (Table 3). Nitrogen is the dominant gas. The methane content is slightly higher at the BdJ spring that at the Kaoris spring. A full analysis of the gas composition will be reported later.

IV.3. Redox potential measurements

The redox potential was measured *in situ* using a standard potential electrode at the same time as pH in the plume of a vent located on the edge of the main carbonate platform of the Bain des Japonais and in the pool of the Kaoris spring (Fig. 4, Table 4). The redox potential varies linearly with pH (Fig. 4) from positive (oxidizing) values at low pH (+28 mV) to negative values at high pH (-288 mV), consistently with the reducing conditions expected for the alkaline waters due to bubbling of a H_2-enriched gas.

The potential of the standard hydrogen electrode is given by:

$$E_h = -\frac{2.303RT}{F}pH - \frac{RT}{2F}\ln p_{H_2} \qquad (0)$$

In the above expression, R is the gas constant, T the absolute temperature, F the Faraday constant and p_{H_2} the hydrogen partial pressure in the gas phase. The measured Eh-pH values are above the H_2-H_2O equilibrium line calculated here for a p_{H_2} of 0.2 bars and a temperature of 25°C as carried out by (Morrill et al., 2013) (Fig. 4). The linear trend depicts the dilution of the reduced hydrothermal fluid by local oxidized seawater. It extrapolates into Eh-pH values reported for a serpentinizing environment (the Cedars site in California; (Morrill et al., 2013)) that lie on the hydrogen-water redox equilibrium line. These results indicate that water is indeed reduced to hydrogen at surface temperature conditions, but only at very high pH values (above 11.5) that are not reached in the Prony Bay. This key point that relates to the redox conditions of the serpentinizing environment, at the surface and at depth with the ultramafic formation, deserves a detailed separate investigation.

IV.4. The composition of the waters

Element concentrations of all the analyzed samples are reported in Table 2 along with in situ temperatures and pH.

The understanding of the hydrologic regime of the hyperalkaline Prony hydrothermal system requires characterizing the high pH end member fluids emitted at each sampling site, in order to investigate their variations from one location to another, and therefore constrain the hydrologic pathways. Ideally a series of water samples covering the pH range from that of the lagoon seawater to the highest measured value should be collected at each site. Then each property (such as temperature or the dissolved element concentrations) should be reported against the concentration of a conservative element used as a measure of mixing and extrapolated (generally to zero) to get the end member characteristics. (Launay and Fontes, 1985) have shown that the highest pH fluids are freshwaters, with salinities lower than 1 g/L. Thus the chloride concentration is a first indication of the extent of mixing.

The element concentrations (Table 2) reported versus Cl (Fig. 5) indeed show that the dilution range is very large, from seawater salinity to freshwater. The freshest samples are the two samples taken at the Kaoris spring for which calcium and hydroxide are the dominant aqueous compounds (the Cl content of these samples are 6 and 8 ppm), leading to a total dissolved load of a few hundred milligrams per liter (Table 2). The 45 water samples follow two trends for all the analyzed elements (but for Si and DIC): one for the BdJ spring, and one for the deep sites including the Kaoris spring. These two trends extrapolate to the same end member at low Cl concentration. This indicates a meteoric origin for the high pH fluids.

At high Cl concentrations (Fig. 5), the trend for the deep sites and the Kaoris spring is consistent with the standard seawater concentrations for Mg^{2+}, Ca^{2+}, K^{+}, Na^{+} and SO_4^{2-} whereas the trend for the BdJ spring is different. Because of the location of the Kaoris spring, i.e. above the sea level at all times including high tide, and about 30 m away from the shore, samples collected there are the only ones that are not contaminated by seawater. The very low salinity of the uncontaminated sample of the Kaoris spring also indicates that seawater does not percolate through the ultramafic rock formation thus preserving the meteoric origin of the high pH fluids, at least at this location.

pH for all the samples ranges from the seawater value of 8.2 to a maximum value of about 11 (Table 2). This is comparable to the pH values reported for Lost City but still far from the highest pH values found on Earth (Table 1; (Mottl, 2009; Mottl et al., 2004)). The question of the upper pH limit in low temperature serpentinizing environments is still open.

Magnesium is a key element in serpentinizing environments where it is released to the water by Mg-silicate (olivine and pyroxenes) dissolution and scavenged from it by serpentine formation. These reactions keep the Mg concentration of high pH waters at very low values.

What the element concentrations reported versus pH depicts is not the evolution of the serpentinizing fluid during its circulation in the ultrabasic formation, but the dilution of the high pH low salinity fluid by seawater at the discharge locations in the lagoon. In Oman these high pH fluids are diluted by the runoff waters (Chavagnac et al., 2013b); Table 1). In the samples that we have collected in the Prony Bay the Mg content drops from the reference seawater value of 54.1 mmol/L at a pH of 8.1 (Millero, 2006) to values as low as 0.006 mmol/L at a pH of 11.08. Note, however, that the Mg content decreases only slightly for pH values between 8.1 and 10 and markedly toward higher pH values with a slope of about -2 (Fig. 6), consistently with a control of the Mg concentration of the waters by brucite formation (see below). The Mg concentrations of the waters of the Kaoris spring (pH 10.80) and of the only sample collected at the deep sites at a pH higher than 10.6 (sample HP11-Site12-W1, Table 2) were not detected by ICP-OES, although very low values (down to 0.01 mmol/L) for the BdJ spring could be measured. This nevertheless shows that the Mg content of the water samples at pH 11.0 for the deep site and at pH 10.8 for the Kaoris spring is very low and that the two distinct trends merge to a very low Mg concentration at high pH (Figs. 5

and 6). At intermediate pH values (10-10.5) the difference between the two trends in the Mg content can be as large as one order of magnitude, as observed for the Ca concentrations (and to a lesser extend for Na and K) (Fig. 6).

The Na and Cl concentrations also exhibit two different trends at pH values above 10, meaning that two waters of the same pH can have different salinities (Fig. 6). Of particular interest is the sample HP11-Site12-W1 which is the water sample of the deep sites having the highest pH value (11). Its chloride and sodium concentrations do plot on the trend defined by the data for the deep sites, but they are higher by more than an order of magnitude than the samples of the BdJ and the Kaoris springs at the same pH values. Also noteworthy its Ca and K concentrations lie on the data trend of the BdJ spring. ST11 located on the eastern side of the bay could be different from the others. Unfortunately no sample with a pH above 10.62 could be collected at the nearby site ST09 (Fig. 1). In a study of the alkaline waters of the Oman and Liguria ophiolites, (Chavagnac et al., 2013b) proposed that the somewhat high salinity of some of these waters could be due to their interaction with the metasedimentary formation underlying the ophiolite nappe, indicating that the circulation of the high pH fluids would not be confined to the ultramafic formation. This could be the case for the Prony Bay.

The data reported in this work for the Kaoris spring are consistent with those given by (Launay and Fontes, 1985) (the same data is given in (Cox et al., 1982) and by (Barnes et al., 1978)), meaning that the composition of the high pH fluids have not markedly changed over the last thirty years or so. This is also the case for the present data for the BdJ spring when compared to the composition given by (Launay and Fontes, 1985). There are similarities but also marked differences between the waters at pH 10.8-11 at the BdJ and the Kaoris springs (Table 2). The waters at BdJ are more saline than at Kaoris. This can be in part explained by a contamination by seawater therefore leading to higher Na, K and Cl concentrations at BdJ compared to Kaoris. The Ca concentration is the same at both locations, but the silica concentration is one order of magnitude higher at Kaoris than at BdJ. This cannot be due to the alteration of the concrete used to build the spa, first because the aqueous silica concentration reported here is the same as the one measured by (Launay and Fontes, 1985) at a time when the spring was not arranged as a pool, and also because at the time of the HYDROPRONY cruise the water flow was significant and the sample was taken at the fluid outlet at the bottom of the pool.

Chloride-normalized concentrations (Fig. 7) allow us to take into account the dilution effects and reducing the dispersion of the data. The variation of chlorine-normalized element concentrations as a function of pH exhibits a major trend break at pH around 10 (Fig. 7), as similarly shown by the Mg data (Fig. 6). They are equal to the reference seawater values at pH values below pH 10 for all the sites but the BdJ spring. The pH value of 10 delimitates the marine environment at low pHs from the hyperalkaline environment (which (Chavagnac et al., 2013b) already observed for Oman and Liguria). Reactive dissolved elements or compounds such as DIC differ from their standard seawater Cl-normalized concentration (when it can be defined, which cannot be done for dissolved silica).

To summarize, the present results show that the hyperalkaline waters emitted at all sites in the Prony Bay are of meteoric origin and that these high pH fluids may mix with seawater at the discharge, but not in the subsurface. The waters of the Kaoris spring appear to be the most pristine. There are differences in water compositions between the deep sites and the other sites in the intermediate pH range, but the end member compositions at the highest pH values are about the same. A difference in salinity may be noticed, but the scarcity of the data at the highest pH values does not allow any firm conclusion for now.

Minerals may form when Ca^{2+}-OH^- type alkaline waters mix with seawater, which we investigate in the following section through the calculation of their saturation states.

V. The mineral saturation states

The number of dissolved elements and compounds determined by the chemical analysis defines the composition of the waters (Table 2) and therefore the chemical system (in a thermodynamic sense) that is used to describe the natural object. Here we analyzed the major elements (along with $SiO_2(aq)$), so that the chemical system in which the compositions of the Prony Bay waters are given is the Na-K-Ca-Mg-Cl-SO_4-DIC-SiO_2-H_2O system. The thermodynamic state of the HYDROPRONY water samples has been addressed through the calculation of the mineral saturation indices using the PHREEQC code. The saturation index is defined as:

$$\Omega = \log\left[\frac{Q}{K_{sp}}\right]$$

in which Q is the ionic product (the product of the ionic activities) and K_{sp} the solubility product of the given mineral.

The choice of the database is of primary importance as different databases contain either different sets of minerals (e.g. portlandite which is not included in the phreeqc.dat database), or different values of the mineral solubility products. It is beyond the scope of the present paper to check the thermodynamic data for all the minerals relevant to the serpentinizing environment. We focused on Ca and Mg carbonates and brucite which have been observed to form in the concretions (Pisapia and the HYDROPRONY scientific team, 2012) and also on various forms of silica (quartz, chalcedony, amorphous silica) that have been shown to play a role in the control of aqueous silica in the alkaline waters of Oman (Chavagnac et al., 2013a; Chavagnac et al., 2013b) .

Values for the brucite solubility product reported in the literature (e.g. (Harvie et al., 1984; Königsberger et al., 1999; Lambert and Clever, 1992) vary over about one order of magnitude. We retained for this mineral the value recently proposed by (Xiong, 2008) in a study based on new solubility data. Thermodynamic data for the Ca-carbonates and for the silica minerals between the various sources (i.e. data bases provided with PHREEQC) were found consistent. However, there are discrepancies between the various values of the thermodynamic properties of the Mg-carbonates available in the literature (see for example (Bénézeth et al., 2011) for magnesite). Values for double salts like dolomite, huntite, etc., are very uncertain likely as a result of the difficulty of synthesizing these minerals at low temperature (Bénézeth et al., 2011). The saturation state values reported here are certainly subject to changes when improved thermodynamic data become available, but they indicate some interesting trends.

The calculations have been carried out using the concentration of all the elements (Table 2) in a molarity scale and pH and the Dissolved Inorganic Carbon content as the input parameter for the carbonate system.

The saturation indices have first been calculated assuming that the relationship between T and pH exhibited for the Bain des Japonais samples (Fig. 3) was valid for all the sites, as a way of estimating the temperature of the fluids at the deep sites.

V.1. Hydroxydes (brucite and portlandite)

The Prony water samples reach saturation with respect to brucite at a pH of 9.5 (Fig. 8) and its saturation state continues to increase up to a pH of 10 where it levels off to a log(Q/K_{sp}) of about 1.5 for the Bain des Japonais. This coincides with the marked change of the Cl-normalized element concentrations (Fig. 7): decrease of Mg/Cl, Na/Cl, SO_4/Cl and increase of K/Cl, Si/Cl, DIC/Cl.

Portlandite ($Ca(OH)_2$) has been found to rarely form in the alkaline springs of Oman (Neal and Stanger, 1984a). It is largely undersaturated in the Prony Bay environment.

V.2. Ca-carbonates and silica

The Prony water samples are supersaturated with respect to calcite (as well as aragonite) throughout the whole pH range at supersaturation values commonly found in the marine environment (Fig. 9).

All forms of silica are undersaturated over the whole pH range. This is the case for marine waters (low pH) and for very alkaline waters in which silica becomes very soluble (see the example of Oman and Liguria in (Chavagnac et al., 2013b).

V.3. Mg-carbonates, dolomite and huntite

Under this heading we designate the Mg-carbonates themselves: magnesite and all forms of hydrated magnesium carbonate: $MgCO_3.pH_2O$ and the double salts Mg-hydroxo-carbonates $mMgCO_3.nMg(OH)_2.pH_2O$ (Table V). The composition of these double salts can be understood as intermediate steps with increasing CO_3/OH ratios from the hydroxide end member brucite to the carbonate magnesite. Hydrated Mg-carbonates $MgCO_3.pH_2O$ and various forms of Mg-hydroxo-carbonates are metastable phases mainly forming through biological processes during the evolution of high pH waters in contact with the atmosphere, such as the Atlin playa lake in British Columbia (Power et al., 2007).

The saturation states of magnesite, hydromagnesite, artinite, huntite and dolomite (Fig. 10) indicate very large supersaturations and a maximum value at pH around 10. These maxima are very well marked for the Bain des Japonais.

VI. Discussion and conclusions

The composition of the waters collected at the hyperalkaline springs of the Prony Bay shows that the high pH fluids are of meteoric origin, as indicated by the low salinity of the highest pH waters. These waters are of the Ca-OH type, as already described in continental serpentinizing environments (Table 1) and clearly shown by the most pristine sample, that of the Kaoris spring, for which aqueous calcium and hydroxide are the dominant dissolved species, all other solutes exhibiting trace concentrations. The highest pH values found at the Prony Bay are close to the values found at Lost City, but lower than the highest alkaline values naturally found to date on Earth (in the Marianna forearc,, Mottl et al., 2004).

A peculiarity of the Prony Bay that makes this site unique is that the low salinity alkaline waters discharge into the marine environment and mix with seawater.

As stated in the introduction (Table 1), hyperalkaline systems can be characterized first by the nature and composition of the high pH end members discharging at springs, but also by the type of environment in which these peculiar high pH fluids discharge and the type of local waters with which they can mix. For the case of the Prony Bay, this translates into two questions: 1) the evolution of the recharge waters (of meteoric origin) during their interaction with the ultramafic basement up to the discharge locations (springs), 2) the mineral formation induced by mixing these high pH low salinity waters with the lagoon seawater (Fig. 11).

The composition of the water samples reported in this work (Fig. 5 and 6) shows that the main difference is between the Bain des Japonais and the other springs, in the intermediate pH range. Within the dispersion of the data, the end member fluids (i.e. the samples with the highest pH values) of the BdJ spring, of the deep sites and of the Kaoris spring are similar. This would mean that even if the flow paths are different, from the recharge zone to the springs (Fig. 11), the residence time of the waters in the ultramafic basement is long enough for the waters to acquire similar compositions. The temperature of the nearby river is up to 15ºC lower than those of the hyperalkaline springs (Launay and Fontes, 1985), arguing for water heating (either due to the geothermal gradient or to heat generated by serpentinization) during its circulation within the ultramafic substratum, and conductively cooling during its ascent to the surface. A tentative value of the geothermal gradient of 20ºC/km in New Caledonia would then suggest that water circulates down to about a kilometer below the surface. The hydrologic regime and pathways of fluid circulation in ophiolites, in New Caledonia and elsewhere (Chavagnac et al., 2013b) are still open questions, that are also addressed in related topics such as carbon capture and sequestration (Arcilla et al., 2011).

The water samples collected at the BdJ spring share common overall characteristics with the other sites, but nevertheless display a different trend. The Bain des Japonais sample with the lowest pH (8.3, Table 2) was collected about 20 m away from any vent. Still this sample has a chloride content (322 mmol/L, Table 2) much lower than that of standard seawater. This can be due to two combined causes. On one hand, the western branch of the Baie du Carénage is very shallow so that the marine waters can be readily diluted by the nearby creek, the Rivière du Carénage (Fig. 1). On the other hand, waters in the southern lagoon of New Caledonia can have a long residence time (i.e. a slow renewal rate) (Ouillon et al., 2010). The tide effects are very attenuated at the end of the Baie du Carenage where the

BdJ spring is located. Such hydrodynamic conditions create an altered "marine" end member that mixes with the high pH fluids produced by serpentinization, thus leading to the trend for the BdJ spring different from that for the other sites where seawater of standard salinity is the marine end member of the mixtures. This is further indicated by the Cl-normalized concentrations of the dissolved elements (Fig. 7).

At intermediate pH values (around 10.5), the Mg content of the fluids is lower by an order of magnitude at the Bain de Japonais compared to the values at the deep sites. Still the two trends show the same major change at pH 10. The thermodynamic calculations reveal that this change occurs when the brucite saturation index reaches a constant value ($\log(Q/K_{sp})$ higher than 1.5) that may be indicative of brucite formation from a supersaturated solution, with a supersaturation at the deep sites higher than that at the Bain des Japonais. Brucite forms at the vents when high pH waters mix with Mg-rich seawater. Brucite formation due to mixing of two water types has already been evidenced in the alkaline springs of Oman where magnesium is brought by the runoff waters and hydroxide by the high pH fluids (Chavagnac et al., 2013a; Chavagnac et al., 2013b). This mode of brucite formation is different from the formation of brucite during the serpentinization process itself, in which magnesium is released by Mg-silicate dissolution, a reaction consuming $H^+(aq)$, therefore increasing the aqueous phase pH leading to the formation of brucite as a secondary mineral (Chavagnac et al., 2013b). In a totally different environment (concrete alteration by drainage waters in Austrian tunnels), (Rinder et al., 2013) have also found that brucite forms at supersaturation values close to those found here. This may indicate that brucite precipitation occurs only when a supersaturation threshold is reached.

The saturation indices of the Mg-bearing carbonate minerals display a maximum value at intermediate pH values (around 10; Fig. 10). These maxima are very large, indicative of marked supersaturation. As stated above, the values of solubility products of these carbonate minerals are still a subject of debate, despite recent improvements (Bénézeth et al., 2011) and the calculated saturation indices may be tentative values. A change in the solubility product of a given mineral would shift the entire data set in Fig. 10, but not change its shape. The supersaturation at pH around 10 may thus indicate the most favorable conditions (the highest driving forces) for these minerals to form through an inorganic process. It is nevertheless well known that magnesite and dolomite do not form at low temperature through simple inorganic precipitation (Morse et al., 2007), although recent works brought new insights into the role of magnesium hydration (Xu et al., 2013) and of surface chemistry (Roberts et al., 2013). This would mean that these high supersaturations at intermediate pH values point to the hindrance of mineral formation (metastability) and not to quantitative precipitation. However, mineralogical observations indicate that organomineralization drives the formation of Mg-carbonates in the concretions (Pisapia et al., 2013). At the Bain des Japonais, there is a marked dominance of brucite, along with the formation of aragonite. Minerals in lesser amounts include magnesium carbonates and double layered hydroxydes (nesquehonite, hydrotalcite, iowaite) (Pisapia et al., 2014). Such mineral assemblages are also observed in the concretions collected at the deep sites actively discharging the high pH fluids. When the vents are no longer active, seawater can percolates deeper into their structure therefore modifying the mineralogical composition of the concretions, with an increasing amount of calcite. These results emphasize the intricate role of the potential energy provided by the inorganic process (mineral supersaturation) and the influence of microorganisms that may take advantage of these favorable energetic conditions to induce mineral formation, thus breaking down the metastability.

The temperature difference between the venting fluids and the lagoon waters is not very large (about at most 15°C). The mixing process depicted by the data in Fig. 5 and 6 creates marked pH, salinity and concentration gradients, leading to mineral supersaturations (Fig. 10) and favorable conditions for the development of adapted ecosystems (Postec et al., submitted; Quéméneur et al., 2014). At active vent sites (especially the deep ones) a combination of inorganic precipitation and bio- and organo-mineralization processes leads to the formation of concretions and needle-like structures that can grow up to the size of the Aiguille de Prony. Some of these formations grow around a central conduit where the high pH fluids circulate. At such places the concretion walls are not very thick so that the pH varies from 8.2 at the outside (seawater in the normal lagoon marine environment) to 11 (the alkaline hydrothermal fluid in the central part) over a distance of 10 cm or so. Also these concretions are very porous. It is then likely that the tortuosity of the flow within the porous material creates complex mixing patterns, with very different conditions of pH, Eh, salinity and temperature over very short distances. The structure of these concretions also depends on the age and on the vigor of the hydrothermal activity of the vent (Pisapia et al., 2013). Inside these concretions alkaliphilic microorganisms can grow in the high pH-low salinity fluid while the outside part is in contact with the normal lagoon marine environment (Pisapia et al., 2013; Quéméneur et al., 2014). The very strong concentration and salinity gradients found in the hydrothermal system of the Prony Bay are unique features. It is very different from the Lost City hydrothermal field where the high pH hydrothermal fluid is altered seawater of the same salinity as normal seawater (Kelley et al., 2001) .

The brucite saturation state has been calculated using the PHREEQC code (with the phreeqc.dat data base) using the input composition data in the Na-K-Ca-Mg-Cl-SO_4-DIC-H_2O chemical system which is here used a model of the real solution (see the discussion in (Monnin and Hoareau, 2010) of the difference between model seawater and seawater models). This procedure neglects eventual dissolved compounds that may act as ligands of aqueous magnesium. Such aqueous complex formation would modify the thermodynamic properties of aqueous magnesium by lowering its total (or stoichiometric) activity coefficient. As a result complexation stabilizes the aqueous phase at the expense of minerals, thereby increasing their solubility. Magnesium is indeed easily complexed by organic molecules (Holm, 2012; Krause et al., 2012) (a common method to analyze magnesium in aqueous solutions is based on a titration using Mg complexation by EDTA).

Serpentinization is a complex combination of dissolution/precipitation and redox reactions. The oxidation of metals (mainly iron) contained in peridotites is accompanied by the reduction of water, leading to the simultaneous production of high pH waters and of hydrogen (Chavagnac et al., 2013b). Further reactions of hydrogen with either organic matter or oxidized carbon compounds may lead to the formation of methane (and to a lesser extend longer chain hydrocarbons or simple organic anions such as formate (Lang et al., 2010) through Fisher-Tropsch type reactions (Prokurovski, 2010). Indeed gases emitted at the alkaline springs of the Prony Bay are enriched in H_2 and CH_4. They serve as important energy and carbon sources for microorganisms that thrive in the porous chimney walls. Various degrees of mixing of the alkaline fluid with oxygenated ambient seawater also provide potential electrons acceptors (such as sulfates, nitrates or oxygen) crucial for many microbial metabolisms. This was recently evidenced by a molecular survey conducted on Prony concretions (Quéméneur et al., 2014) which showed the dominance of microbial metabolic groups using either of H_2 or CH_4 as electron donors for their growth under the anaerobic conditions found in the high pH fluids. These metabolic groups notably include Methanosarcinales, a group of archaea including both hydrogenotrophic methanogens and members responsible for the anaerobic oxydation of methane, a reaction thermodynamically unfavorable unless coupled with sulfate or nitrate reduction via syntrophic association (consortia) with sulfate or nitrates reducing bacteria (Knittel and Boetius, 2009). Remarkably the Methanosarcinales described in Prony are very similar to those previously detected in the Lost City hydrothermal field (Brazelton et al., 2006a; Schrenk et al., 2004). In the high pH springs of the Prony Bay, sulfate-reducing bacteria of the delta-proteobacteria group are also well represented (Quéméneur et al., 2014) as is the case at Lost City (Brazelton et al., 2006a).

Aerobic respiration of hydrogen or methane (and other C1 compounds) is also most likely active in the concretions as strongly suggested by the abundance of sequences related to hydrogenotrophic bacteria of the Burkholderia class, such as Hydrogenophaga and many taxa representing methylotrophic bacteria (Quéméneur et al., 2014).

Lastly, the carbonate concretions and the hyperalkaline springs of the Prony hydrothermal system provide a unique example of the interface between a continental ultramafic formation and the marine environment, with peculiar links between geology, fluid chemistry and microbial activity (Perner et al., 2013; Toner et al., 2013).

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Table list

Table 1 – High pH waters worldwide. The first column (marine or continental) is the general geological environment in which the springs are found. ”Input water" is the type of waters entering the local hydrologic cycle. The “discharge environment” is the location of the springs, on continental surfaces or in the deep or shallow marine environment. "Local waters" are the waters that are found in the type of geological environment (for example formation waters of continental kimberlites or river waters on continental surface) that mix with the high pH waters at some point of the hydrologic pathways.

Table 2 – Major and minor elemental composition and temperature of the waters collected in the Prony Bay during the HYDROPRONY cruise (*b.d.l.:* below detection level; DIC: dissolved inorganic carbon).

Table 3 – The hydrogen, methane and nitrogen contents of the gases (in volumetric percentage) collected at the springs of the Bain des Japonais and of the Rivière des Kaoris.

Table 4 – Redox potential and pH measured *in situ* (April 24, 2013) at the springs of the Bain des Japonais and of the Rivière des Kaoris.

Table 5 – Chemical formula of various magnesium-calcium carbonates (the numbers m, n and p correspond to the following formula: $mMgCO_3.nMg(OH)_2.pH_2O = (m+n)Mg.mCO_3.nOH.pH_2O$)

	Input water	Discharge environment	Location	Geological environment	Highest pH	Local waters	Reference
Continental	*meteoric (river)*	*continental*	Ontario	continental kimberlites	12.5	formation porewaters	Sader et al., 2007
			Oman	ophiolite	12.2	continental runoff	Chavagnac et al., 2013; Neal and Stanger, 1984
			Portugal	ophiolite	10.9	continental runoff	Marques et al., 2008
			Phillipines	ophiolite	11.7	continental runoff	(Fujii et al., 2010)
			Northern Italy	ophiolite	11.9	continental runoff	Cipolli et al., 2004 Boschetti and Toscani, 2008 (Boschetti and Toscani, 2008) Chavagnac et al., 2013
			Cyprus	ophiolite	11.6	continental runoff	(Neal and Shand, 2002)
			The Cedars (California)	ophiolite	11.9	continental runoff/formation porewaters	Morrill et al., 2013
			Newfoundland	ophiolite	12.3	continental runoff	Szponar et al., 2012
Marine	*marine (seawater)*	*marine (deep)*	Lost City (Mid Atlantic Ridge)	seafloor peridotites	11.0	ocean bottom seawater	Kelley et al., 2005
			Marianna forearc (Southwest pacific)	marine sediments / mud volcanoes	12.5	marine sediment porewaters	Mottl et al., 2004
Mixed	*meteoric (river)*	*marine (shallow)*	Baie de Prony (New Caledonia)	ophiolite	11.2	lagoon seawater	Launay and Fontes, 1985 This work

Site	Sample name	pH	T	Si mmol/l	DIC mmol/l	Mg mmol/l	Ca mmol/l	Na mmol/l	K mmol/l	F- mmol/l	Cl- mmol/l	SO4 mmol/l
Standard seawater (Millero, 2006)					2.07	54.10	10.53	480.47	10.46		559.14	28.93
Bain des Japonais	HP11-BdJ-Ilot1-W1C	11.08		0.0009	0.3921	0.006	0.518	2.38	0.32	0.0071	2.22	0.10
	HP11-BdJ-Ilot1-W2	10.48		0.0028	0.3573	0.198	0.525	7.29	0.42	0.0055	5.47	0.28
	HP11-BdJ-Ilot1-W3	10.01		0.0102	0.4737	2.344	0.957	26.14	0.81	0.0059	21.61	1.24
	HP11-BdJ-Ilot1-W5	11.07		0.0025	0.4601	*b.d.l.*	0.444	1.28	0.30	0.0055	0.41	0.01
	HP11-BdJ-Ilot1-W6	10.68		0.0059	0.3616	0.092	0.667	5.68	0.41	0.0061	4.02	0.19
	HP11-BdJ-Ilot2-W1	10.87		*b.d.l.*	0.4096	0.029	0.594	2.98	0.36	0.0069	1.84	0.07
	HP11-BdJ-Dil1	10.05	36.0	0.0073	0.4599	3.98	1.29	22.63	1.54	0.0053	52.67	3.36
	HP11-BdJ-Dil2	9.13	31.1	0.0432	1.2946	23.83	5.00	197.98	4.75	0.0064	179.27	11.85
	HP11-BdJ-Dil3	8.66	29.8	0.0498	1.6152	33.58	6.87	284.15	6.36	0.0204	241.80	16.09
	HP11-BdJ-Dil4	10.20	36.8	0.0052	0.4774	1.34	0.97	1.91	1.15	0.0055	34.52	2.16
	HP11-BdJ-Dil5	8.30	28.2	0.0316	1.7884	45.16	9.16	392.81	8.52	0.0257	322.05	21.45
	HP11-BdJ-Dil6	11.00	37.1	0.0039	*b.d.l.*	0.028	0.21	2.55	0.43	0.0269	1.44	0.06
	HP11-BdJ-Dil7	10.92	37.6	0.0029	0.3097	0.024	0.22	1.65	0.39	0.0109	0.66	0.02
	HP11-BdJ-Dil8	10.88	36.9	0.0025	0.3996	0.036	0.41	1.75	0.40	0.0064	0.76	0.02
Rivière des Kaoris	HP11-CarKao-W1	10.80	31.0	0.0662	0.1440	*b.d.l.*	0.36	0.65	0.08	0.0032	0.23	*b.d.l.*
	HP11-CarKao-W2	10.80	31.0	0.0656	0.0000	*b.d.l.*	0.38	0.58	0.08	0.0025	0.19	*b.d.l.*
Site ST11	HP11-Site11-W1	10.64		0.0502	0.5376	2.516	2.28	40.52	0.00		45.78	1.54
	HP11-Site11-W4	9.58		0.0394	1.1156	31.69	7.28	270.85	5.09		327.74	16.16
	HP11-Site11-W5	8.76		0.0116	1.8450	45.44	9.45	386.58	7.36		451.96	22.56
	HP11-Site11-W10	9.06		0.0344	1.5244	31.37	7.19	263.71	4.87		319.18	15.79
	HP11-Site11-W11	9.38		0.0432	1.2131	22.75	6.31	199.40	3.69		248.69	12.13
Site ST12	HP11-Site12-W1	11.00		0.0298	0.3824	*b.d.l.*	0.55	40.05	0.14		41.74	0.38

	HP11-Site12-W3	8.92	0.0249	1.3080	44.02	8.27	384.52	7.56		432.70	21.50
	HP11-Site12-W4	9.50	0.0207	0.6818	22.18	4.43	191.24	3.91		247.31	11.53
	HP11-Site12-W5	8.85	0.0121	1.6377	45.18	8.69	385.32	7.49		440.03	21.79
	HP11-Site12-W6	9.34	0.0158	0.9075	37.44	6.32	323.69	6.47		371.92	18.20
	HP11-Site12-W7	8.60	0.0108	1.8849	45.34	8.90	393.22	7.79		447.21	22.17
	HP11-Site12-W8	8.15	0.0077	0.4070	54.65	10.28	475.50	9.28		515.39	25.89
Site ST7	HP11-Site7-W1	9.73	*b.d.l.*	0.5830	23.32	4.91	190.96	3.69		252.37	12.24
	HP11-Site7-W2	9.66	*b.d.l.*	0.6666	22.92	4.96	187.73	3.62		250.44	12.14
	HP11-Site7-W3	9.67	*b.d.l.*	0.6721	18.69	4.43	154.31	2.93		212.43	10.17
	HP11-Site7-W4	9.61	*b.d.l.*	0.6342	20.42	4.59	167.61	3.40		225.87	10.82
	HP11-Site7-W5	9.72	*b.d.l.*	0.7691	24.43	5.17	198.08	3.74		262.81	12.78
	HP11-Site7-W6	9.61	*b.d.l.*	0.7067	28.73	5.74	235.44	4.53		297.38	14.59
	HP11-Site7-W3Ti	9.44	0.0138	0.6870	41.14	7.16	346.46	7.33		400.87	19.95
	HP11-Site7-W7	10.00	0.0001	0.5377	27.95	5.46	232.61	4.81		290.68	14.20
	HP11-Site7-W8	10.13	*b.d.l.*	0.4945	20.08	4.41	163.75	3.32		223.03	10.64
	HP11-Site7-W9	9.91	0.0006	0.4971	29.36	5.76	249.17	4.95		309.31	15.19
	HP11-Site7-W10	10.14	*b.d.l.*	0.4482	12.43	3.49	97.32	2.00		163.85	7.53
	HP11-Site7-W11	9.96	*b.d.l.*	0.5121	28.02	5.45	228.89	4.58		292.43	14.25
Site ST9	HP11-Site9-W1	10.45	0.0119	0.5280	3.60	2.95	36.67	1.51		81.52	3.31
	HP11-Site9-W3	10.62	0.0127	0.3985	2.768	2.76	6.46	0.98		50.58	1.72
	HP11-Site9-W4	10.46	0.0118	0.4094	4.80	2.98	44.96	1.76		91.62	3.82
	HP11-Site9-W6	9.18	0.0079	1.6885	38.77	8.56	337.76	7.34		380.77	18.85
	HP11-Site9-W7	10.51	0.0137	0.6342	4.96	3.22	47.54	1.78		95.84	4.03

Spring	**Number of samples**	**H2 (%V)**	**CH4 (%V)**	**N2 (%V)**
Bain des Japonais	18	19±11	13±4	67±11
Rivière des Kaoris	11	24±11	6±1	69±11

Spring	T°C	pH	Eh (mV)
Bain des Japonais	34.7	10.48	-288
	31.5	10.13	-216
	29.1	9.68	-172
	26.5	8.88	-50
	35.4	10.77	-352
	30.4	10.17	-219
	29.7	9.93	-198
	28.4	9.68	-171
	28.9	9.53	-163
	26.9	8.73	5
	27.4	8.47	33
	27.2	8.44	19
	28.6	9.46	-151
	27.4	8.38	28
Rivière des Kaoris	30.5	10.95	-195

m	**n**	**p**	**Name**	**Formula**
1	0	0	Magnesite	$MgCO_3$
1	0	2	Barringtonite	$MgCO_3.2H_2O$
1	0	3	Nesquehonite	$MgCO_3.3H_2O$
1	0	5	Lansfordite	$MgCO_3.5H_2O$
1	1	3	Artinite	$MgCO_3.Mg(OH)_2.3H_2O$
4	1	5	Dypingite	$4MgCO_3.Mg(OH)_2.5H_2O$
4	1	5	Hydromagnesite	$4MgCO_3.Mg(OH)_2.4H_2O$
0	1	0	Brucite	$Mg(OH)_2$

Figure captions

Figure 1 – Simplified geological map of the Prony Bay (after (Maurizot and Vendé-Leclerc, 2009) with the location of the sampling sites.

Figure 2 – The Bain des Japonais spring (abbreviated as BdJ spring in the text). The carbonate platform is uncovered at low tide. It is surrounded by several underwater vents discharging high pH waters and gas bubbles. Note the brick walls built by the convicts of the Prony penitentiary in the XIXth century.

Figure 3 –*In situ* temperature of the Prony Bay water samples versus pH.

Figure 4 – Redox potential measured *in situ* at the springs of the Bain des Japonais and of the Rivière des Kaoris springs (this work) and of The Cedars site (California; (Morrill et al., 2013). The plain line represent the redox potential calculated at a temperature of 25°C for the equilibrium between water and hydrogen at a H_2(g) partial pressure of 1 bar and the dashed line at a H_2(g) partial pressure of 0.0001 bar.

Figure 5 – Element concentrations versus the chloride content of the water samples (cross: standard seawater; open circles: Site ST07 (Aiguille de Prony); filled diamonds: Site ST12; open diamonds: Site ST09; triangles: Site ST11; filled circles: Bain des Japonais; star: Rivière des Kaoris; inverted triangle: data of (Launay and Fontes, 1985) for the Bain des Japonais and the Rivière des Kaoris.

Figure 6 – Element concentrations of the collected water samples versus pH. Same symbols as for Fig. 5.

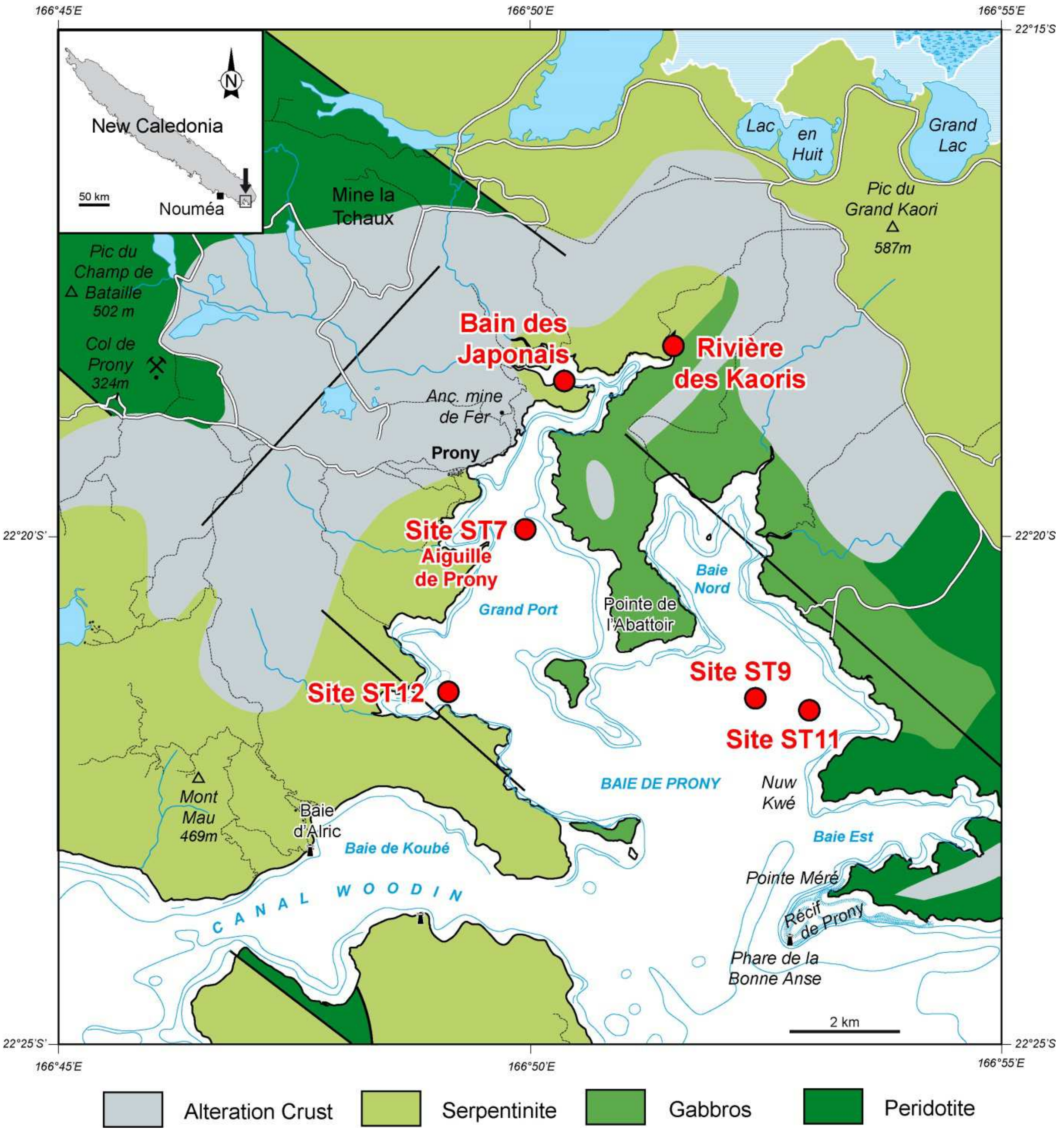
Figure 7 – Chloride-normalized element concentrations versus pH. Same symbols as for Fig. 5. The dashed line represents the value for standard seawater (Millero, 2006).

Figure 8 – The brucite saturation state of the Prony waters versus pH. Same symbols as for Fig. 5. The horizontal dashed line represents the chemical equilibrium.

Figure 9 – The calcite saturation state of the Prony waters versus pH. Same symbols as for Fig. 5. The horizontal dashed line represents the chemical equilibrium.

Figure 10 – The saturation state of various magnesium/calcium carbonates of the Prony waters versus pH. Same symbols as for Fig. 5. The horizontal dashed line represents the chemical equilibrium.

Figure 11 – A sketch of the general geological setting of the Prony hydrothermal field (PHF, not to scale). The ophiolite nappe is covered by a thick lateritic cover. The hydrothermal system is fed by meteoric waters that percolate through the densely fractured peridotites and discharge at springs in the lagoon where the high pH waters mix with seawater. Note the position of the spring of the Rivière des Kaoris above sea level, while the Bain des Japonais is uncovered at low tide and the other springs always under water. The arrows tentatively indicate the pathways of the fluid percolation and point to the question of the nature of the geological formations leached by the waters: ophiolite nappe, continental basement and/or coral formations.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Mine la Tchaux
Lac en Huit
Grand Lac
Pic du Grand Kaori
587m
Pic du Champ de Bataille
502 m
Col de Prony
324m
Bain des Japonais
Rivière des Kaoris
Anc. mine de Fer
Prony
Site ST7
Aiguille de Prony
Grand Port
Pointe de l'Abattoir
Baie Nord
Site ST9
Site ST12
Site ST11
BAIE DE PRONY
Nuw Kwé
Mont Mau
469m
Baie d'Alric
Baie de Koubé
Baie Est
Pointe Méré
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Alteration Crust
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Peridotite


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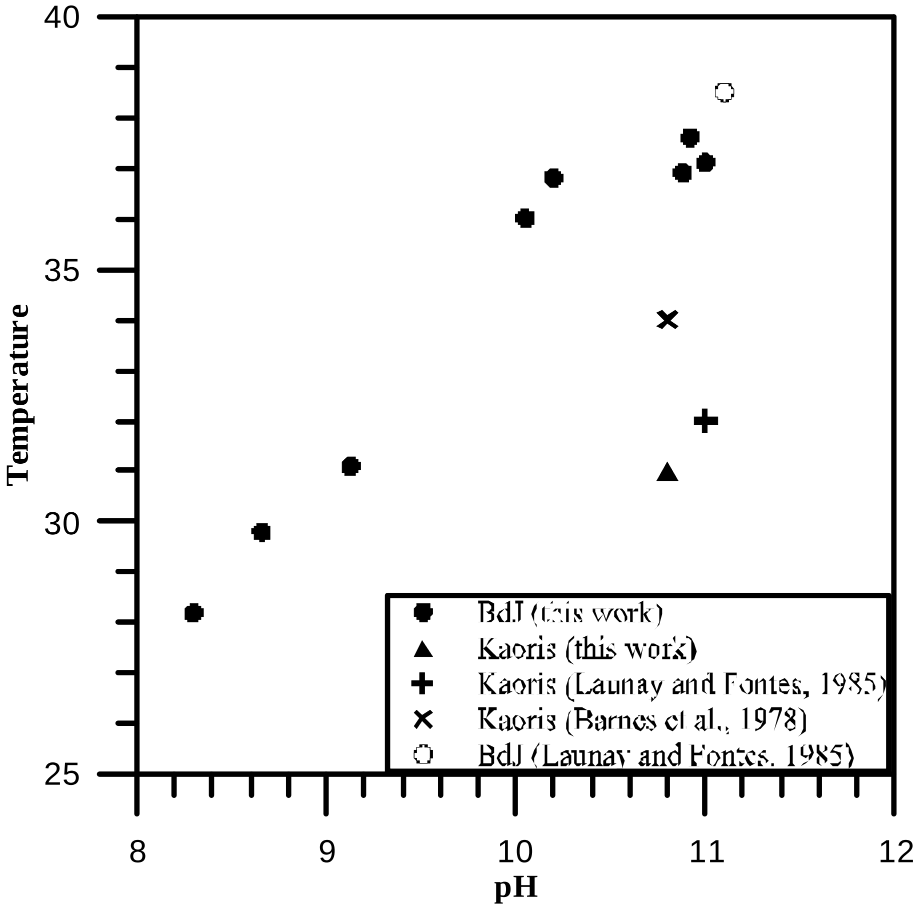
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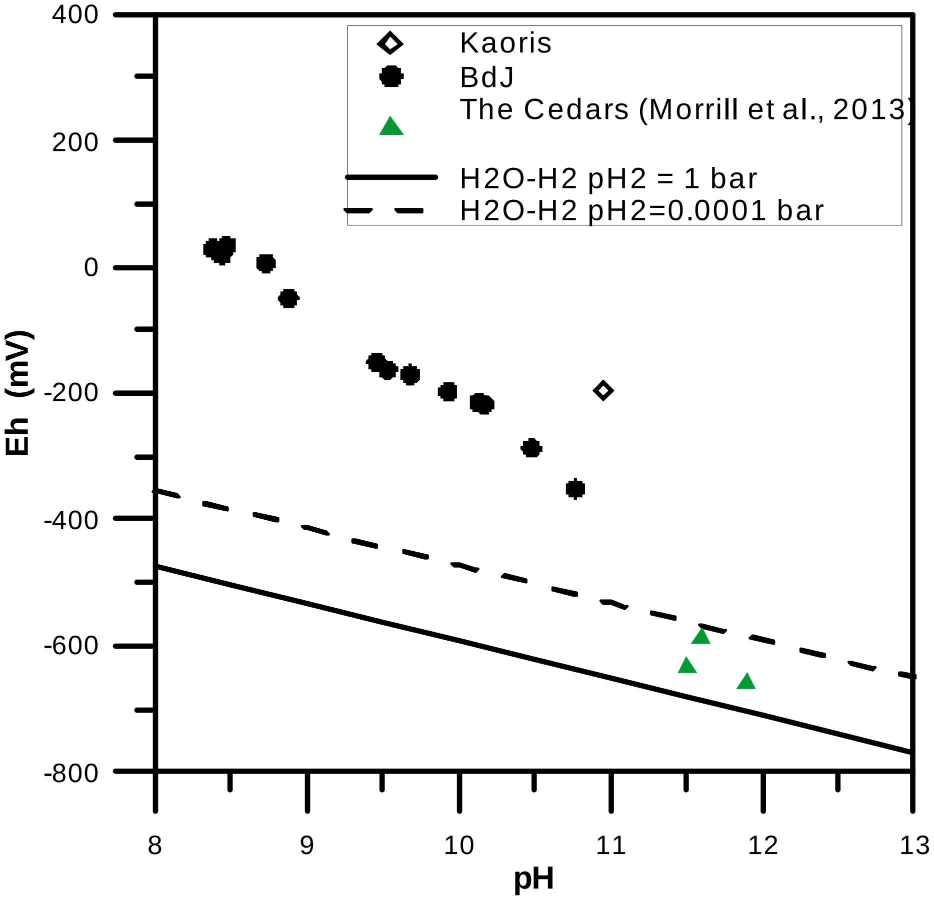
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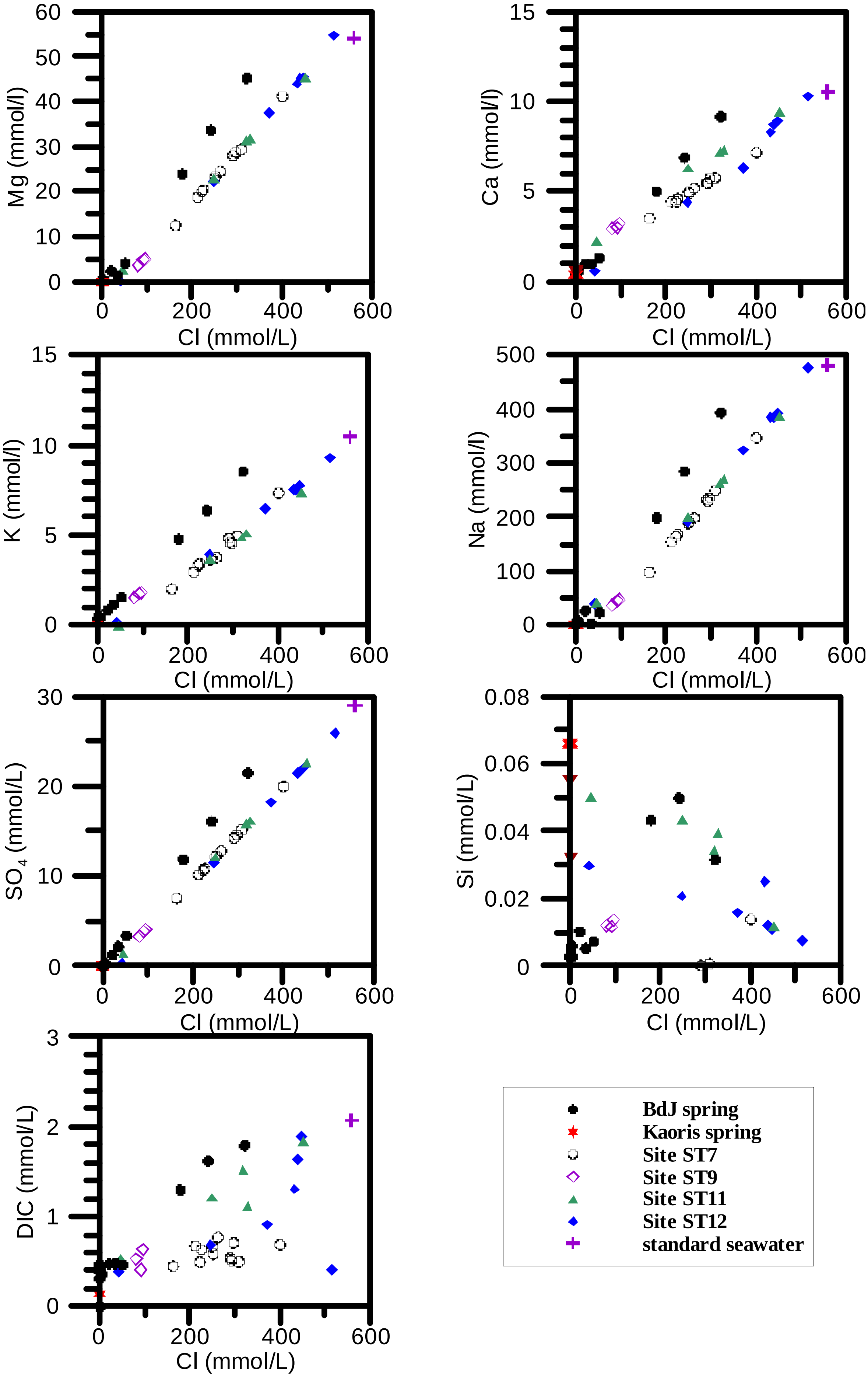
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BdJ spring
Kaoris spring
Site ST7
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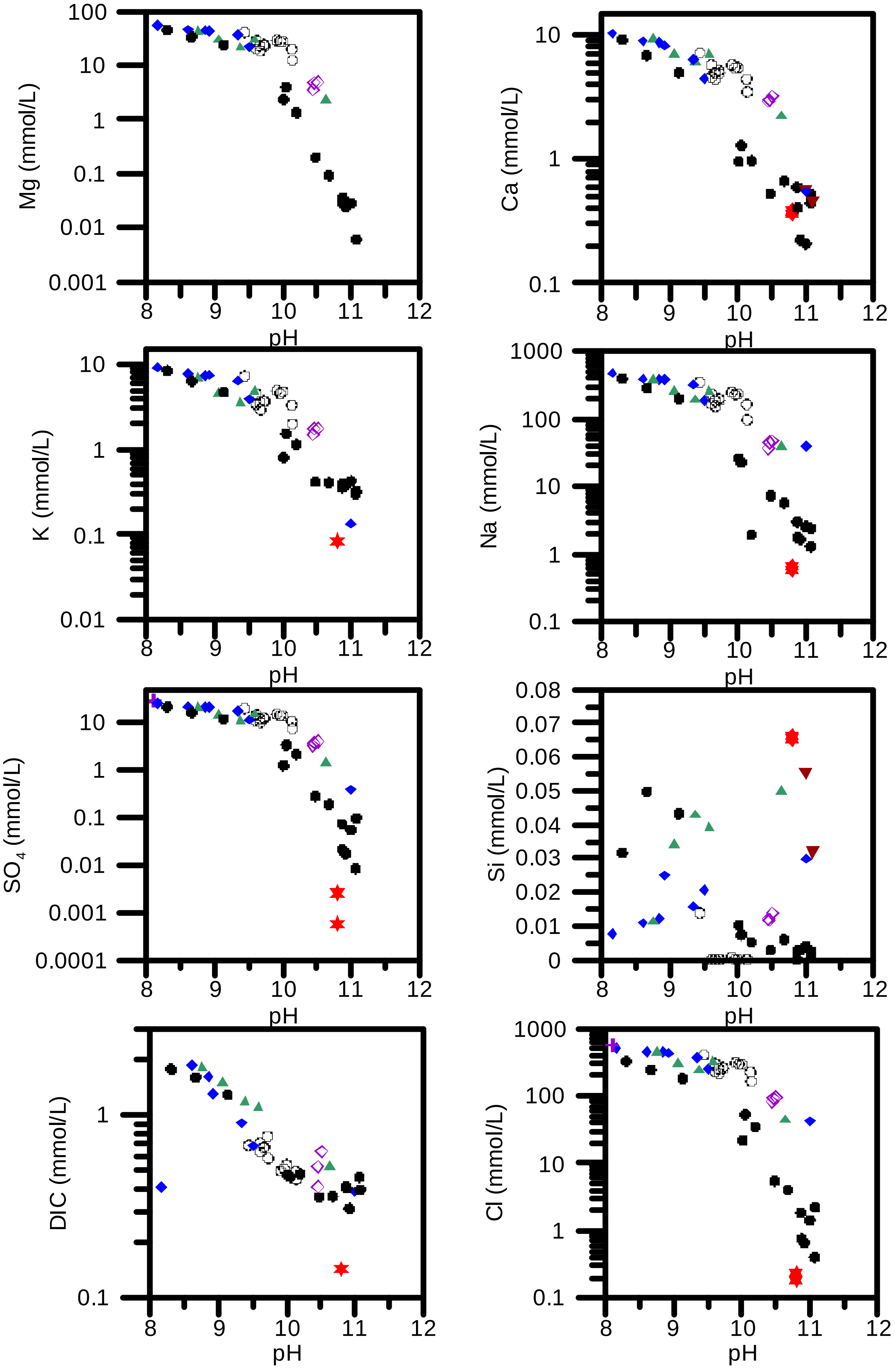
Site ST11
Site ST12
standard seawater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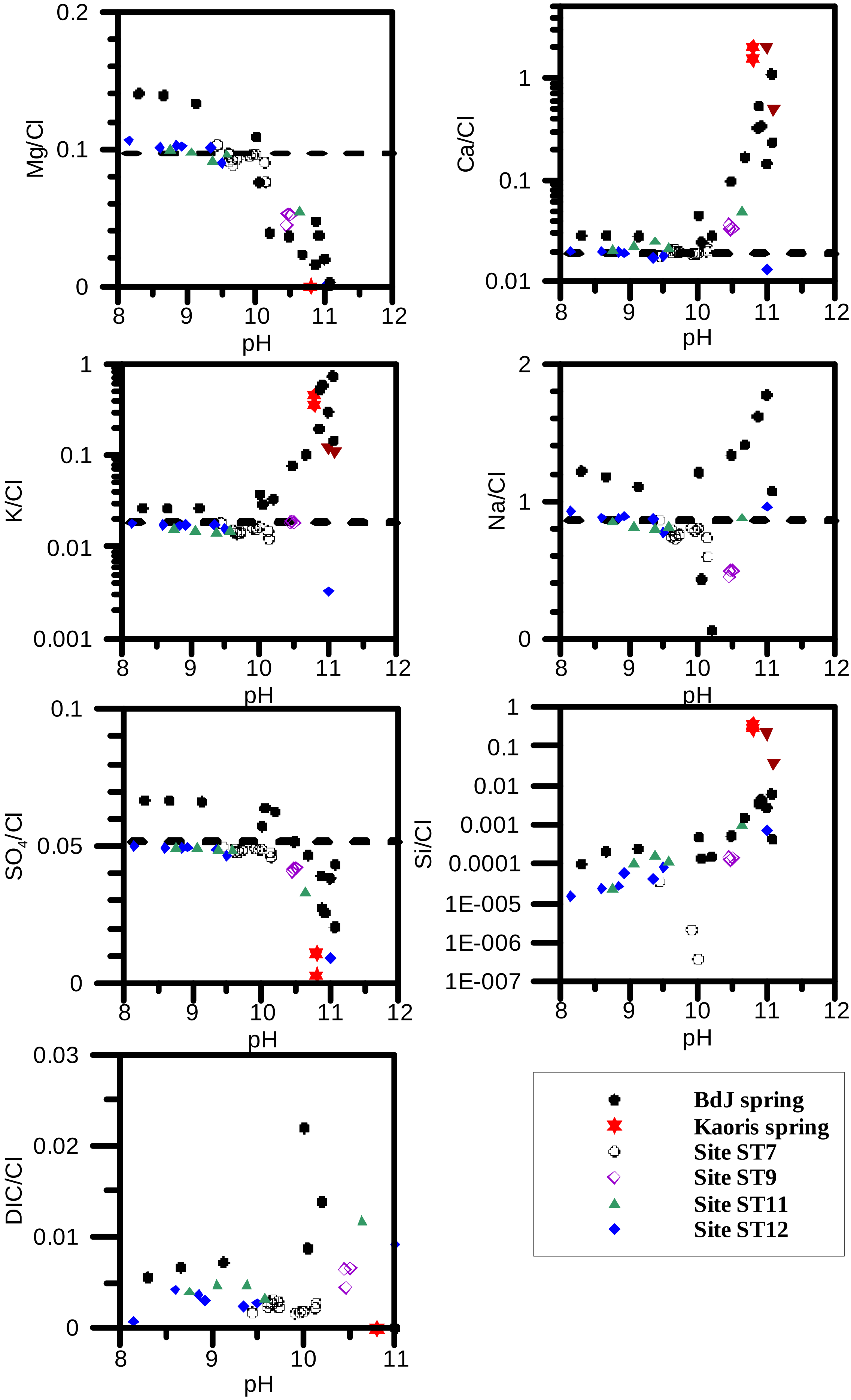
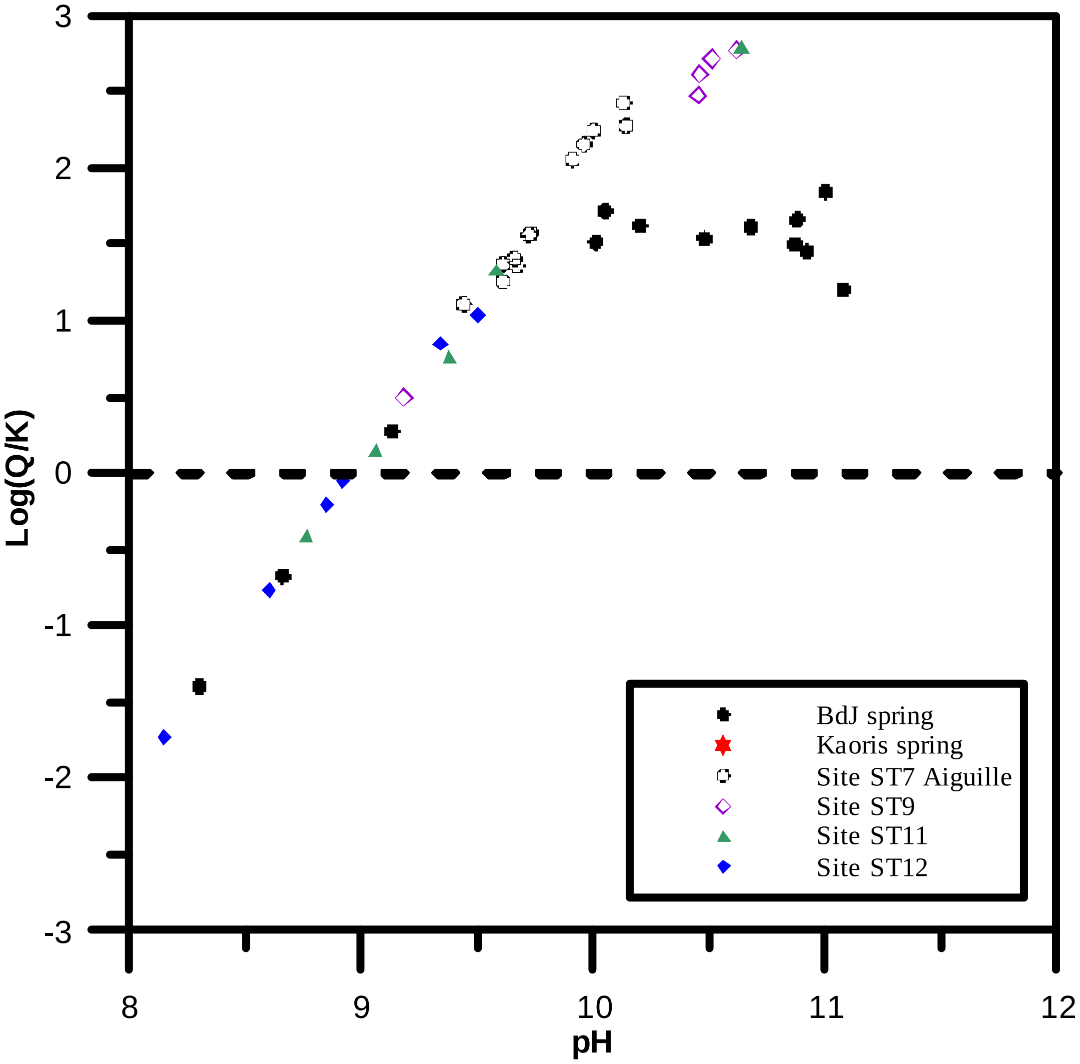
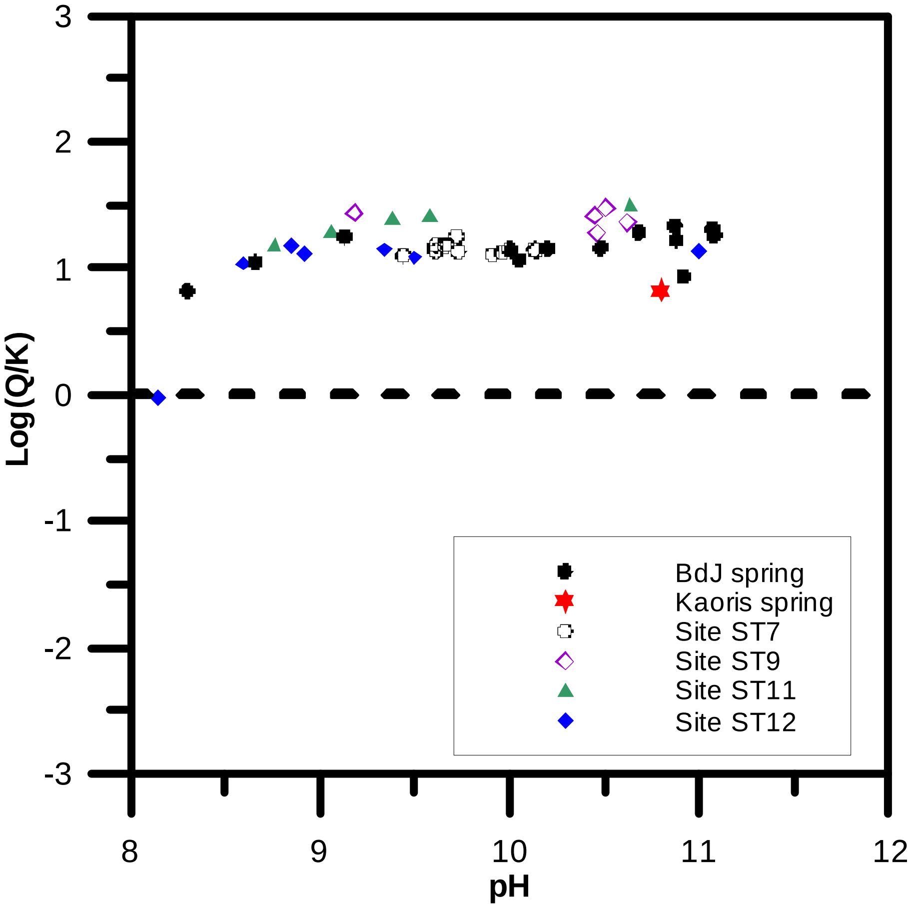
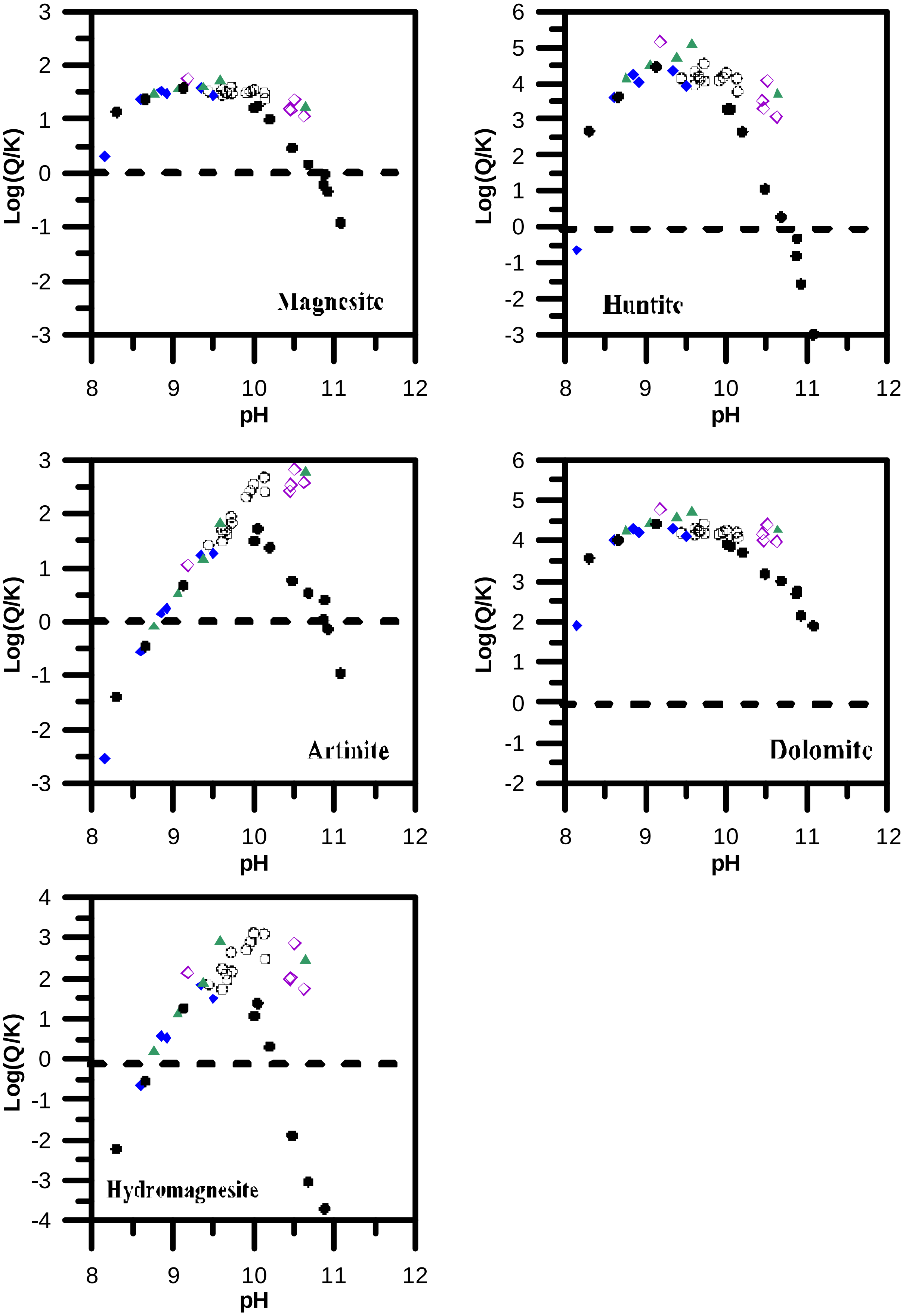
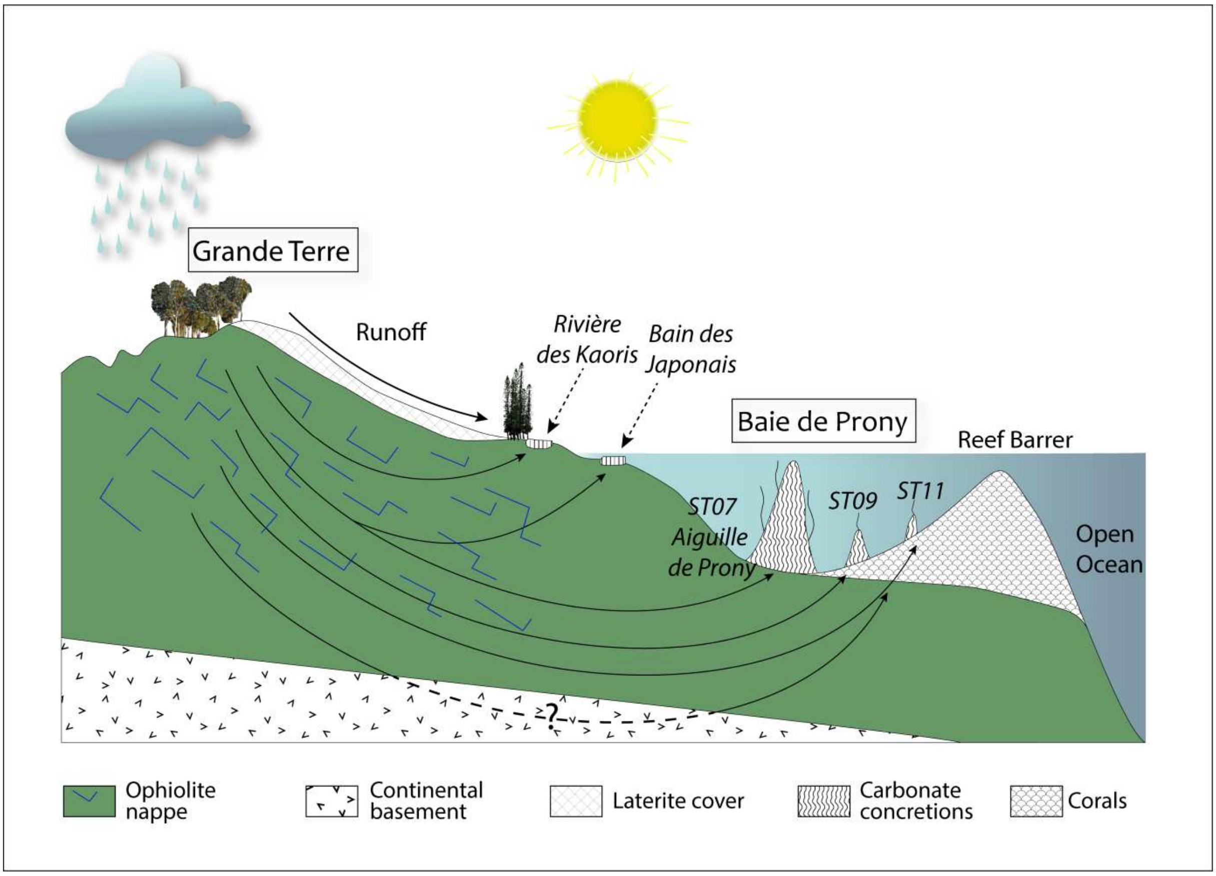
12
pH


Mg/Cl
0.2
0.1
0
Ca/Cl
1
0.1
0.01
K/Cl
1
0.1
0.01
0.001
Na/Cl
2
1
0
SO4/Cl
0.1
0.05
0
Si/Cl
1
0.1
0.01
0.001
0.0001
1E-005
1E-006
1E-007
DIC/Cl
0.03
0.02
0.01
0
8
9
10
11
12
pH
BdJ spring
Kaoris spring
Site ST7
Site ST9
Site ST11
Site ST12


3
2
1
0
-1
-2
-3
Log(Q/K)
8
9
10
11
12
pH
BdJ spring
Kaoris spring
Site ST7 Aiguille
Site ST9
Site ST11
Site ST12


3
2
1
0
-1
-2
-3
Log(Q/K)
8
9
10
11
12
pH
BdJ spring
Kaoris spring
Site ST7
Site ST9
Site ST11
Site ST12


Log(Q/K)
pH
Magnesite
Huntite
Artinite
Dolomite
Hydromagnesite
3
2
1
0
-1
-2
-3
6
5
4
-4
8
9
10
11
12


Grande Terre
Runoff
Rivière des Kaoris
Bain des Japonais
Baie de Prony
Reef Barrer
ST07 Aiguille de Prony
ST09
ST11
Open Ocean
?
Ophiolite nappe
Continental basement
Laterite cover
Carbonate concretions
Corals