

# **Stable isotope study of rainfall, river drainage and hot springs of the kerguelen archipelago, SW Indian Ocean**

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22 x  $\delta^{18}O$  rainfall + 11) and a summer runoff line ( $\delta D$  river drainage = 7.45 x  $\delta^{18}O$  river drainage + 6). Surface waters with low- ion concentrations, chlorine facies and stable isotope values infiltrate through fractures and lava flows recharging deeper groundwaters. Thermal 25 groundwater with low- (7 to 50 °C) and high- (50 to 100 °C) temperatures emerges in different localities in the volcanic archipelago. The low-temperature thermal waters might represent a mixture of high-temperature water with rainfall, thermal gradient changes or shallower infiltration compared to that for high-temperature thermal waters. The Rallier du Baty and Val Travers areas contain geothermal fluids with high-temperature springs, fumaroles and a large water flow. In the Rallier du Baty, the major ion chemistry and O, H, C 31 and S stable isotope ratio of low (7 to 50 °C) temperature spring waters in Rallier du Baty area demonstrate a geothermal-system recharged by meteoric water ( $δD$  H<sub>2O liquid</sub> = 7.0 x  $δ<sup>18</sup>O$  $_{\text{H2O}$  liquid + 0.5) rather than sea water. The chemical and isotopic compositions of elevated 34 temperature spring waters (50 to 100 $^{\circ}$ C) have a long and complex history of meteoric water 35 interacting with cooling magmas ( $\delta D$  H<sub>2O liquid</sub> = 1.78 x  $\delta^{18}O$  H<sub>2O liquid</sub> – 23). Surficial precipitation of aragonite, kaolinite, pyrite, native sulfur attest to a long livied geothermal system. A temperature of the geothermal reservoir has been estimated between 193 and 259 °C by cation geothermometry. The combination of minerals observed, major ion composition of water with thermodynamic modeling and stable isotope data suggest a geothermal system 40 with a series of water/rock interactions from 50 to 250 °C. The conductive cooling of rising of  $H_2O-CO_2$ -rich fluids have produced a  $H_2O-CO_2$  phase separation with the precipitation of secondary minerals.

Keywords: Kerguelen archipelago, geothermal springs, stable isotope composition, water-rock interaction

#### 1 Introduction

A prolonged record of continuous magmatic activity has been documented for the Kerguelen archipelago (Fig 1A; Giret, 1990; Weis and Giret, 1994; Weis et al., 1998; Mathieu et al., 2011), but little attention has been paid to the type of hydrothermal system responsible for the generation of hot springs and fumarolic activity. The volcanic archipelago of Kerguelen hosts several geothermal centers expressed by continuous fumaroles and thermal springs (Fig. 1B to E). Local rainfall and geothermal waters collected over the years by the permanent scientific base and episodic fieldwork (1981 to 1983 and 2002 to 2009) allow a survey of chemical and stable isotope values.

This survey involves of rainfall and fumarolic fields associated with thermal springs at temperatures below the boiling point of water. Heat and fluid flow in these areas have been 59 related to a magmatic source releasing  $CO<sub>2</sub>$  (e.g., Delorme et al., 1994) and periods of volcanism throughout the Kerguelen archipelago. However, there is a lack of observational data cataloguing recent volcanic eruptions due to the remoteness of the Kerguelen archipelago. Various authors have interpreted local magmatic petrogenesis and temperature in the Kerguelen archipelago (Giret, 1990; Luyendick and Rennick, 1977; Weis and Giret, 1994; Weis et al., 1998; Mathieu et al., 2011). Fewer authors have focused on seawater and meteoric water exchanged by hydrothermal water/rock interaction of geothermal systems associated with magma (Ballestracci and Nougier, 1984; Delorme et al., 1994; Verdier, 1989) and almost very few papers deal with present-day hydrology (Berthois and Le Provost, 1971), 68 hydrogeology or geothermal fluids ( $\delta^{13}C$  co<sub>2</sub>: Javoy et al., 1982).



mildly alkaline basalts and trachyte associated with a silicic peralkaline volcanic activity (Bonin et al., 2004; Weis and Giret, 1994) dated from 115 Ma to 39 Ma ago (Duncan, 2002; Grégoire et al., 1997; Luyendick and Rennick, 1977). The emerged part of the archipelago rises to 1850 m above sea-level (Fig. 1A) is a series of younger basalt flows and intercalated ashes with ages ranging from 30 Ma to 0.13 Ma (Giret, 1990; Weis and Giret, 1994; Weis et al., 1993, 1998; Gagnevin et al., 2003).

The rugged geomorphology (Fig. 1A) of the Kerguelen archipelago induces large rainfall volumes in the west (estimated ca. 8000 mm/y) and drier conditions on the eastern side of the island (~ 800 mm/y). This eastward difference relates to the Cook Ice Cap and Mount Ross (Rallier du Baty area, RdB; Fig. 1B) with a permanent snow line at ca. 1200 m. This mountainous system produces a cold and desertic climate with peat formation on the 103 archipelago. At the French weather station in Port aux Français (PaF: 49 ° 21'S: 70 ° 13'E: 104 Fig. 1A) the average daily temperature is 4.6 °C  $\pm$ 0.4 with 760 mm/y of rain (1951 to 2008: data source Météo-France; cf. Lebouvier et al., 2011). Interpretation of satellite images taken recently (cf. Berthier et al., 2009; Frenot et al., 1993; Vallon, 1977) suggests a glacial retreat of 10 m/y. This ice retreat has been interpreted as related to current worldwide temperature changes (Bergstrom et al., 2006; Smith, 2002) which in Port aux Français records +0.2 °C/y and -10 mm/y of rain during the last twenty years. The large "Rivière du Chateau" watershed 110 shows seasonal flow changes from 1 to 25  $\mathrm{m}^3$ /s and low dissolved solids content of waters. The low dissolved solids content of the water is related to a significant proportion of melted snow and rainfall rather than a contribution from sea sprays (Berthois and Le Provost, 1971). The Scientific base of Port au Français (150 people during summer) uses drinkable water from a river in the Loranchet area, while the hydrology and hydrogeology of the Kerguelen  $\left($  ca. 7215 km<sup>2</sup> with maximum 150 human being), is totally unknown.

The basaltic Kerguelen plateau hosts disseminated occurrences of altered tholeiitic lavas with clay minerals, sulfide, silica precipitation, zeolite and carbonates (Delorme et al., 1994; Renac et al., 2010; Verdier, 1989). The 'Rallier du Baty' (RdB) and 'Presqu'îles de la Société de Géographie' (PSG; Fig. 1A) locations represent visible, modern and large hydrothermal areas with a geothermal activity witnessed by fumarolic activity (Ballestracci and Nougier, 1984; 121 Gagnevin et al., 2003). The largest fumarolic area is located at 49 ° 37'S, 68 ° 47'E (Fig. 1B; Ballestracci and Nougier, 1984); and the highest flow of thermal waters recognized in the Val 123 Travers (49 ° 19' 41S, 69 ° 24' 10E; Fig. 1C, Berthois and Le Provost, 1971; Delorme et al., 1994).

3 Field measurements, water sampling, and chemical preparation

From 1981 to 1983 B. Blavoux and J. Nougier collected rainwaters (18 months) at the French meteorological station of PaF (Table 1, unpublished data provided by Bernard Blavoux). During summer camps (1981 to 1983) a series of river drainages and thermal springs throughout the whole archipelago were sampled (Fig. 1A; Tables 1, 2, 3). A digital elevation model and Qgis treatments associated these samplings (river drainage and springs) with tens 133 of small catchment areas  $(1 \text{ km}^2)$  and a larger watershed  $(30 \text{ km}^2)$  Fig. 1 B to E). These outlets are each other separated from 50 to 500 m (surface distance). Further scientific programs from 2002 to 2009 (Carbonatoker Dylioker and Hotvir IPEV program) allow summer sampling of river drainages, material from fumaroles, spring waters with low- to high-temperatures at Rallier du Baty, the Central-Plateau and Gallièni. Hot springs emerge in large ponds with thermal waters or as steam vents from fissures cutting lava flows or

pyroclastic rocks. Some outcrops and ponds are surrounded by centimeters to decimeters wide muddy fringes of gray to red altered volcanic rocks.



## 4 Chemical and isotope methods of fluid analysis





- 188 We measured  $\delta^{18}O$  H<sub>2O</sub>,  $\delta^{D}$  H<sub>2O</sub>,  $\delta^{13}C$  D<sub>IC</sub>,  $\delta^{34}S$  so<sub>4</sub> values by double (1981 to 1983 samples:
- 189 VG602 E) and 2002 to 2009 samples on triple collectors (ISOPRIME) isotope ratio mass
- 190 spectrometers equipped with a dual-inlet and a continuous flow system for  $\delta^{34}S$
- 191 measurements. All stable isotope values are reported as per mil (‰) relative to V-SMOW for
- 192 O and H in silicates and water (Coplen, 1988),  $\delta^{34}S$  values relative to V-CDT and  $\delta^{13}C$  values
- 193 relative to V-PDB. Analytical error and reproducibility for standards (NBS 18, NBS 19, NBS
- 194 123, NBS 127) and replicates are  $\pm 0.05\%$  for the  $\delta^{13}C$  Baco3 equivalent of  $\delta^{13}C$  DIC  $\pm 0.2\%$
- 195 for  $\delta^{34}S$  Baso4 and  $\pm 0.1\%$  for  $\delta^{18}O$  of water, and  $\pm 1\%$  for  $\delta D$  (2 $\delta$ ) of water
- 196 We quantified the anhydrous gases collected on charcoal  $(Ar, N_2)$  with an ISOPRIME dual
- 197 inlet system. The mass calibration was realized on mass 36 for Ar mass 28 for  $N_2$  and mass 44
- 198 for  $CO<sub>2</sub>$  and peak jumps. We measured the relative proportions of argon and nitrogen with a
- 199 calibration curve obtained with mixtures anhydrous gas (Ar/N2: 0.9/78; 2/ 98; 10/90; 20/ 80).
- 200
- 201 5 Results
- 202

#### 203 5.1 Rainwater and river drainage at Kerguelen.

204

Rainwater volume and temperature measured from 1981 to 1983 are similar to the recent data obtained from the meteorological station at Port aux Français (PaF; Table 1). Meteoric waters at Port aux Français have low-concentrations with dominant Na and Cl contents with a 1:1 208 Na/Cl molar ratio for temperatures between 1 and 12 °C (Table 1; Fig. 2A). The  $\delta^{18}O$  rainfall



221 Figure 2 and Tables 1 to 3

222

223 5.2 Geothermal localities

224

225 Thermal waters (from 7 to 100  $^{\circ}$ C) usually appear as isolated ponds. The RdB area hosts many springs with a lower flow rate than in VT and Gallièni areas (Val Travers in the Plateau Central; Fig. 1C). In the RdB area, many small ponds can be found within a few square kilometers (Rallier du Baty; Fig. 3A). Thermal waters from rocks to ponds flow through channels stained by iron oxides, and along clay-rich horizons (Fig. 3B) intercalated in lava units associated with basaltic scoria (Fig. 3C). Some thermal outlets are surrounded by precipitation of kaolinite (XRD: 1Md polytype), goethite, pyrite, and native sulfur (RdB). The 232 water temperature varies from an average surficial temperature of 6 to steam fumaroles at 100

°C. We arbitrarily define low-temperature springs as waters with temperatures higher than the 234 average surficial temperature (6 °C) up to a maximum of ~50 °C. This range of temperature corresponds to a majority of thermal waters disseminated through the archipelago with variable flow rates with traces of mineral precipitation (Infernet valley, Fallot glacier, and Gallièni Massif; Table 3). The Val Travers area and the active fumaroles in the Rallier du 238 Baty (RdB) area have both low- (7 to 50  $^{\circ}$ C, Fig. 3D and E) and high- temperature waters (50 to 100 °C; Figs. 1A and 3F).

240 In the RdB area, thermal springs (7 to 100  $^{\circ}$ C) are distributed from mean sea level to an 241 altitude of 500 m above sea level (a.s.l.). Thermal water flow rates vary from 10s' L/ s (50 to 242 220 m) to low-flow rates represented by condensed H<sub>2</sub>O liquid  $+H_2O$  vapor in a bubbling 243 oxide-rich ponds (ca. l L/ hour) located above 220 m. springs. The low-temperature thermal 244 waters occur from sea level to 220 m and high-temperature fluids  $(H<sub>2</sub>O$  liquid + vapor and 245  $CO_2$ ; 97 °C, Fig. 3F) between 220 m and 450 m above sea level.

246

247 5.3 Chemical and isotopic compositions of thermal fluids and hydrothermal 248 precipitates

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250 Low-temperature thermal waters, from sea level to 220 m, have dominant Ca, Mg, Na and 251 HCO<sub>3</sub> ion compositions (Table 3) with neutral pH and rare springs with a basic pH (Fig. 3B). 252 The Na/Cl molar ratios are higher than those measured at rainfall river drainages (Fig. 4A). 253 Some of the low-temperature thermal waters have high-Ca, K, Mg,  $NO_3$ <sup>-</sup>,  $SO_4$ <sup>2-</sup> and Br ion 254 contents with Na/Cl molar ratio < 1.9 below diluted seawater content and EC > 300 µS/cm 255 (Fig. 4A). These waters have been further described as mineral waters. The high- temperature 256 thermal waters ( $> 220$  m above sea-level) have neutral to acid pH ( $\sim$  3), low EC and Total

257 Dissolved Solids (TDS; Table 3) with Na, Cl to Na, Cl,  $SO<sub>4</sub><sup>2</sup>$  ion concentrations and very 258 low-Na/Cl molar ratios.

259 Oxygen and hydrogen stable isotopic values of mineral and low- temperature thermal waters 260 (7 to 50 °C) plot on or beside the local meteoric water line and define a line ( $\delta$ D  $_{H2O\;Hauid}= 7.0$ 261  $\times \delta^{18}O_{\text{H2O liquid}} + 0.5$ ; R<sup>2</sup>= 0.904) (LMWL). A large number of high- temperature thermal 262 waters (50 to 100 °C) are located on both sides of this LMWL. Nevertheless, some  $\delta^{18}O$  and **263**  $\delta$ D values of high- temperature thermal waters form a trend line ( $\delta$ D H2O liquid = 1.78 x  $\delta^{18}$ O 264  $_{\text{H2O liquid}} - 23$ , R<sup>2</sup> = 0.65; Fig. 4B) from LMWL toward more positive values of  $\delta^{18}$ O and  $\delta$ D 265 values.

266 In low- and high- temperature thermal waters dissolved carbon and sulfur species define a 267 wide range of stable isotopic values. The low-temperature thermal waters have  $\delta^{13}C$  DIC and 268  $\delta^{34}$ S so<sub>4</sub> values ranging from -5.6 to -23 ‰, and of +5 to +12 ‰, respectively (Table 3). The 269 spring having high-Ca, K, Mg, NO<sub>3</sub>, SO<sub>4</sub><sup>2</sup>, and Br ion contents has the highest  $\delta^{34}S$  s<sub>O4</sub> value 270 (11.6 ‰) and the lowest  $\delta^{13}C$  DIC value (-23 ‰). High-temperature thermal springs, with 271 lower TDS contents than low- temperature springs (7 to 50 °C), have  $\delta^{13}C$  DIC and  $\delta^{34}S$  so4 272 values ranging from -5 to -10  $\%$  and +3 to +9  $\%$  e, respectively (Table 3). 273 The two steamers associated with high-temperature waters consist of  $H_2O$  vapor dominant 274 (approximately 95 %) with CO<sub>2</sub> ( $\delta^{13}$ C co<sub>2</sub> = -5.1 %  $\leq$  0.2), and S-rich gas attested by the odor

275 and native sulfur in muddy deposits. The measured anhydrous gases in vapor dominant steam 276 have a total pressure lower than atmospheric pressure (0.09 MPa) with dominant N<sub>2</sub> (98.7 %) 277 minor Ar  $(1.2\%)$  and traces of He and CO (close to detection limit= 1 ppmv).

278 The X-ray diffraction of mineral precipitates in the zone of low-temperature springs (0 to 220 279 m) identified precipitates of aragonite (Fig. 3D) or amorphous silica and goethite (Fig. 3E).



The river drainages during the summer are slightly more saline with O and H isotopes data forming a restricted domain of values as rainfalls (Table 1, Fig. 2A). The increasing salinities from West to East (Gallièni, Jeanne d'Arc, Ronarc'h and Loranchet plateau) suggest that runoff is Na-enriched either by leaching of a Na-rich surface of rocks or by storms in the eastern archipelago. We favor higher proportion of sea spray mixed with rainfall during storm events considering the low-altitude of the eastern part of the archipelago. Whereas, mountains on the western side of the archipelago reduce the inland incursion of storms as shown by the western-side watershed basins (Fig. 1A).

The O and H stable isotope values of river drainages aligned and centered with the LMWL 311 confirm that they are meteoric water (rainfall and snowmelt: lowest  $\delta^{18}O$  and  $\delta D$ ) runoff and can percolate throughout the Kerguelen volcanic plateaus. The river drainages from the western side of the Archipelago (RdB) have the lowest Na-Cl concentrations, and similar to slightly higher O-H stable isotope values (Table 2, Fig. 2B). We interpreted this data as dominant meteoric waters with low salinity related to the dilution of sea spray by more rain (orographic effect: estimated around 8000 mm per year on the western coast and 800 m per year on the Eastern side PaF).

#### 6.2 Organic contamination of thermal water

Flowing thermal springs or larger geothermal areas in Rallier du Baty and Val Travers have different recharge areas (Fig. 1B and 1C) and geothermal reservoirs. Each of these geothermal areas may represent one or several sources of steam; high-temperature thermal water derived from condensed steam and mixtures with meteoric water (e.g., Giggenbach and Stewart, 1982; Marini, 2004). Moreover, thermal springs (the Infernet Valley, Fig. 1B) located on the



350 infiltration than the high-temperature waters. However, the lack of a time series of analysis 351 did not permit the characterization of this phenomenon. In both cases, the meteoric recharge 352 would be driven by the topography and infiltration through fractures, or along discontinuities 353 between lava-flows and pyroclastic rocks (Fig. 3F). Their  $\delta^{13}C$  <sub>DIC</sub> and  $\delta^{34}S$  <sub>SO4</sub> data (Table 3) 354 confirm dominant sources of inorganic carbon (magmatic- mantle=  $-6.0\%$   $\geq 1$ ; e.g., Javoy et 355 al., 1982) and sulfur (Hattori and Muehlenbachs, 1980; Watanabe and Sakai, 1983). 356 Moreover, the substantial precipitation of aragonite observed (Fig. 3D) with  $\delta^{13}C$  values 357 recognized in hydrothermal systems (eg., Pichler and Veizer, 2004) suggests an even more 358 important proportion of inorganic  $CO<sub>2</sub>$  in the past than the present-day.

359

#### 360 6.4 Origin of 50 to 100 °C waters

361

362 The high-temperature thermal waters and fumaroles are the most representatives of a 363 significant thermal flux or magma-derived fluids. The fluid flow of hot springs with thick 364 kaolinite precipitates suggest a long-lived period of fluid circulation. The other thermal 365 springs was not sufficient nor the composition stable enough for analysis. Therefore, the long-366 lived flow, temperature, and chemistry was not estimated for other localities. This kaolinite 367 may have precipitated from fluids different from the present-day ones. Consequently,  $\delta^{18}O$ 368 H<sub>2O liquid</sub> (-5.1 ‰) and  $\delta$ D <sub>H2O liquid</sub> (-39 ‰) in equilibrium with kaolinite were first calculated 369 (Savin and Lee, 1988; Sheppard and Gilg, 1996) with the present-day temperature of steam (T 370 measured = 97 °C; Table 3). The calculated  $\delta^{18}O_{H2O}$  liquid and  $\delta D_{H2O}$  liquid are comparable to 371 present-day O-H stable isotope values  $(\delta^{18}O_{H2O~liquid}$  measured: -4‰;  $\delta D_{H2O~liquid}$  measured: -372 32 ‰). Secondly, we used an equilibrium temperature of 105 °C (T measured = 97 °C) with 373  $\delta^{18}$ O kln and δD kln of kaolinite (cf. paragraph 5.2) and its spring water (δ<sup>18</sup>O H2O liquid= -4 ‰;



meteoric recharge is in agreement with the low-salinity of all thermal springs in the Kerguelen archipelago. The meteoric recharge in the RdB area is delimited by a watershed in the surrounding volcanic plateaus with an average altitude of 700 m a.s.l. (Figs. 1B and 2) and the permanent snow line at a maximum altitude of ~1200 m (Table 2). Consequently, the higher  $394 \delta^{18}$ O and  $\delta$ D values of the intercept suggests, a meteoric water recharge less influenced by melted snow than river drainage or a similar recharge affected by additional processes such as 396 vapor-condensed liquid separation (Giggenbach and Stewart, 1982), H<sub>2</sub>S- CO<sub>2</sub> -H<sub>2</sub>O isotope exchange, and water-rock interaction (reference aforementioned). These processes are

398 evidenced by the composition of fumarole steam with anhydrous gas and an  $N_2/$  Ar molar 399 ratio of 80, similar to that of atmospheric air (84; cf. Fischer et al., 1998; Giggenbach, 1995; 400 Shaw et al., 2003), as well as the inorganic carbon ( $\delta^{13}$ C co<sub>2</sub>= -5.1 ‰ ±0.2) and the native 401 sulfur  $(\delta^{34}S)$  native sulfur= 3.5 ‰; Table 3; e.g., Craig, 1963; Javoy et al., 1982; Hoefs, 1980; 402 Lowenstern et al., 1999). These additions of gas through hydration may contribute to an 403 increase in the proportion of sulfuric and carbonic acids (Ohmoto and Rye, 1979) and kinetic 404 water/rock interaction (Fritz and Fontes, 1986; Giggenbach, 1991; Liebscher and Heinrich, 405 2007).

406

407 6.5 Process changing stable isotope compositions of high-temperature of thermal 408 waters

409

410 In the RdB hydrothermal systems, condensed fumarole steam (steamers:  $\delta^{18}O_{H2O\text{ vapor}} = +3\%$ 411 and  $\delta$ D <sub>H2O vapor</sub> = -20 ‰; Table 3) is O and D enriched compared to fluids from other high-412 temperature springs (Fig. 4B). The calculated  $\delta^{18}O$  H<sub>2O liquid</sub> (2.24 ‰) and  $\delta D$  H<sub>2O liquid</sub> (-7.8 ‰) 413 values in equilibrium (oxygen and hydrogen fractionation factors; Majoube, 1971; Horita and 414 Wesolowski, 1994; Table 2) with these vapors for a temperature of 100  $\degree$ C are more positive 415 that of the estimated meteoric recharge ( $\delta^{18}O_{\text{H2O liquid}} \sim -5\%$   $\epsilon$  ±1 and  $\delta D_{\text{H2O liquid}} \sim -35\%$   $\epsilon$ ; 416 part. 6.4). This calculation suggests either a different recharge or a vapor-liquid separation 417 associated with a stable isotopes kinetic-exchange. 418 This kinetic exchange can be estimated looking at the slope of  $\delta^{18}O_{H2O}$  and  $\delta D_{H2O}$  values for

419 high-temperature springs with a dominant H<sub>2</sub>O- liquid in RdB. The trend line with  $\delta$ D <sub>H2O</sub>

420  $_{\text{liquid}}$   $\delta^{18}$ O <sub>H2O liquid</sub> with a slope of 1.78 then integrates buoyancy and changing vapor/liquid

421 ratios from depth to atmospheric pressure. The calculated  $\delta D$  H<sub>2O liquid</sub>  $\delta^{18}O$  H<sub>2O liquid</sub> ratio, 422 equivalent to the  $\delta D$  H<sub>2O liquid-vapor</sub>/ $\delta^{18}O$  H<sub>2O liquid-vapor</sub> ratio, is lower than the predicted ratio 423 obtained by equilibrium or kinetic evaporation at  $\leq 100$  °C (below 100 °C: equilibrium= 5.3, 424 Majoube 1971 and kinetic evaporation= 2 to 5, Dansgaard 1964; Gonfiantini et al. 1973; Fig. 425 4B). This  $\delta D_{\text{H2O liquid}} / \delta^{18}O_{\text{H2O liquid}}$  ratio below 2 exclude the equilibrium and kinetic process 426 of liquid- vapor separation below  $\leq 100$  °C. These O and H stable isotope changes may also 427 relate to (i) isotopic fluid exchange  $(CO_2, H_2S,$  and  $H_2O)$ , ii) fluid/rock interaction with O-H 428 isotopic exchange (Craig et al. 1956)., iii) Mixing of meteoric water and magmatic-like water 429 (cf.  $\delta^{18}O = +9$  to  $+10\%$  and  $\delta D = -8$  to  $-18\%$  c; Giggenbach, 1992b).

430 Firstly, we established a conceptual model that considers the lower part of the RdB reservoir

431 as a rock-dominated system and the upper part of the reservoir with a steam dominated cell

432 (Giggenbach, 1992b). We examined, the  $CO_2$ ,  $H_2S$  and  $H_2O$  interactions able to produce

433 dominant "horizontal" <sup>18</sup>O shifts (cf. Giggenbach, 1992a) related to a  $CO<sub>2</sub>-H<sub>2</sub>O$  oxygen

434 isotopic exchange (Majoube, 1971) and a  $H_2S-H_2O$  H isotopic exchange (cf. Galley et al.,

435 1972). In both cases, the low-CO<sub>2</sub> (measured CO<sub>2</sub>  $\leq$  5 wt. %) and estimated H<sub>2</sub>S proportion

436 (H<sub>2</sub>S odor) and their C and S isotopic values would not produce an <sup>18</sup>O shift as observed

437 (Table 3; Fig. 4B; cf. Chiodini et al., 1993; Giggenbach, 1987).

438 The second hypothesis (i),  $\delta^{18}O$  and  $\delta D$  on both above and below of the LMWL may

439 represent vapor and condensed liquid separation. The oxygen and hydrogen stable isotope

440 values of condensed liquid on the LMWL and vapor above the LMWL (Fig. 4B) with a δD

441 H<sub>2O liquid</sub>  $\delta^{18}$ O <sub>H2O liquid</sub> ratio of 1.78 would represent a high-temperature H<sub>2</sub>O liquid-vapor

442 system at  $\sim 250$  °C with a phase separation probably occurring in ascending fluids. Finally,

443 hypotheses ii) and iii) are difficult to separate since water/rock interaction may produce large

444 O isotope shifts driven by a thermal meteoric fluid/ magmatic rock interaction (Craig et al.,

1956). The stable isotope values tend toward this large domain so-called "magmatic-like water" (cf. Capasso et al., 1997; Chiodini et al., 2000; Giggenbach, 1992b). In this case, the 447 hydrothermal alteration may shift the  $\delta^{18}O$  H<sub>2O liquid</sub> and  $\delta D$  H<sub>2O liquid</sub> toward the field of magmatic-like water. However, no high-temperature hydrothermal mineral (K-feldspar, epidote) has been observed in the RdB area. 450 We also calculated temperatures derived from different S isotopes in  $SO<sub>4</sub><sup>2</sup>$ -rich water and pyrite (S-isotopes fractionation factor: Ohmoto and Rye, 1979; Robinson, 1973). Assuming 452 equilibrium, the calculation of  $\delta^{34}S$  so42- $\delta^{34}S$  pyrite suggest a temperature varying from 240 to 300 °C. This calculation indicates either an inappropriate assumption of equilibrium or hot-454 springs with a fluctuation of temperature (dominant kaolinite ca. 100 °C, minor pyrite 240 to 455 300 °C). For a similar assumption of equilibrium, the C stable isotope values of  $CO<sub>2</sub>$  gas and  $CO<sub>3</sub><sup>2</sup>$ - rich water (C isotope fractionation factor: Mook et al., 1974).  $CO<sub>2</sub>$  and HCO<sub>3</sub><sup>-</sup> 457 equilibrium would be between 50 and 115  $\degree$ C. The range of calculated temperatures indicate 458 temperatures varying from 300 to 50 °C, with phase separation to water/rock interaction.

6.6 Ion concentration ternary diagrams and cation thermometers for water

The temperature range of the RdB geothermal reservoir was bracketed by the major element composition. The large surface of this geothermal area is attested by the volcanic context of the archipelago, and warm soils in the Infernet valley (Fig. 1B), where thousands of animals breed. This thermal flux could be regional or a local convective heat flux (Ballestracci and Nougier, 1984). The calculated critical points of water (NaCl between 0.001 467 and 0.1 weight %;  $CO_2$  varying from 1 to 10 weight %; Table 2) between 340 and 370 °C for

22 MPa to 23 MPa (Duan and Sun, 2003) will limit the maximum temperature of the hydrous geothermal reservoir.

The low- to high-temperature springs tend to have low- Na -Cl for acid and sulfate-rich thermal waters. These chemical compositions may be the consequence of several processes and the geometry of the geothermal reservoir. Processes can be due to hydrothermal cells with steam or condensed steam (e.g., Giggenbach and Stewart, 1982; Marini, 2004), mixtures of 474 low-Na rainfall with a Na-precipitating phase,  $SO_4^2$  enrichment for low Cl concentrations with water-rock interaction (cf. Hedenquist et al., 1994; Sheppard, 1986; Taylor, 1979), and up-flow circulation (Giggenbach, 1988).

We estimated the temperatures of the geothermal reservoir with a cation thermometer. The calculated temperatures assume a chemical equilibrium between water and mineral in the

geothermal reservoir (e.g., Bowers and Taylor, 1985; Fournier and Potter, 1982; Pope et al.,

1987; Giggenbach, 1988; Fournier, 1991; Simsek and Gülec, 1994; White et al., 1971).

481 Thermal springs with steam loss with CO<sub>2</sub>, acid pH, or amorphous silica, kaolinite, and

aragonite indicate under-saturation or saturation of carbonates and silicates during conductive

undercooling or fluid transport. These conditions exclude the assumption of chemical

equilibrium for Si, Ca compounds and the use of Si-Ca geothermometry.

Consequently, a preliminary calculation of the temperature of the thermal reservoir used

information on conservative elements such as cationic diagram and thermometry (Fig. 5A;

Giggenbach, 1988). Nevertheless, the cation diagram shows that most low and high-

temperature spring waters are not classified as "fully equilibrated mineral waters" (Arnórsson,

2000; Arnórsson et al., 1983; Giggenbach, 1988). One acid and two basic thermal fluids plot

490 in the field of fully equilibrated water. A Cl<sup>-</sup>,  $SO_4^2$  and HCO<sub>3</sub> diagram (Fig. 5B) and the

491  $SO_4^2$ -rich water suggest of volcanic origin; whereas the HCO<sub>3</sub> -rich waters are reported in

the literature as related to peripheral waters or mature fluids.



6.7 Thermodynamic modeling of water/rock interaction in Rallier du Baty

Whole fluid-rock interaction and associated chemical changes have been reconstructed with the thermodynamic model (PhREEQC 3.3 software, with the Lawrence Livermore National Laboratory thermodynamic database: LLNL database, July 2017; Parkhurst and Appelo 1999). We selected chemical compositions of the thermal spring waters in the fully equilibrated field (Fig. 5A) with an estimated temperature of the geothermal reservoir between 200 and 300 °C (Table 2). This model uses the influx of meteoric water with a chemical composition of river drainage in RdB (Cap Bourbon) representing the meteoric and hydraulic recharge of the geothermal reservoir (Table 1). This meteoric recharge can interact with the anorthite, albite, olivine, Ca-pyroxene, pyrite, and quartz for volcanic glass, considered a primary mineral of the surrounding rocks (Beaux, 1986; Moine et al., 2004), and produce secondary minerals observed in the RdB area (goethite, amorphous silica, aragonite, kaolinite, and pyrite) or found in the Kerguelen archipelago (analcime, clinoptilolite, stilbite, illite, smectite, quartz, K-feldspar (adularia) and carbonates; cf. Renac et al., 2010; Verdier, 1989).

This modeling assumes a first stage with the injection of meteoric water into a geothermal reservoir where reactions reach equilibrium. The second stage will examine chemical changes in fluids produced from the geothermal reservoir toward the surface. Temperature and 520 pressure in the first stage vary from 6  $\degree$ C to a maximum temperature of 306  $\degree$ C and from atmospheric pressure to 24 MPa. In order to follow chemical changes 6 cells with a dT/dP 522 gradient of  $+50 \degree C$ / $+4 \text{ MPa}$  were separated. In summary, a calculation with increasing temperature and pressure predicts the dissolution of ferromagnesian minerals, feldspars in 524 trachyte and the production of a Na, Ca, H<sub>2</sub>S and  $SO_4^2$  acid brine (pH ~ 4.5) well known to exist in oceanic hydrothermal areas (Brombach et al., 2000; D'Amore and Panichi, 1980; Pope et al., 2009). Such fluids in RdB and VT would represent the most thermal and pristine geothermal fluids. Nevertheless, acid thermal waters represent a small number of recognized hot springs in the Kerguelen archipelago (Table 3). The results of these calculations combined with stable isotope values indicate that the analyzed geothermal waters have evolved 530 chemically. Consequently, the high-temperature  $H_2O$  liquid-vapor or  $CO_2$ -HCO<sub>3</sub> represent a phase change and a separation during fluid ascent from the geothermal reservoir to the surface (adiabatic cooling). This modeling predicts the formation of secondary minerals (smectite, 533 smectite-illite below 200 °C, quartz and K-feldspar (adularia) from 150 to 306 °C) that haven't been recognized in the RdB or VT areas but described by Verdier (1989) in highly altered rocks.

536 The second stage of this thermodynamic model deal with ascending fluids and mineral 537 changes from the geothermal reservoir (306 °C) through conductively cooling trachyte (50 to 538 100 °C). As observed, the calculation predicted the alteration of a primary mineral and the 539 precipitation of kaolinite (stable isotopes ca. 100 °C) and amorphous silica (Fournier and 540 Rowe, 1966) with pyrite at temperature starting at 150 °C. These secondary minerals 541 equilibrate with acid pH, a low-Si concentration with high-Na-Ca and  $SO_4^2$  concentrations.

The low-Na concentration of the thermal waters suggests the precipitation of Na-rich secondary minerals (zeolite or smectite).

The differences between the analyzed composition of the thermal waters and the calculated 545 composition combined with the interpretation of  $\delta^{18}$ O,  $\delta$ D,  $\delta^{13}$ C and  $\delta^{34}$ S values suggest that the RdB area consists either of several hydrothermal cells (heated groundwater) and/or a 547 progressive separation of fluids (H<sub>2</sub>O liquid-vapor, cation-anion changes,  $CO<sub>2</sub>$  dissolved -gas) 548 takes place. The  $\delta^{18}O$  and  $\delta D$  hypothesis of an 'incomplete water-rock interaction' would be derived from several hydrothermal cells with different liquid-vapor separation as suggested by 550  $a$  SO<sub>4</sub><sup>2</sup>-rich water related to volcanic-sourced steam (part 6.3).

We combined these different hypotheses in a schematic cross-section in the RdB (Fig. 6).

This cartoon indicates a high-temperature geothermal reservoir with acid brine and water-rock 553 interaction between 250 and 300 °C. The final stage is represented by a  $CO<sub>2 gas</sub>$ -HCO<sub>3</sub><sup>-</sup> phase 554 separation (50 °C) associated with an N<sub>2</sub>/Ar ratio similar to the atmospheric ratio. Between these two stages, conductive cooling of rising fluids has produced carbonates, amorphous 556 silica, and kaolinite ( $\sim 100 \degree C$ ). The depth of the RdB geothermal reservoir is difficult to determine because of the unknown geothermal gradient. Therefore, the meteoric origin of the water recharging the RdB hydrothermal system (surrounding plateau: 700 to 1200 m, Fig. 1) promotes a maximum hydraulic pressure of 7 to 12 MPa. Assuming a maximum pressure of about 23 MPa (critical point of liquid water) then their differences would represent the hydrostatic pressure below sea level. The difference ranges between 16 (23-7 MPa) and 11 (23-12) MPa equivalent to a depth of 1.6 km to 1.1 km or 0.4 to 0.6 km under hydrostatic or lithostatic pressure. In such a context, the RdB geothermal gradient (300 °C/ 0.4 km or 300 564 °C/0.6 km or 300 °C/ 1.1 km or 300 °C/1.6 km) is equivalent to the Iceland or Guadeloupe active geothermal fields (Pope et al., 2009; Brombach et al., 2000).



7 Summary and conclusions

The results of the comparison of chemical composition and stable isotope values for rainwater, river drainage, minerals, and thermal spring waters supports the concept of meteoric recharge and geothermal activity. The large volcanic plateau with issuing low- to high- thermal waters in the different areas of the Kerguelen suggest that heated groundwater might represent shallow and deep fluids and thermal water diluted with meteoric recharge. Nevertheless, the fumarole field of Rallier du Baty and other geothermal locations in the Kerguelen archipelago represent the surficial expression of meteoric-water hydrothermal systems. In the Rallier du Baty, meteoric thermal waters are chemically modified by boiling and gas-water-rock interaction. Meteoric recharge and thermal fluids such as acid brines have interacted with anhydrous gas from magma to alter igneous rocks and to precipitate kaolinite (ca; 100 °C), amorphous silica, carbonate on the surface and presumably adularia and zeolite at depth.

The O, H and S stable isotope ratios confirmed a high-enthalpy hydrothermal system with 584 temperatures between 250 to 300 °C and HCO<sub>3</sub> separation to CO<sub>2</sub> between 50 and 115 °C 585 associated with an  $N_2/Ar$ - like atmospheric ratio gas and the precipitation of kaolinite. The depth of 400 to 1600 m below sea level of the geothermal reservoir was calculated using values for lithostatic and hydrostatic pressure.

The stable isotope and chemical data presented in this paper could encourage further comparisons to be made with infrared thermography, and fluid-inclusion microthermometry

to obtain a realistic interpretation of earlier magmatic activity in the simulation of active

geothermal systems throughout the Kerguelen archipelago.

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digital elevation model of the Jeanne d'Arc area with locations of sampled rivers and their

watersheds; E) digital elevation model of the Gallièni area with sampling locations of river and thermal springs and watershed associated.



Figure 3: A) Fumarole field of Rallier du Baty (420 m a.s.l.), B) Thermal water iron oxides and silica particles in the Upper Infernet valley, C) Steam and thermal water emergence in an altered pumice level at the Infernet valley in the Rallier du Baty area, D) aragonite crust encountered nearby low-temperature thermal springs in Plage du Feu de Joie E) modern opal precipitates on Plage du Feu de Joie, F) Steamer sampled at Mount des fumarole for fluids (H<sub>2</sub>O and CO<sub>2</sub>, anhydrous gas) and alteration phases (kaolinite and pyrite).

Figure 4: A) Na vs. Cl concentration (mg/l) of mineral and thermal spring waters of

634 Kerguelen (7 to 50 °C: blue circle; 50 to 100 °C red circle); B)  $\delta$ D vs.  $\delta^{18}$ O diagram, showing

635 the isotope composition 7 to 50 °C (blue circle) and 50 to 100 °C (red circle) of mineral and

thermal spring waters of the Kerguelen archipelago. Springs with carbonate, opal, kaolinite

precipitates are marked. Also shown are the GMWL (dashed line), the composition of

'andesite type magmatic waters' (Giggenbach, 1992) and Na, Cl and O-H stable isotope composition of RdB watershed water A trend line for O- H stable isotope values is shown for 50 to 100 °C spring waters from the RdB (plain line).

Figure 5: Mineral and thermal water composition of Kerguelen (blue circle: 7 to 50 °C waters; red circles: 50 to 100 °C waters and composition fields for rainwater and watershed waters) in 644 A) Na–K–Mg<sup>1/2</sup> triangular diagram, and B)  $SO_4^2$ –HCO<sub>3</sub>–Cl (%) triangular diagram and fields of immature and fully equilibrated waters as well as some calculated temperatures using Na-K and Mg-K geothermometers (after Giggenbach 1988).

Figure 6: Schematic model of the Rallier du Baty geothermal field based on interpretations of the water chemistry and stable isotope values. The model presents infiltration of meteoric water into the geothermal reservoir followed by the upflow conductive cooling and a liquid-vapor separation.

Table 1: Sampling of rainwater (month), average temperature, amount of rainfall (mm), , electrical conductivities (µS/cm), pH, total dissolved species (mg/l), chemical composition 655 (concentrations in mg/l), calculated amount of  $HCO<sub>3</sub>^-$  (mg/l), and stable isotope values ( $\delta D$ 656 and  $\delta^{18}$ O) of rainwater in Port aux français (n.d. not detected; n.a. not analyzed)

Table 2: Location, GPS position and altitude of sampled river drainage in the Kerguelen archipelago (Rallier du Baty, Val Travers, Galliéni, Ronarc'h…) with temperatures (°C),

660 electrical conductivities (μm/cm), pH, cation and anion concentrations (mg/L) and  $\delta^{18}O - \delta D$ stable isotope values.



ice-capped geothermal system in Kerguelen Archipelago. J Volc Geotherm Res. 20, 85-100.













Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus. 16, 436-467.

- Delorme, H., Verdier, O., Cheminée, J-L., Giret, A., Pineau, F., Javoy, M., 1994. Etude
- chimique et rapport isotopique du carbone des fumerolles de la Péninsule Rallier du Baty (Iles
- Kerguelen). Mém. Soc. Géol. France. 166, 25–30.

- Duan, Z., Sun, R., 2003. An improved model calculating CO2 solubility in pure water and
- aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. Chem. Geol. 193, 257- 271.

Duncan, R.A., 2002. A time frame for construction of the Kerguelen Plateau and Broken Ridge. J. Petrol. 43 (7), 1109-1120.

- Fischer, T.P., Giggenbach, W.F., Sano, Y., Williams, S.N., 1998. Fluxes and sources of
- volatiles discharged from Kudryavy, a subduction zone volcano, Kurile Islands. Earth Planet.
- Sci. Lett. 160, 81–96.

- Fournier, R.O., 1991. Water geothermometers applied to geothermal energy, In: D'Amore, F.
- (coordinator). Application of Geochemistry in Geothermal Reservoir Development.
- UNITAR/UNDP publication, Rome, 37-69.
- 
- Fournier, R O., Potter, R.W., 1982. A revised and expanded silica (quartz) geothermometer.
- Geotherm Resourc Council Bull. 11, 3–12.

- Fournier, R. O., Rowe, J.J., 1966. The deposition of silica in hot springs. Bulletin
- Volcanologique. 29, 585–587.

Fournier, R.O., Truesdell, A.H., 1974. Geochemical indicators of subsurface temperature. Part 2, estimation of temperature and fraction of hot water mixed with cold water. U.S. Geological 777 Survey Journal of Research. 2 (3), 263–270.

Frenot, Y., Gloaguen, J-C., Picot, G., Bougère, J., Benjamin, D., 1993. Azorella selago Hook used to estimate glacier fluctuations and climatic history in the Kerguelen Islands over the last two centuries. Oecologia, 95, 140–144.

783 Fritz, P., Fontes, J-C., (Eds.) 1986. Handbook of Environmental Isotope Geochemistry. 1<sup>st</sup> ed.

Vol. I., II. and III. The Terrestrial Environment, A. and B. Ed. Elsevier. Scientific Publishing

Company. New York. EE.UU. 545-557-428.

- Gagnevin, D., Ethien, R., Bonin, B., Moine, B., Féraud, G., Gerbe, M-C., Cottin, J-Y.,
- Michon, G., Tourpin, S., Mamias, G., Perrache, C., Giret, A., 2003. Open-system processes in
- the genesis of silica-oversaturated alkaline rocks of Rallier-du-Baty Peninsula, Kerguelen
- Archipelago (Indian Ocean). J. Volcanol. Geotherm. Res. 123, 267–300.







821 Giret, A., 1990. Typology, evolution and origin of the Kerguelen plutonic series. Indian Ocean: a review, Geol. J. 25, 239–247.

Gonfiantini, R., Borsi, S., Ferara, G., Panichi, C., 1973. Isotopic Composition of Waters from the Danakil Depression (Ethiopia). Earth Planet. Sci. Lett. 18, 13-21.

- Grégoire, M., Lorand, J-P., Cottin, J-Y., Giret, A., Mattelli, N., Weis, D., 1997. Xenoliths
- evidence for a refractory oceanic mantle percolated by basaltic melts beneath the Kerguelen

archipelago. Eur. J. Mineral. 9, 1085–1100.

Hattori, K., Muehlenbachs, K., 1980. Marine hydrothermal alteration at a Kuroko ore deposit, Kosaka. Japan, Contrib. Mineral. Petrol. 74, 285–292.



Geology, geochemistry, and origin of high sulfidation Cu-Au mineralization in the Nansatsu district. Japan, Econ. Geol. 89, 1-30.

Hoefs, J., 1980. Stable Isotope Geochemistry. 2nd edition. 208 pp., 52 figs, 23 tables. Berlin,

Heidelberg, New York: Springer-Verlag, ISBN 3 540.

- Horita, J., Wesolowski, D.J. 1994. Liquid-vapor fractionation of oxygen and hydrogen
- isotopes of water from freezing to the critical temperature. Geochim. Cosmochim. Acta. 58,

3425–3437.

- Javoy, M., Pineau, F., Allegre, C.J., 1982. Carbon geodynamic cycle. Nature. 300, 171- 173.
- Lebouvier, M., Laparie, M., Hullé, M., Marais, A., Cozic, Y., Lalouette, L., Vernon, P.,
- Candresse, T., Frénot, Y., Renault, D., 2011. The significance of the sub-Antarctic Kerguelen
- Islands for the assessment of the vulnerability of native communities to climate change, alien
- insect invasions and plant viruses. Biol Invasions. 13, 1195–1208.

Liebscher, A., Heinrich, C.A., 2007. Fluid-fluid interactions in the Earth's lithosphere. MSA Reviews in Mineralogy and Geochemistry. 65, 430 p.











magma flux, lithosphere assimilation and composition of the Kerguelen Plume. J. Petrol. 39, 973–994.

- White, D.E., Muffler, L.P.J., Truesdell, A.H., 1971. Vapor-dominated hydrothermal systems
- compared with hot water systems. Econ. Geol. 66, 75-97.



46.6532 S; 44.8835 W

61.7821 S; 44.8835W











Figure 2





Figure 4



Figure 5



Figure 6





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# **Geochemical exploration of** *geothermal* **activity in the Kerguelen archipelago, SW Indian Ocean**

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This paper described the geothermal water of Kerguelen and its active geothermal system. We reconstruct the meteoric origin, and the hydrothermal processes from chemical and isotopic data of rain water and thermal water. Interpretations indicate series of reactions from 6 up to 260°C and few hundred meters below the surface.

