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### ► To cite this version:

Gabriel Pasquet, Amin Mohamed Idriss, Lou Ronjon-Magand, Magali Ranchou-Peyruse, Marion Guignard, et al.. Natural hydrogen potential and basaltic alteration in the Asal–Ghoubbet rift, Republic of Djibouti.. *Bulletin de la Société Géologique de France*, 2023, 194, 9 (24 p.). 10.1051/bsgf/2023004 . hal-04062062

**HAL Id: hal-04062062**

**<https://univ-pau.hal.science/hal-04062062>**

Submitted on 7 Apr 2023

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1 Natural hydrogen potential and basaltic alteration in the Asal–Ghoubbet rift, Republic of Djibouti.

2 Potentiel en hydrogène naturel et altération basaltique dans le rift d'Asal-Ghoubbet, République  
3 de Djibouti.

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12

### 13 **Résumé :**

14 Le rift actif d'Asal-Ghoubbet en République de Djibouti est un site d'intérêt pour l'énergie géothermique et  
15 l'hydrogène naturel, et des études précédentes ont indiqué que du dihydrogène (H<sub>2</sub>) émane de ce rift.

16 Cependant, la réaction de serpentinisation bien connue ne semble pas être le principal mécanisme de  
17 production de H<sub>2</sub> sur ce site. L'H<sub>2</sub> est plutôt généré de la manière suivante : (1) par altération de la lave  
18 basaltique en profondeur via une réaction avec l'eau de mer s'écoulant de la baie de Ghoubbet vers le lac Asal ;  
19 (2) par simple dégazage de la chambre volcanique située à quelques kilomètres sous la caldeira de Fiale dans  
20 l'axe du rift ; ou (3) à la suite de processus de pyritisation via l'oxydation de H<sub>2</sub>S. L'étude des micro-organismes  
21 n'a pas indiqué de production ou de consommation de H<sub>2</sub>, CO<sub>2</sub> ou CH<sub>4</sub> ; il est donc peu probable que les micro-  
22 organismes aient affecté les teneurs en gaz H<sub>2</sub> mesurées à la surface. Cependant, la contamination de l'air dans  
23 les fumerolles est généralement considérable et peut limiter l'interprétation de tels processus.

24 Les déblais de forage des puits Fiale 1 (F1) et Gale le Goma 1 (Glc1) (situés respectivement sur les marges  
25 intérieure et extérieure du rift) ont été analysés pour déterminer où l'H<sub>2</sub> est généré. Les analyses de la roche

26 totale ont indiqué des zones distinctes à des profondeurs de 464 m et 280 m pour F1 et Glc1, respectivement,  
27 représentant la limite entre les basaltes d'Asal et Stratoïd. Les analyses  $^{57}\text{Fe}$  Mössbauer montrent une  
28 diminution du pourcentage de  $\text{Fe}^{3+}$  en profondeur, ce qui indique que les minéraux riches en  $\text{Fe}^{2+}$ , notamment  
29 dans les basaltes Stratoïd, peuvent être une source de  $\text{H}_2$ .

30 D'après les données des puits du centre du rift et de la marge externe du rift, il est évident que l' $\text{H}_2$  est présent  
31 à la surface dans l'axe du rift et que cette zone offre un bon potentiel rémanent en raison de la présence de  
32 chlorite riche en Fe. À l'inverse, peu d'émissions d' $\text{H}_2$  ont été mesurées à la surface sur les marges extérieures  
33 du rift, bien que les données de puits aient montré la présence d' $\text{H}_2$  (~0,25 %) en profondeur. La présence  
34 d'une roche de couverture dans l'axe du rift n'a pas encore été prouvée ; cependant, la forte perte au feu et la  
35 minéralogie dans le puits Glc1 peuvent indiquer que les roches sont suffisamment altérées sous forme  
36 argileuse pour offrir un potentiel en tant que couverture à l' $\text{H}_2$ . Si tel est le cas, les marges du rift offriraient un  
37 plus grand potentiel d'exploration que le centre du rift.

38 **Mots clés :** Hydrogène naturel, Géothermie, Djibouti, Rift d'Asal, Altération, Basaltes.

39 **Abstract:**

40 The Asal–Ghoubbet active rift in the Republic of Djibouti is a site of interest for geothermal energy and natural  
41 hydrogen, and previous studies have indicated that dihydrogen ( $\text{H}_2$ ) emanates from this rift. However, the well-  
42 known serpentinization reaction does not appear to be the main mechanism generating  $\text{H}_2$  at this site. Rather,  
43 the  $\text{H}_2$  is generated as follows: (1) by alteration of basaltic lava at depth *via* reaction with seawater flowing  
44 from Ghoubbet Bay towards Lake Asal; (2) by simple degassing of the volcanic chamber located a few  
45 kilometers below the Fiale Caldera in the rift axis; or (3) as a result of pyritization processes *via* the oxidation of  
46  $\text{H}_2\text{S}$ . Study of microorganisms did not indicate any production or consumption of  $\text{H}_2$ ,  $\text{CO}_2$ , or  $\text{CH}_4$ ; therefore, it is  
47 unlikely that microorganisms affected  $\text{H}_2$  gas contents measured at the surface. However, air contamination at  
48 fumaroles is typically considerable and may limit interpretation of such processes.

49 Drill cuttings from the Fiale 1 (F1) and Gale le Goma 1 (Glc1) wells (located on the inner and outer rift margins,  
50 respectively) were analyzed to determine where  $\text{H}_2$  is generated. Total rock analyses indicated distinct zones at  
51 depths of 464 m and 280 m for F1 and Glc1, respectively, representing the boundary between the Asal and

52 Stratoïd Basalts. <sup>57</sup>Fe Mössbauer analyses show a decrease in the percentage of Fe<sup>3+</sup> at depth, indicating that  
53 Fe<sup>2+</sup>-rich minerals, particularly in the Stratoïd Basalts, may be a source of H<sub>2</sub>.

54 Based on well data from the rift center and the outer rift margin, it is evident that H<sub>2</sub> is present at the surface in  
55 the rift axis and that this area offers good remnant potential because of the presence of Fe-rich chlorite.  
56 Conversely, few H<sub>2</sub> emissions were measured at the surface on the outer rift margins, although well data  
57 showed some H<sub>2</sub> (~0.25%) at depth. The presence of a cap rock in the rift axis has not yet been proven;  
58 however, the high loss on ignition and the mineralogy in well Glc1 may indicate that the rocks are sufficiently  
59 altered into clays to offer potential as a H<sub>2</sub> seal. If so, the rift margins would offer greater exploration potential  
60 than the rift center.

61 **Keywords:** Natural hydrogen, Geothermal energy, Djibouti, Asal Rift, Alteration, Basalts.

## 62 1. Introduction

63 Dihydrogen (H<sub>2</sub>) is a key element in the energy transition and is often used as an energy carrier (e.g., for  
64 storage) rather than as a primary energy source (Moretti, 2019; Lapi et al., 2022). At present, H<sub>2</sub> is produced  
65 primarily from hydrocarbons through a process that emits high volumes of CO<sub>2</sub>; this is known as “grey”  
66 hydrogen (Prinzhofer and Rigollet, 2022). However, lower emission sources of H<sub>2</sub> exist and are more  
67 appropriate in the context of current global environmental conditions. Dihydrogen is referred to as “blue”  
68 when CO<sub>2</sub> emissions are captured and stored during grey hydrogen processing and as “green” when it is  
69 produced by the electrolysis of water using a decarbonized source of electricity. “White” dihydrogen is H<sub>2</sub> in its  
70 natural state (Rigollet and Prinzhofer, 2022) and is generated mainly through fluid rock interactions reactions  
71 (Smith et al., 2005; Gaucher, 2020; Moretti and Webber, 2021).

72 This natural dihydrogen has been observed in various geological contexts (Truche et al., 2020; Zgonnik, 2020),  
73 including mid-oceanic ridges (Charlou et al., 1998, 2002; Kelley et al., 2001; Kelley, 2005); ophiolitic massifs  
74 such as the Sultanate of Oman, New Caledonia, or the Philippines (Neal and Stanger, 1983; Abrajano et al.,  
75 1988; Sano et al., 1993; Deville and Prinzhofer, 2016; Vacquand et al., 2018); and Archean and Proterozoic  
76 cratonic basins such as those in Namibia, Mali, Russia, Australia, and Brazil (Larin et al., 2015; Prinzhofer et al.,  
77 2018, 2019; Boreham et al., 2021; Moretti et al., 2021, 2022; Malvoisin and Brunet, 2023). Steam at the high-  
78 temperature geothermal sites of Italy, Iceland, and Djibouti (Oskarsson, 1984; Ármannsson et al., 1989; Leila et

79 al., 2021; Pasquet et al., 2021, 2022; Combaudon et al., 2022) has also been shown to contain H<sub>2</sub>, possibly from  
80 multiple sources.

81 Many H<sub>2</sub> emission zones have been discovered, yet the production of natural hydrogen (as in Mali; Prinzhofer  
82 et al., 2018) remains rare and natural dihydrogen exploration is still in its infancy. The geological and  
83 geothermal context of the active rift in the Afar Depression is favorable for natural H<sub>2</sub> production, with several  
84 sources proposed previously: alteration of iron minerals in basaltic material, pyritization, or volcanic degassing  
85 (Holloway and O'Day, 2000; Klein et al., 2020; Pasquet et al., 2021). Following surface gas surveys, analysis of  
86 cuttings from two wells is presented below and aims to improve our understanding of basalt alteration and  
87 Fe<sup>2+</sup>/Fe<sup>3+</sup> evolution at depth across the Asal–Ghoubbet rift in order to assess its potential H<sub>2</sub> resource.

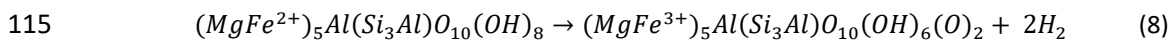
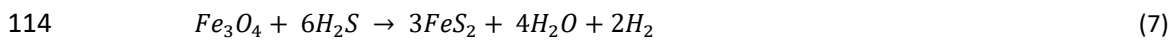
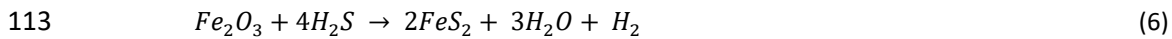
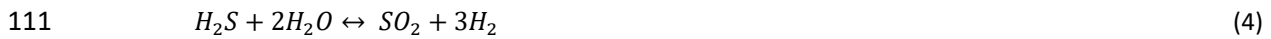
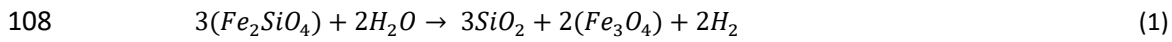
### 88 1.1. Hydrogen system

89 Many reactions can produce H<sub>2</sub> (Worman et al., 2020), depending on the protolith, fluid, and physical  
90 parameters (*i.e.*, temperature, pressure) of the environment; some of these reactions are oxidation–reduction  
91 processes. The ferrous iron contained in a mineral is oxidized when in contact with water to become ferric iron,  
92 whereas the water is reduced to form H<sub>2</sub>. The more ferrous iron a rock contains, the greater its ability to  
93 produce H<sub>2</sub> during alteration processes. Basalt is composed mainly of plagioclase, with smaller amounts of  
94 pyroxene and olivine (olivine typically less than 20%). Olivine, including the iron-rich end-member fayalite, is  
95 highly unstable at the surface and will deteriorate more rapidly than the other minerals present in basalt  
96 (Stevens and McKinley, 2000; Sissmann et al., 2014; Kularatne et al., 2018). In contrast, plagioclase, the major  
97 phase, has less or no iron and is kinetically more stable. Accordingly, the production of H<sub>2</sub> from a basaltic  
98 protolith is typically limited by its high plagioclase content.

99 Despite this limitation, volcanic zones such as Iceland (Combaudon et al., 2022) offer other advantages for  
100 natural hydrogen production. These include the relatively regular renewal of crustal material (and thus of  
101 potentially oxidizable minerals), high temperature gradient, significant water resource (meteoric, glacial, or  
102 marine), and production of H<sub>2</sub>S due to volcanic activity.

103 The present study will focus on several oxidation–reduction equations that generate H<sub>2</sub>: oxidation of Fe<sup>2+</sup> from  
104 fayalite to magnetite (1); oxidation of Fe<sup>2+</sup> from magnetite to hematite (2); oxidation of Fe<sup>2+</sup> from mesostasis to  
105 hematite (3); oxidation from H<sub>2</sub>S to SO<sub>2</sub> in the gas phase (4); iron sulphides pyritization (5); oxidation of H<sub>2</sub>S to

106 form pyrite from hematite (6) and magnetite (7) (Arrouvel and Prinzhofer, 2021); and oxidation of chlorite from  
107  $Fe^{2+}$  to  $Fe^{3+}$  (8) (Steudel et al., 2016; Lempart et al., 2018).



116 Additionally, different clay phases can be formed by basalt alteration at different temperatures, with smectites  
117 at low temperatures and chlorites at higher temperatures. This argillization of basalt does not necessarily lead  
118 to direct production of  $H_2$ , because the iron remains ferrous (Reed and Palandri, 2008). However, once chlorite  
119 is formed, it can oxidize (Brindley and Youell, 1953); here, we discuss whether this could represent an  
120 intermediary phase for  $H_2$  production. As in hydrocarbon systems, in addition to defining the source rock (here,  
121 the reactive minerals) for  $H_2$  generation, it is also necessary to define a reservoir, migration pathways, and a  
122 seal.

## 123 1.2. The Asal–Ghoubbet context

### 124 1.2.1. Geological context

125 The Asal–Ghoubbet rift is part of a large spreading system, the East African Rift (EAR), that extends from the  
126 Red Sea in the north to Mozambique in the south. In the Republic of Djibouti (Figure 1), in the north of the  
127 magmatic east branch of the EAR, this rift is an emergent segment of the Aden Ridge (Stieltjes et al., 1976).  
128 Although continental extension started earlier, the first evidence of oceanic crust accretion in the Gulf of Aden  
129 has been dated to 20–17 Ma (Nonn et al., 2017, 2019). In the Red Sea, extension started approximately 25 Ma  
130 and ocean formation approximately 4 Ma. In the southern Red Sea, Gulf of Aden, and Afar region, after various

131 phases of extension, volcanism, and thinning (Barberi et al., 1972, 1975b), a large series of fissural basaltic  
132 eruptions resulted in the Afar Stratoïd Series (Barberi et al., 1975a). This series is composed of basalts with an  
133 alkaline tendency (Varet, 1978; Fournier et al., 1984) at its base and rhyolitic rocks at its top and has been  
134 dated to 4–1 Ma. These eruptions were followed by the Axial Series, from 1 Ma to the present day; this series  
135 comprises more evolved tholeiitic and porphyritic basalts. These series represent the accretionary segments of  
136 the present axial volcanic ranges, linked together by transform faults, such as the Asal–Ghoubbet rift (Barberi  
137 and Varet, 1970; Stieltjes et al., 1976; Barberi and Varet, 1977). The N130° oriented Asal–Ghoubbet rift has an  
138 opening rate of approximately 1.5–2 cm/year (Delibrias et al., 1975) with a N40° direction. The last major  
139 eruption in the rift zone was that of the Ardoukoba shield volcano in 1978 (Demange et al., 1980). The rift  
140 comprises three main zones: the axial volcanic zone, the inner margins, and the outer margins. The lavas evolve  
141 from porphyritic on the margins to aphyritic in the center and from magnesian to ferrous towards the center of  
142 the rift zone (Stieltjes et al., 1976; Varet, 1978).

### 143 1.2.2. Geothermal exploration

144 The geodynamic activity of this rift has prompted numerous geothermal exploration campaigns since the  
145 1970s, and temperatures observed in exploration wells have been encouraging with an average thermal  
146 gradient of 180°C/km to 200°C/km in the axis as on the margins. In 1975, the BRGM (Bureau de Recherches  
147 Géologiques et Minières) drilled two wells on the southwestern outer margin of the rift: wells A1 (260°C) and  
148 A2 were drilled to depths of 1154 and 1554 m, respectively (Abdillahi, 2014). A second phase of drilling, carried  
149 out by Aquater between 1987 and 1988, created three new wells on the outer margins of the rift: wells A3  
150 (265°C), A4 (344°C), and A6 (281°C) were drilled to depths of 1316, 2011, and 1761 m, respectively, while well  
151 A5 (located in the center of the rift) was drilled to 2105 m (359°C) (D'Amore et al., 1997; Abdillahi, 2014). Since  
152 2016, further drilling has been undertaken in the rift: the Gale le Goma 1 (Glc1) well was drilled to 600 m on  
153 the southern outer margin near A3 and A1 (138°C) (Ahmed, 2018); and, more recently, wells F1 (363°C), F2  
154 (352°C), and F3 (363°C) were drilled around the Fiale Caldera to depths of 2475, 2237, and 2402 m, respectively  
155 (Turk et al., 2019).

156 Seismic velocity anomaly studies have identified a magma chamber beneath the Fiale Caldera at a depth of  
157 more than 5 km (Dobre et al., 2007). Combined velocity anomaly data and well data indicate cold marine  
158 water intrusions between 0 and 1 km depth in the center of the rift (Zan et al., 1990; Dobre et al., 2007;

159 Doubre and Peltzer, 2007). Seawater flows from Ghoubbet Bay to Lake Asal through numerous NW–SE faults.  
160 This temperature inversion at shallow depth has been noted in wells A5, F1, F2, and F3, i.e., at the center of the  
161 rift (Zan et al., 1990; Doubre et al., 2007; Turk et al., 2019). At the rift margins, these hypersaline fluids are  
162 warmer and the flow is weaker (Mlynarski and Zlotnicki, 2001).

### 163 1.2.3. H<sub>2</sub> in the Asal–Ghoubbet rift

164 Well data and a field campaign (2019) across the rift highlighted the presence of H<sub>2</sub> at depth in the area (Figure  
165 2), in some geothermal wells along the southwestern margin (wells A3 and A6; D’Amore et al., 1997), and in  
166 the fumaroles along the southern inner margin near well A5 and the Fiale Caldera (Pasquet et al., 2021). The  
167 well data indicate H<sub>2</sub> percentages of ~0.25% (in dry gas, excluding air and water vapor); however, no H<sub>2</sub> sources  
168 were measured at the surface in the vicinity of the wells during the field campaign. Along the inner margins and  
169 in the axial volcanic zone, although no gas data were acquired at depth, the intense hydrothermal activity  
170 present at the surface made it possible to measure gas contents: after correction for air, H<sub>2</sub> contents were  
171 found to be up to 3%, with an average value of 1% and a mean value of 0.77% (Pasquet et al., 2021). Gas  
172 analysis following the 1978 Ardoukoba eruption (in the volcanic core zone) also indicated 0.15% H<sub>2</sub> in the  
173 magma gas (Allard et al., 1979). At the surface, H<sub>2</sub> concentrations were found to increase towards the center of  
174 the rift (Pasquet et al., 2021).

175 Several hypotheses have been proposed for the origin of this H<sub>2</sub>: (1) alteration of basalts by hot hypersaline  
176 fluids circulating at depth; (2) alteration of basalts at lower temperatures due to marine intrusion at shallow  
177 depth in the rift axis; (3) pyritization; and (4) volcanic degassing as magma ascends through major active faults  
178 rooted near the magma chamber (Pasquet et al., 2021).

179 In summary, H<sub>2</sub> has been measured at depth in geothermal wells along the margins of the Asal–Ghoubbet  
180 system but has not yet been detected at the surface in these areas. Conversely, in the center of the rift, H<sub>2</sub> has  
181 been measured at the surface in fumaroles but no subsurface data are available.

## 182 2. Materials and Methods

183 We first conducted a preliminary analysis of surface gases in the axial volcanic zone. Gas measurements were  
184 acquired in the field during two campaigns in 2019 and 2020 using the BIOGAS 5000 analyzer; some of this  
185 dataset has been published previously (Pasquet et al., 2021). Soil samples were acquired primarily during the



186 first campaign in 2019, although one sample was acquired in 2021.

187 The drill cuttings from the Fiale 1 (F1) and Glc1 wells were studied based on total rock analysis: ICP–OES  
188 (Inductif Coupled Plasma Optical Emission Spectrometry), XRD (X-ray diffraction) and Mössbauer spectroscopy.  
189 The ICP–OES analyses were carried out by the Service d'Analyse des Roches et des Minéraux of the CRPG at  
190 Nancy.

## 191 2.1. Gas sampling

192 Surface gas measurements were acquired on three different days. The studied site is located near the Asal 5  
193 (A5) and F1 geothermal wells, along the inner margins of the rift along a major N140°-oriented fault that runs  
194 between Ghoubbet Bay and Lake Asal (Pasquet et al., 2021; Pasquet, 2023). This site includes a set of  
195 fumaroles with hydrothermal alteration around them (Figure 3). Steam is present over approximately 70 m  
196 wide and the Afar people living in this area have installed tubes to induce condensation and take advantage of  
197 the drinking water contained in the hot steam. To obtain measurements, a perforated stainless steel tube was  
198 inserted into the fumaroles; drilling tools were not necessary as the soil was soft. The tube was then connected  
199 by silicone tubes to the BIOGAS 5000 field analyzer. Also, to increase gas capture for fumaroles, a funnel can be  
200 placed in the vent and connected directly to the analyzer. Gas contents were monitored in real time, although  
201 only peak values for each 2-min interval were recorded. CH<sub>4</sub>, CO<sub>2</sub>, and O<sub>2</sub> were measured in % and H<sub>2</sub>, CO, and  
202 H<sub>2</sub>S in ppm. The remaining unanalyzed gases were grouped under the term “Balance” and measured in %. This  
203 balance is often considered to be N<sub>2</sub> but might also include, in this volcanic context, gases such as SO<sub>2</sub> or HCl.  
204 H<sub>2</sub>O<sub>(g)</sub> was not analyzed owing to the presence of a water vapor filter. Measurements uncertainties were as  
205 follows: ±0.5% of the CH<sub>4</sub> and CO<sub>2</sub> contents; ±1.0% of the O<sub>2</sub> content; ±2.5% of the H<sub>2</sub> content; and ±2.0% of the  
206 CO and H<sub>2</sub>S contents.

207 As H<sub>2</sub> contents have been shown to vary both within and between days in some geological settings (Prinzhofer  
208 et al., 2019; Moretti et al., 2021, 2022), we recorded the time each measurement was obtained and will  
209 present the results versus time. Although samples were obtained from various locations along the leaking zone  
210 (Figure 3), no SE–NW trends in concentrations were noted; accordingly, we did not attempt to map H<sub>2</sub>  
211 concentrations spatially.

## 212 2.2. Microbiological approaches

213 H<sub>2</sub> can be an electron donor and an energy source for many aerobic, sulfate-reducing, (homo)acetogenic and  
214 methanogenic microorganisms. We identified the microbial families present and considered the metabolic  
215 processes associated and described in the literature, in particular their ability to consume H<sub>2</sub>. Extraction of  
216 genomic DNA was performed on 250 mg of soil using the DNeasy PowerSoil Pro kit (Qiagen). gDNA was  
217 quantified by fluorescence, using the Quant-it kit (Invitrogen), following the supplier's instructions. A Synergy  
218 HTX multi-mode reader (BioTek) microplate reader using the Gen5 software was used. Amplifications of 16S  
219 rRNA genes were performed by PCR for soil diversity analysis by Illumina MiSeq sequencing. Universal primers  
220 515F-III (CTTCCCTACACGACGCTCTCCGATCTGTGYCAGCMGCCGCGGTA) and 928R-III  
221 (GGAGTTCAGACGTGCTCTCCGATCTCCCGYCAATTCMTTTRAGT) (region V4–V5; Wang et al., 2015) were used,  
222 containing the tags required for sequencing, according to the following PCR cycle: 94°C-2 min; (94°C-30 s; 65°C-  
223 30 s; 72°C-40 s) x30; 72°C-7 min. The core PCR kit (Roche) supplemented with 1 mg/mL (final concentration) of  
224 BSA (Bovine Serum Albumin, supplied by NEB-B9200S) was used, with a 2720 Thermal Cycler (Applied  
225 Biosystems). The amplicons were sequenced using the MiSeq Illumina 2 x 250 bp technique, *via* the GenoToul  
226 sequencing platform (Toulouse, France) and analyzed with the FROGS analysis pipeline as described in Haddad  
227 et al. (2022).

228 In order to monitor metabolic activity based on gas phase variations in soil samples from the 2021 Djibouti  
229 campaign, soil samples weighing 2 g were introduced into sterile 100 mL penicillin vials. Two conditions were  
230 defined: in anaerobiosis and in aerobiosis. The anoxic vials were hermetically sealed (butyl stopper, aluminum  
231 cap) and flushed with nitrogen; then, 10 mL of sterile nitrogen-degassed distilled water was added to the soil.  
232 Finally, these bottles were flushed with H<sub>2</sub>/CO<sub>2</sub> (80/20; 1 bar). The oxic flasks were treated in the same way  
233 except for the initial gaseous phase, which was air and sterile distilled water that had not been degassed in  
234 order to maintain aerobic conditions. H<sub>2</sub>/CO<sub>2</sub> was added under slight overpressure in the sealed bottles (1 bar).  
235 The vials were then incubated at 95°C. After 10 days of incubation, the composition of the gaseous phase was  
236 again analyzed to compare the gaseous phases versus T0; in this way, we were able to monitor the evolution of  
237 the system (GC- $\mu$ TCD, Micro GC Fusion, Chemlys, France). The cultures were placed in an oven at 37°C for 30  
238 minutes before analysis and the pressure of the gaseous phase quantified before and after analysis by a  
239 manometer (Digitron 2022P) in order to quantify the moles of gases present under the same conditions.

240 Materials from two field campaigns (in 2019 and 2021) have been studied. Soil samples were collected in  
241 triplicate at Site 4 (Figure 3). During the 2021 campaign, three locations along the leaking zone were sampled  
242 and named zones 13, 15 and 16.

### 243 2.3. XRD

244 The well cuttings were reduced to powder to obtain XRD measurements. The analyses were carried out at the  
245 Université de Pau et des Pays de l'Adour using a D2 PHASER diffractometer (Bruker). XRD allowed us to obtain  
246 information about the crystalline phases of our rock samples and thus to determine both qualitatively and  
247 quantitatively the presence of specific minerals. For this analysis, the powdered samples were mounted on a  
248 base and the intensity of scattered X-rays analyzed to determine mineral composition.

249 The analyses were performed under conditions of 10 mA, 300 W, and 30 kV and a PSD (Position Sensitive  
250 Detector) of 1.6 s. The front slot, blade, and back slot had openings at 0.2, 1.0, and 3.0 mm, respectively. The  
251 observed  $2\theta$  angle was between 10 and 80° with an X-ray wavelength of 1.54184 Å.

### 252 2.4. Mössbauer spectroscopy

253 Once the mineral phases were identified, their  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios were measured to determine potential for  
254 oxidation to produce  $\text{H}_2$ . For this purpose,  $^{57}\text{Fe}$  Mössbauer spectroscopic analyses were carried out at the  
255 "Resonance Spectroscopies" facility of the Institute of Condensed Matter Chemistry of Bordeaux (ICMCB). This  
256 analysis is based on the Fe oxidation state, magnetic state, and crystalline chemistry of iron-containing  
257 minerals. In particular, it allows characterization of the valence of iron and the sites at which iron is present  
258 within crystals.

259 The measurements were carried out at room temperature using a constant acceleration spectrometer  
260 operating in transmission geometry. The gamma emitter used in the experimental setup is a  $^{57}\text{Co}$  radioactive  
261 source (activity: 1.85 GBq) embedded in a rhodium matrix kept at room temperature (293 K). Thin absorbers  
262 were prepared with about 250 mg of sample powder and placed between the source of gamma rays and a  
263 NaI(Tl) scintillation detector. The recorded  $^{57}\text{Fe}$  Mössbauer spectra are then the sum of various components  
264 (sub-spectra) associated with the different iron-bearing minerals in the analyzed rock samples. Each sub-  
265 spectrum is characterized by Mössbauer hyperfine parameters: isomer shift ( $\delta$ , in mm/s, relative to  $\alpha\text{-FeO}$  at  
266 room temperature), quadrupole splitting ( $\Delta$ , in mm/s) or quadrupole shift ( $2\epsilon$ , in mm/s), hyperfine magnetic

267 field (Bhf, in T) and resonance line width ( $\Gamma$ , in mm/s). Refinement of hyperfine parameters and relative  
268 absorption areas were performed with the WinNormos® software (Wissenschaftliche Elektronik GmbH).

### 269 3. Results

270 Here, we present our results based on the analysis of *in situ* gas measurements obtained at Site 4 (Figure 3).  
271 This fumarole site ( $T > 96^\circ\text{C}$ ) was measured on three different days (one in November 2019 and two in August  
272 2020), with measurements taken at regular intervals from 09:30 to 17:00 (UTC +3) to record diurnal variations  
273 in  $\text{H}_2$  activity. In November 2019, measurements were collected throughout the study site; accordingly, the  
274 measurement values for this period (*i.e.*, orange dots in Figure 4) were obtained from slightly different  
275 locations. To consider conditions at depth, we discuss here the results from drill cuttings obtained from the F1  
276 and Glc1 geothermal wells; we collected 37 samples down to 1118 m and 10 samples down to 458 m for F1 and  
277 Glc1, respectively.

#### 278 3.1. Gas emissions

279 Site 4 is an active hydrothermal site along the inner margins of the Asal–Ghoubbet rift, located to the  
280 southwest of the Fiale Caldera near wells F1 and A5 (Figure 2). Fumaroles escape from a major rift fault with a  
281 gas temperature exceeding  $96^\circ\text{C}$ . This site has been shown to exhibit the highest surface  $\text{H}_2$  concentrations in  
282 the area, with values exceeding 1000 ppm (Pasquet et al., 2021). The temporal evolution of  $\text{H}_2$  and  $\text{CO}_2$  at this  
283 site is illustrated in Figure 4, with data points color coded according to sampling day.

284 For our uncorrected dataset, bell trends in *in situ*  $\text{H}_2$  concentrations were observed, with the highest values  
285 (900–1000 ppm) were typically observed between 13:00 and 15:00 (Figure 4a). In contrast, *in situ*  $\text{CO}_2$   
286 measurements increased with time to a maximum value of approximately 6% (Figure 4b).

287 A major problem encountered in this region, as in many volcanic emissions, is that the sampled gas is a mixture  
288 of volcanic gas and atmospheric air. The volcanic gases can be diluted with air by the thermal contrast between  
289 the emanations and the atmospheric air, by the lava corridors formed during previous eruptions, or by the  
290 large faults in the vegetation-free landscape, which induce high vertical and horizontal permeability. The field  
291 analyzer measured  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{S}$ , and the balance. As already stated, a water filter was placed  
292 upstream of the analyzer to obtain the dry gas concentration; volcanic gas typically contains approximately  
293 80% water vapor. Then, having measured the  $\text{O}_2$  concentration and if the balance is considered to contain

294 mostly N<sub>2</sub> (*i.e.*, if the balance/O<sub>2</sub> ratio is higher than that of the atmosphere), the measured gas can be  
295 corrected. To do this, we subtracted the O<sub>2</sub> compound, which we considered to be outside the system, and  
296 removed the equivalent volume of N<sub>2</sub> from the balance according to the atmospheric ratio  $N_{2(atm)}/O_{2(atm)} =$   
297 3.727. Similarly, argon was removed from the balance according to the ratio  $Ar_{(atm)}/O_{2(atm)} = 0.044$ . We  
298 observed a temporal trend in the balance/O<sub>2</sub> for samples taken on two days (*i.e.*, blue and orange points in  
299 Figure 4c), which allowed us to make this correction. This ratio was higher than 3.7, indicating that the balance  
300 contains other gases than atmospheric N<sub>2</sub> (Ar, He, SO<sub>2</sub>...). In contrast, a different temporal trend was observed  
301 for the other sampling day (*i.e.*, gray points in Figure 4c): we observed a constant decrease of the balance/O<sub>2</sub>  
302 ratio between 4.3% and 3.8%, associated with an increase in O<sub>2</sub> concentration from 18.2% to 20.5% (Figure 4c).

303 Once these air corrections were made, H<sub>2</sub> concentration was found to remain relatively constant throughout  
304 the day for samples collected in November 2019 and on August 12<sup>th</sup> 2020, with values between 0.57% and  
305 0.89%. However, after correction, the H<sub>2</sub> concentrations obtained on August 13<sup>th</sup> 2020 exhibited a strong  
306 positive diurnal trend, increasing from 0.31% to 3% over the course of the day (Figure 4d). This could be  
307 explained by a higher concentration of O<sub>2</sub>, and so a bigger correction on air (raw data are available in  
308 supplementary data 1).

309 Our corrected CO<sub>2</sub> concentrations exhibit no notable trend for the samples collected in November 2019.  
310 Concentrations measured on August 12<sup>th</sup> 2020 increased from 21% to 36% over the course of the day, while  
311 the strongest positive correlation was observed on August 13<sup>th</sup> 2020 (Figure 4e). Finally, we observed a positive  
312 correlation between H<sub>2</sub> and CO<sub>2</sub> (Figure 4f), as shown previously by Pasquet et al. (2021).

### 313 3.2. Microbial taxonomic diversity

314 Following microbial analysis of soil samples collected at Site 4 in 2019, samples were collected in three  
315 different locations in 2021. DNA samples were extracted from these soils and the 16S rRNA genes were  
316 amplified and sequenced to taxonomically identify the prokaryotes present. The number of sequences  
317 analyzed (following high-throughput sequencing and the removal of low-quality reads and chimera) was as  
318 follows: 19,038, 15,467 and 17,338 sequences for Site 4 2019; 15,359, 17,993, and 18,144 sequences for Site 4  
319 2021 (zone 13); 18,454, 19,663 and 18,368 sequences for Site 4 2021 (zone 15); and 17,614, 18,462 and 13,611  
320 sequences for site 4 2021 (zone 16). The analysis of these sequences indicated a very high dissimilarity between  
321 the communities collected in 2019 and 2021, as illustrated by the Heatmap (Figure 5).

322 As shown in Figure 6, the microbial community of 2019 included few archaea (>2%), while the 2021 community  
323 was dominated by these prokaryotes (with  $91 \pm 13\%$  for Site 4 2021 (zone 13) and  $93 \pm 3\%$  for Site 4 2021(zone  
324 15)). Site 4 2021 (zone 16) revealed another equilibrium between bacteria and archaea ( $37 \pm 4\%$ ), which could  
325 be explained by the presence of abundant chloroplasts ( $28 \pm 3\%$ ). The archaea belonged primarily to the  
326 phylum Crenarchaeota, including the classes Nitrososphaeria and Thermoprotei, and to the orders SCGC AB-  
327 179-E04 (from  $33 \pm 4\%$  to  $79 \pm 13\%$ ) and Geoarchaeales (from  $4 \pm 0\%$  to  $19 \pm 16\%$ ), respectively. No archaea  
328 similar to methanogens were identified at this site during either sampling campaign. In addition, enrichments  
329 carried out in the dark under anoxic and oxic conditions showed no significant consumption of  $H_2$  or  $CO_2$   
330 present in the gas phase, during incubation carried out for 10 days.

331 Regarding bacteria, the community from Site 4 in 2019 included mainly the following orders: Kapabacteriales  
332 ( $15 \pm 1\%$ ), Thermoflexales (family of *Thermoflexaceae*;  $8 \pm 3\%$ ), Thermomicrobiales (*Thermomicrobiaceae*;  $8$   
333  $\pm 4\%$ ), Cyanobacteriales (*Nostocaceae*;  $14 \pm 3\%$ ), Brevibacillales (*Brevibacillaceae*;  $10 \pm 4\%$ ), Paenibacillales  
334 (*Paenibacillaceae*;  $5 \pm 2\%$ ), and Symbiobacteriales (*Symbiobacteraceae*;  $3 \pm 2\%$ ). The presence of organisms  
335 affiliated to the class of Hydrothermae ( $14 \pm 3\%$ ) should also be noted. For the second sampling campaign, in  
336 zones 13 and 15, bacteria represented only 6–8% of the relative abundance of the communities present. Only  
337 the community at Site 4 2021(16) exhibited a relatively high abundance, with 63% of bacteria belonging to the  
338 orders Pseudonocardiales (*Pseudonocardiaceae*;  $7 \pm 1\%$ ), Ktedonobacterales (*Ktedonobacteraceae*;  $5 \pm 1\%$ ),  
339 and Gemmatales (*Gemmataceae*;  $7 \pm 2\%$ ).

### 340 3.3. Bulk analysis

341 The total rock analyses performed by ICP–OES for the F1 and Glc1 wells (Table 1) demonstrate elemental  
342 variations with depth in the inner and outer margins. For the F1 well,  $SiO_2$  concentrations remained relatively  
343 constant with depth, typically in the range 44–47%, although  $SiO_2$  values closer to 50% were observed at a few  
344 depths. In contrast, sample 15 (304 m) was particularly poor in  $SiO_2$  (31.86%). For Glc1,  $SiO_2$  concentrations  
345 were more variable: typically, these were lower than 45% for the first 280 m and higher than 45% in the rest of  
346 the cuttings, reaching up to 66% for sample 10 (458 m).

347 A transition is apparent in well F1 at 464 m depth (Figure 7).  $Al_2O_3$  concentrations were higher at depths of 0–  
348 464 m, typically varying between 18.86 and 25.32%, compared to 11.95–21.21% in the rest of the well. Most

349 other parameters analyzed generally exhibited lower values at shallower depths (i.e., 0–464 m), including total  
350 iron (4.45 to 8.81%), TiO<sub>2</sub> (0.67 to 1.47%), Na<sub>2</sub>O + K<sub>2</sub>O (2.18 to 2.46%), and loss on ignition (LOI; 1.31 to 5.69).  
351 However, concentrations of CaO were higher at these depths (12.18 to 15.39%) than elsewhere. Values at 518–  
352 1118 m were as follows: 5.51–15.83% for Fe<sub>2</sub>O<sub>3</sub>; 0.97–3.48% for TiO<sub>2</sub>; 2.67–6.20% for Na<sub>2</sub>O + K<sub>2</sub>O; 2.07–9.37%  
353 for LOI; and 5.12–13.54% for CaO.

354 In well Glc1, a transition was also observed at 280 m depth (Figure 7), with lower SiO<sub>2</sub> contents and higher  
355 Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, and TiO<sub>2</sub> contents at depths of 0–280 m relative to the rest of the well. In contrast, Al<sub>2</sub>O<sub>3</sub>  
356 contents remained relatively constant with depth (~13 ± 1.5%).

357 A global decrease in LOI with depth was found for well Glc1, whereas LOI was found to increase slightly with  
358 depth in well F1. In both wells, Fe<sub>2</sub>O<sub>3</sub> peaks were associated with TiO<sub>2</sub> peaks (e.g., at 250 m and 280 m for Glc1;  
359 at 616 m, 894 m, 954 m, and 1016 m for F1).

360 Sample 15 from well F1 is totally different from the surrounding basalts, with SiO<sub>2</sub>, CaO, and LOI values of  
361 31.86%, 30.28%, and 25.87%, respectively.

362 On a total alkali–silica (TAS) diagram (Figure 8), the F1 well cuttings are concentrated in the area of basalts with  
363 relatively homogeneous SiO<sub>2</sub> concentrations (44% < SiO<sub>2</sub> < 47%). However, some of the samples exhibited  
364 higher silica concentrations and could be described as hawaiite-type trachybasalts or andesitic basalts (SiO<sub>2</sub> >  
365 50%). All of the basalts are distributed close to the straight line separating alkaline basalts from tholeiitic  
366 basalts, with samples from proximal levels in the tholeiitic domain and the deeper samples in the alkaline  
367 domain. A few samples exhibited SiO<sub>2</sub> concentrations below 45%, placing them closer to picro-basalts and  
368 basanites, which are more basic and richer in normative olivine.

369 The data from the Glc1 well cuttings are more heterogeneous, despite remaining predominantly within the  
370 basaltic domain. Samples from shallower levels tend towards alkaline basalts, whereas those from deeper  
371 levels are typically tholeiitic basalts. However, point 10, from 548 m, is particularly rich in SiO<sub>2</sub> (66%) and is  
372 therefore more acidic and located within the dacite zone.

Sample	Depth	Temp.	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> *	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	LOI	Total
D4-1	0	95	38,79	23,91	11,57	0,17	2,94	1,61	0,10	0,05	2,45	0,26	17,60	99,44
D4-13	0	95	46,61	23,28	6,41	0,10	3,55	14,47	1,96	0,17	1,30	0,16	1,48	99,51
<b>Fiale 1</b>														
12	149	32	46,43	22,94	7,09	0,091	3,78	14,52	2,01	0,17	1,47	0,15	1,31	99,95
13	208	32	46,12	22,45	7,17	0,096	4,73	13,99	2,04	0,21	1,14	0,13	1,79	99,84
14	254	35	46,03	19,89	8,32	0,12	5,97	13,04	2,22	0,23	1,43	0,18	2,27	99,70
15	304	47	31,86	4,19	4,49	0,065	1,23	30,28	0,50	0,20	0,36	0,13	25,87	99,17
16	354	85	44,69	18,86	8,81	0,12	4,94	12,18	2,29	0,31	1,57	0,22	5,69	99,68
17	404	145	44,18	23,84	5,47	0,10	3,21	14,86	2,01	0,22	1,08	0,00	4,46	99,42
18	437	160	44,76	23,44	5,68	0,090	4,17	14,25	2,02	0,22	1,01	0,00	3,72	99,35
19	464	168	44,63	25,32	4,45	0,083	2,81	15,39	1,83	0,57	0,67	0,00	3,71	99,46
21	518	190	44,66	18,78	9,65	0,14	3,96	11,16	2,65	0,81	1,63	0,22	5,94	99,59
22	536	195	43,73	17,85	8,52	0,14	3,91	13,54	2,36	0,41	1,42	0,20	7,94	100,02
23	552	200	44,78	17,36	10,20	0,17	3,70	10,24	2,73	0,75	2,13	0,37	6,54	98,96
24	574	205	50,77	13,50	10,11	0,21	4,15	5,36	2,41	3,44	2,34	0,42	6,65	99,36
25	592	205	47,66	15,57	10,23	0,22	3,78	8,71	2,37	2,10	2,03	0,33	6,21	99,21
26	616	207	47,02	12,75	15,83	0,28	4,59	8,17	3,39	0,63	3,48	0,51	2,07	98,73
27	634	207	46,13	17,74	9,85	0,20	5,02	7,55	3,16	1,80	2,27	0,53	5,29	99,53
28	654	208	46,58	16,19	10,84	0,21	5,19	6,48	2,96	1,79	2,38	0,45	6,50	99,57
29	674	209	45,13	18,88	8,06	0,21	3,65	9,87	3,18	1,53	1,53	0,23	6,64	98,94
30	694	210	46,82	14,23	12,33	0,16	4,91	5,12	2,46	2,48	2,43	0,37	7,82	99,14
31	714	205	51,20	18,19	6,98	0,13	3,32	7,35	2,04	4,16	1,29	0,20	4,80	99,64
32	734	190	44,94	14,07	11,66	0,29	5,12	8,55	3,26	0,67	2,34	0,32	7,80	99,03
33	754	180	46,62	17,36	7,45	0,19	3,85	10,56	3,35	1,17	1,38	0,19	7,07	99,18
34	774	170	47,19	21,21	5,51	0,13	3,39	10,82	3,74	0,93	0,97	0,14	5,91	99,93
35	794	162	44,76	18,14	8,54	0,17	4,26	10,73	3,41	0,77	1,60	0,22	6,60	99,20
37	838	150	47,22	17,22	9,34	0,19	4,27	8,56	3,16	1,20	1,84	0,29	6,04	99,33
38	854	145	45,73	11,91	10,41	0,20	3,72	11,26	3,32	0,90	2,11	0,37	9,37	99,29
39	871	135	44,66	17,52	8,10	0,19	2,64	11,64	3,06	1,85	1,55	0,24	7,99	99,43
40	894	127	46,27	14,93	12,82	0,23	5,09	10,34	3,08	0,35	2,64	0,37	3,38	99,51
41	914	120	47,61	15,64	9,97	0,23	3,92	9,29	3,65	0,62	1,85	0,32	6,37	99,47
42	934	115	52,44	11,95	8,87	0,19	3,25	9,73	3,05	0,19	1,67	0,35	7,57	99,26
43	954	110	45,58	13,35	13,37	0,23	5,17	10,82	2,49	0,18	2,70	0,39	4,89	99,16
44	974	107	45,54	18,89	9,60	0,17	3,96	11,94	2,76	0,11	2,02	0,23	4,43	99,64
45	994	100	44,94	18,15	9,37	0,16	4,62	12,01	2,54	0,12	1,72	0,20	5,93	99,76
46	1016	95	45,83	14,45	12,55	0,20	5,93	12,24	2,50	0,19	2,61	0,35	2,43	99,28
47	1034	92	47,49	18,86	9,04	0,16	4,52	12,34	3,13	0,13	1,61	0,21	2,82	100,29
48	1054	90	47,16	16,09	9,68	0,16	3,54	10,28	3,63	0,17	1,99	0,33	6,09	99,12
50	1091	85	46,24	19,30	9,29	0,17	4,10	12,08	3,03	0,32	1,78	0,23	2,93	99,46
51	1118	77	45,58	17,75	8,33	0,17	3,45	13,07	2,78	0,10	1,77	0,23	6,90	100,14
<b>Glc 1</b>														
1	76	35	36,75	11,29	11,26	0,16	4,08	12,52	2,07	0,78	2,33	0,48	17,88	99,60
2	160	50	38,09	14,41	8,34	0,15	5,01	10,12	1,84	0,68	1,54	0,28	18,75	99,21
3	250	90	43,37	13,38	14,52	0,22	4,97	10,83	2,73	1,10	3,06	0,53	4,34	99,06
4	280	110	42,90	14,57	13,66	0,22	6,49	11,01	2,61	0,41	2,67	0,36	4,68	99,58
5	310	115	49,68	13,06	9,22	0,24	3,19	4,82	1,87	2,25	1,38	0,27	14,08	100,06
6	340	120	48,65	13,12	9,42	0,19	3,19	5,51	1,18	1,60	1,45	0,34	14,89	99,54
7	370	125	45,98	14,57	9,65	0,20	4,31	8,61	2,45	1,16	1,56	0,29	10,92	99,69
8	400	130	51,81	13,90	9,85	0,14	3,86	4,30	1,59	3,36	1,28	0,30	9,85	100,22
9	420	130	50,20	12,50	8,09	0,15	3,23	8,18	1,66	3,07	1,08	0,26	11,98	100,39
10	458	130	66,50	10,53	4,56	0,12	1,73	4,48	0,88	3,28	0,59	0,11	7,59	100,36

Table 1 – Chemical compositions of Fiale 1 and Glc1 cuttings in Ox%. Samples D4-1 and D4-13 are from Pasquet et al. (2021). Fe<sub>2</sub>O<sub>3</sub>\* is for total iron.



375 In addition to the major primary minerals, such as plagioclase (mainly labradorite and bytownite),  
376 clinopyroxene (solid solution between diopside and augite), the XRD analyses revealed the appearance at  
377 depth of secondary minerals (Figure 9). Some minerals, such as olivine or zeolites, which are present in low  
378 amounts, were difficult to detect due to poor because the signal-over-noise ratio is too low to distinguish their  
379 weak concentrations. In addition, many peaks overlap each other.

380 In well F1 (37 samples; XRD patterns in supplementary data), the secondary minerals found include smectite at  
381 208 m and calcite at 464 m; quartz was detected in sample 21 at 518 m, chlorite at 536 m, and epidote at 854  
382 m. Pyrite began to appear at 694 m, although in very low concentrations. Magnetite-rich sections were found  
383 between 518 m and 616 m depth and from 894 m to 1118 m. Zeolites were very rare.

384 In well Glc1 (10 samples; XRD profiles in supplementary data), kaolinite, calcite and quartz are present in the  
385 samples extracted from the top of the well. No secondary minerals were observed between 250 and 280 m.  
386 Analcime zeolites were observed in the first 160 m of the well, whereas smectite began to appear below 280  
387 m. Secondary minerals typical of higher temperatures, such as chlorite, epidote, and pyrite, were not detected  
388 by XRD.

### 389 3.5. Mössbauer spectroscopy analysis

390 <sup>57</sup>Fe Mössbauer analyses were performed on 20 samples from well F1 and 10 samples from well Glc1 (Table 2).  
391 These data allowed the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios in the rocks to be determined and allowed iron-bearing minerals to be  
392 identified. The main minerals found were ferrihydrite (Fe<sup>3+</sup><sub>5</sub>HO<sub>8</sub>.4H<sub>2</sub>O), clinopyroxene  
393 ((Ca,Na,Mg,Fe<sup>2+</sup>,Al,Ti)<sub>2</sub>(Si,Al)<sub>2</sub>O<sub>6</sub>), olivine ((Fe<sup>2+</sup>,Mg)<sub>2</sub>SiO<sub>4</sub>), ilmenite (Fe<sup>2+</sup>TiO<sub>3</sub>), hematite (Fe<sup>3+</sup><sub>2</sub>O<sub>3</sub>), magnetite  
394 (Fe<sup>2+</sup>O. Fe<sup>3+</sup><sub>2</sub>O<sub>3</sub>), and maghemite (γ-Fe<sup>3+</sup><sub>2</sub>O<sub>3</sub>) in the first part of the well (i.e., depths up to 464 m). At greater  
395 depths, a Fe-rich chlorite like chamosite (iron end-member of chlorite: (Al,Fe<sup>2+</sup>,Fe<sup>3+</sup>,Mg)<sub>6</sub>(Si<sub>3</sub>Al)O<sub>10</sub>(OH)<sub>8</sub>) was  
396 found in place of olivine and maghemite disappeared (Table 2).

397 The phase mixtures in these rocks are quite complex and the Mössbauer spectra exhibit various components  
398 (quadrupole doublets and magnetic sextets) associated with different Fe-bearing minerals. The analyses were  
399 carried out at room temperature; accordingly, there is some uncertainty in the attribution of some  
400 components. Indeed, the Fe<sup>3+</sup> doublets characterized by isomer shift (δ) values ranging from 0.35 to 0.38 mm/s  
401 and rather large quadrupole splitting (0.60 ≤ Δ ≤ 0.84 mm/s) could correspond to either ferrihydrite or Fe<sup>3+</sup>-

402 chlorite (Figure 10). Moreover, this component often exhibits broad resonance lines ( $\Gamma > 0.60$  mm/s) that could  
403 hide a low-intensity doublet associated with pyrite ( $\text{Fe}^{2+}\text{S}_2$ ) which is characterized by  $\delta \approx 0.30$  mm/s and  
404  $\Delta \approx 0.5$  mm/s. Similarly, the  $^{57}\text{Fe}$  Mössbauer hyperfine parameters of the  $\text{Fe}^{2+}$  doublets due to olivine and  $\text{Fe}^{2+}$ -  
405 chlorite are very similar. Further analysis at different temperatures would allow these  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$ -bearing  
406 phases to be distinguished. This study has taken the approach of interpreting these doublets and sextets  
407 considering the results of XRD analyses and especially, the detection of chlorite XRD pattern in the  
408 diffractograms. Thus, the concentration of chlorite is likely to be overestimated in comparison with olivine and  
409 the proportion of pyrite likely underestimated.

410  $\text{Fe}^{3+}$  was found to be carried by ferrihydrite, maghemite, and hematite at depths of 0–464 m but primarily by  
411 Fe-rich chlorite and magnetite at greater depths (Table 2). An additional threshold was observed at 518 m,  
412 where ferrihydrite, maghemite, and Fe-clinopyroxene were replaced by Fe-chlorite. Despite the highest  
413 concentrations of  $\text{Fe}_{\text{total}}$  being observed below 464 m depth, the percentage of  $\text{Fe}^{3+}$  in the rock was significantly  
414 lower (24–55%) at greater depths than at depths less than 464 m (63–77%; Figure 11).

Sample	Depth (m)	Cpx	Frh	Olivine	Fe-Chlorite		Hematite	Magnetite		Ilmenite	Maghemite	Pyrite	Fe <sup>3+</sup> /Fe <sub>total</sub>
		Fe <sup>2+</sup>	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Fe <sup>3+</sup>	Fe <sup>2+/3+</sup>	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Fe <sup>2+</sup>	(%)
12	149	31	24	3	-	-	14	6	6	-	16	-	63.0
13	208	24	22	-	-	-	20	3	3	-	28	-	74.5
14	254	26	23	3	-	-	8	5	5	4	30	-	68.5
16	354	28	26	8	-	-	8	12	12	8	12	-	64.0
17	404	14	36	11	-	-	6	6	6	8	13	-	64.0
18	434	15	31	9	-	-	16	6	6	3	14	-	70.0
19	464	4	26	11	-	-	15	8	8	4	24	-	77.0
21	518	10	16	12	-	-	20	11	11	2	18	-	68.5
22	536	-	-	-	18	30	31	9	9	-	-	-	62.5
23	552	-	-	-	20	48	13	8	8	3	-	-	45.0
26	616	17	-	-	16	13	7	16	17	14	-	-	47.5
30	694	-	-	18	37	28	-	-	-	-	-	17	37.0
33	754	-	-	-	17	45	21	7	7	3	-	-	48.5
38	854	-	-	-	12	42	28	5	5	-	-	-	55.5
39	871	-	-	-	20	59	7	5	5	4	-	-	34.5
43	954	11	-	-	14	30	6	14	15	10	-	-	41.5
47	1034	27	-	-	19	28	-	12	14	-	-	-	38.0
48	1054	-	-	-	11	49	8	13	13	6	-	-	38.5
50	1091	17	-	-	15	38	3	9	9	9	-	-	31.5
51	1118	-	-	-	11	64	-	9	8	8	-	-	24.0
1	76	4	80	-	-	-	-	2	2	12	-	-	95.0
2	160	-	78	-	-	-	22	-	-	-	-	-	100.0
3	250	19	25	-	-	-	20	3	3	30	-	-	79.5
4	280	24	19	-	-	-	23	5	5	24	-	-	73.5
5	310	-	76	4	-	-	20	-	-	-	-	-	96.0
6	340	-	44	56	-	-	-	-	-	-	-	-	44.0
7	370	19	36	30	-	-	-	4	4	-	7	-	42.0
8	400	-	39	26	-	-	35	-	-	-	-	-	74.0
9	420	-	35	17	-	-	48	-	-	-	-	-	83.0
10	458	-	47	19	-	-	19	-	-	-	-	-	66.0

Table 2 - Distribution of iron content in mineral phases after Mössbauer spectroscopic analysis of F1 (12 to 51) and Glc1 (1 to 10) cuttings.

## 415 4. Discussion

416 Here, we discuss how our results allow us to better define the dihydrogen system of the Asal–Ghoubbet rift;  
417 this includes inferring the H<sub>2</sub> source rock, migration pathways, reservoir rock, and a seal in the Fiale area.

### 418 4.1. Well lithologies

419 We produced simplified lithological logs (Figure 12) by comparing our XRD and bulk rock analysis results; the  
420 resolution of these logs is based on the spacing of the well cuttings, *i.e.* 20–50 m for F1 and 20–90 m for Glc1.

421 Unsurprisingly, the rocks in these two wells are mainly basalts. These basalts are transitional, essentially  
422 composed of plagioclase (solid solution between labradorite and bytownite) and clinopyroxene (solid solution  
423 between diopside and augite). They can be divided into two domains: basalt with a tholeiitic tendency (0–464  
424 m for F1) and basalt with an alkaline tendency (464–1118 m for F1) (Figure 7 & 8). The first domain  
425 corresponds to the basalts of the Asal Series (1 Ma to present) and the second to the Afar Stratoid Series (4–1  
426 Ma). The basalts of the Asal Series are richer in plagioclase so richer in CaO%.

427 The transition between the two series, although marked in both wells, is less pronounced in well Glc1. Indeed,  
428 the composition of the lavas here are known to have varied with time, with the basalts of the Asal Series along  
429 the external rift margins exhibiting compositions that are more intermediate than tholeiitic (Stieltjes et al.,  
430 1976). In our dataset, the transition from the basalts of the Asal Series to the Stratoid Series was observed to  
431 occur at 280 m. The Asal Series is thicker along the rift axis.

432 Basalts with a Fe<sub>2</sub>O<sub>3</sub> (total iron) composition above 15% (Ox%) are considered to be ferrobasalts (Stieltjes et al.,  
433 1976) and are associated with high TiO<sub>2</sub> concentrations (>3.48%) (Table 1). Many of these basalts are rich in  
434 iron (>10%) and titanium (>2%) but cannot be classed as ferrobasalts because their Fe<sub>2</sub>O<sub>3</sub> content is lower than  
435 15%. This correlation suggests high levels of ilmenite and titanomagnetite (Fe<sup>2+</sup>(Fe<sup>3+</sup>,Ti)<sub>2</sub>O<sub>4</sub>). SiO<sub>2</sub> peaks are  
436 often correlated with Na<sub>2</sub>O + K<sub>2</sub>O peaks, corresponding to more acidic rocks such as andesite basalts or  
437 trachybasalts.

438 LOI can be used as a proxy for the alteration rate of basalts; here, many samples exceeded 5%, which indicates  
439 argillization/chloritization of the rock. At shallow depths in well Glc1 (160–200 m), LOI values above 15% are  
440 considered to indicate hyaloclastites, which were formed under seawater. Conversely, the first cuttings from

441 well F1 (i.e., from depths up to 250 m) exhibited LOI values lower than 2.5%. These basalts can be considered  
442 unaltered or slightly altered; the XRD data support this interpretation, with less pronounced clay signals.

443 Finally, a sedimentary layer was observed at 300 m depth in F1; this layer was composed primarily of calcium  
444 carbonates and quartz. Thus, the high Fe<sup>3+</sup> concentration in the hyaloclastites at the margins indicates almost  
445 complete oxidation of the submarine basalts, in contrast to the open-air conditions along the axis. The  
446 underlying Stratoid Basalts, richer in total iron and also more altered, indicate a reconcentration of iron after  
447 alteration.

#### 448 4.2. Secondary mineral occurrence

449 Secondary minerals provide information about the alteration degree of the basalts and the physicochemical  
450 conditions at depth. Based on our knowledge of conditions and the mineral phases present, it is possible to  
451 consider potential redox reactions leading to H<sub>2</sub> formation and to determine whether a rock has already  
452 produced or could produce H<sub>2</sub>.

453 For well F1 (axial zone), temperatures reach a maximum of 210°C at 694 m depth, and 130°C at 400 m for Glc1  
454 (external margins). Then, in the axial zone, temperature decreases from this 210°C maximum to approximately  
455 60°C (see Table 1) owing to marine water intrusion (Zan et al., 1990; Varet, 2014).

456 For well F1, we observed the successive appearance of smectites, calcite, quartz, chlorite, and then epidote  
457 with increasing temperature (Figure 13); this is similar to the characteristics of well A5 as described previously  
458 (Zan et al., 1990). Indeed, these minerals can be utilized to define temperature domains according to their  
459 dominance (Franzson et al., 2008): 50 to 200°C for smectite–zeolites; 220°C to 240°C for chlorite; and 240°C to  
460 280°C for the chlorite–epidote mixture. Chlorite was first observed by XRD and Mössbauer spectroscopy at  
461 190°C, according to the well temperature profile. However, high-temperature minerals such as chlorite and  
462 epidote are not affected by this sudden geothermal water temperature drop. Therefore, it can be inferred that  
463 the secondary minerals are not currently in equilibrium with the fluid.

464 Secondary magnetite is a good proxy for H<sub>2</sub> production, but we assume that the titano-magnetite is principally  
465 of primary origin here, because there is a strong and uniform positive correlation between TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> (Total)  
466 in our data (Figure 14). Little pyrite was found in our samples. For well Glc1, a clear zeolite layer is evident in  
467 the first 160 m of depth. Deeper than 310 m, smectite and mixed-clay layers start to appear.

468 When considering H<sub>2</sub> production, both the observation of these alteration minerals and the alteration ratio are  
469 key to constraining potential cap rocks at depth. Despite the presence of a clay-rich layer around 850 m in well  
470 F1, it has not been possible to confirm that this layer is a good seal based on the LOI values (Table 1, Figure 7).  
471 However, at the external margin of the rift in well Glc1, fully weathered layers were observed over almost the  
472 first 400 m of depth; despite the presence of some unweathered layers, these locations may represent a  
473 suitable cap rock.

#### 474 4.3. H<sub>2</sub> production

475 As already stated, continuous H<sub>2</sub> flow has been measured at the surface next to the Fiale Caldera, and some H<sub>2</sub>  
476 content has been detected in wells F1 and A5. The relative H<sub>2</sub> concentrations have been found to be 0.57–  
477 0.89% of the dry gas phase. This concentration is higher than that measured at depth in well A3 (0.25% of the  
478 dry gas phase) and also higher than a purely volcanic degassing such as that during the Ardoukoba eruption in  
479 1978 (0.145% of the dry gas phase; Allard et al., 1979). After the volcanic degassing, this surface fumarolic H<sub>2</sub>  
480 may have been enriched by other processes, including redox reactions between iron-rich mineral phases and  
481 other liquid or gaseous phases.

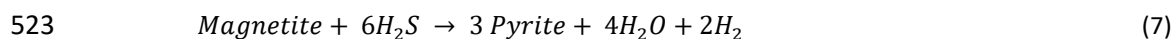
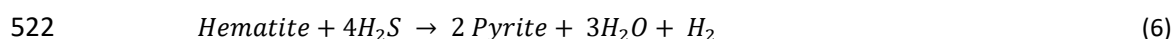
482 Microbial communities in continuous H<sub>2</sub> flow have been studied in order to characterize their *in situ* taxonomic  
483 diversity and their potential to use H<sub>2</sub> as a source of energy and electrons from enrichment cultures. Indeed, it  
484 is known that microbial ecosystems can be hydrogen-based (Stevens and McKinley, 1995) with sulfate, carbon,  
485 dioxide or oxygen, for example, as acceptor electron. Given the environmental conditions at this site, in  
486 particular the high temperatures, our study of taxonomic diversity unsurprisingly revealed the presence of  
487 microorganisms known to be extremophiles; this includes the archaea, which are very well represented but not  
488 very diversified at this location. All of the archaea identified belong to the orders SCGC AB 179 E04 and  
489 Geoarchaeales, which have been described in thermal springs in the US (Havig and Hamilton, 2019). Similarly,  
490 the bacteria identified also belong to taxonomic groups already known to populate hot springs, such as the  
491 *Pseudonocardiaceae* (Ningsih et al., 2019), Kapabacteriales (Guajardo-Leiva et al., 2021), *Thermoflexaceae*  
492 (Dodsworth et al., 2014), *Thermomicrobiaceae* (AlSaade et al., 2022), *Ktedonobacteraceae* (Arif et al., 2021),  
493 *Nostocaceae* (Ansary et al., 2017), *Brevibacillaceae* (Inan et al., 2016), *Paenibacillaceae* (Panosyan et al., 2020),  
494 and Hydrothermae (Smrhova et al., 2022). Much affiliation remains vague at the order or even class level, since  
495 hot springs are extreme environments from which few microorganisms can be cultured and studied (López-

496 López et al., 2013; Marín-Paredes et al., 2021); this justifies the need to multiply the studies of these extreme  
497 environments in order to better understand them. Our results illustrate variation in taxonomic diversity both  
498 spatially (*i.e.*, between Site 4 2021 (zone 13), Site 4 2021 (zone 15), and Site 4 2021 (zone 16)) and, particularly,  
499 temporally (*i.e.*, between 2019 and 2021). This seems to suggest that unstable environmental conditions are  
500 strongly influencing the structuring of communities. Most of the microorganisms identified are aerobic and the  
501 presence of cyanobacteria and chloroplasts (algae) suggest the influence of oxygenic photosynthesis as a key  
502 metabolism of two of the communities (Site 4 2019 and Site 4 2021 (zone 16)). The dominance of aerobic  
503 microorganisms explains the absence of functional groups such as sulfate-reducers and methanogenic archaea,  
504 which harbor numerous hydrogenotrophs. The absence of methanogens is consistent with the non-detection  
505 of methane during gas analyses. Laboratory tests have shown no H<sub>2</sub> consumption in either anaerobiosis or  
506 aerobiosis. The absence of photosynthetic or hydrogenotrophic autotrophic organisms raises the question of  
507 maintenance in such ecosystems, in particular for the communities at Site 4 2021 (zone 13) and (zone 15).  
508 However, some members of the Nitrososphaeria class have been shown to be thermophilic autotrophic  
509 ammonia-oxidizers (Hatzenpichler et al., 2008). This capacity would explain the very strong dominance of these  
510 kinds of archaea (up to 79% of the relative abundance), since they would be key players in the microbial  
511 communities, capable of using ammonium as an electron donor, oxygen as electron acceptor, and CO<sub>2</sub> as a  
512 carbon source.

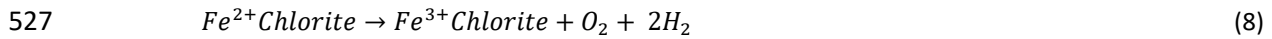
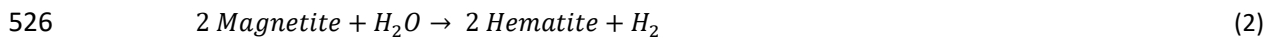
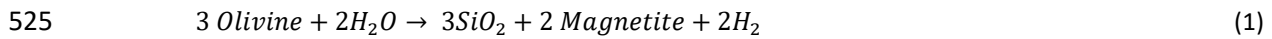
513 It remains to evaluate the internal reactions of the iron-rich minerals of different basalts in order to conclude  
514 whether enrichment of the H<sub>2</sub> phase at depth is likely to be possible. Based on the Mössbauer data, we were  
515 able to establish remnant H<sub>2</sub> generation using the calculations of Geymond et al. (2022). These results give an  
516 idea of the maximum H<sub>2</sub> potential of the rock if the corresponding minerals undergo the associated reaction.  
517 From the reactions presented in the introduction and based on the minerals present in the basalts of the Asal-  
518 Ghoubbet rift, two main groups of reactions can be isolated: pyritization reactions involving H<sub>2</sub>S oxidation and  
519 Fe<sup>3+</sup> reduction; and reactions involving H<sub>2</sub>O reduction and Fe<sup>2+</sup> oxidation.

520

521 ***Fe<sup>3+</sup> reduction and pyritization:***



524 **Fe<sup>2+</sup> oxidation:**



528 According to Figure 15, H<sub>2</sub> production is low in the upper part of the wells, i.e., in the basalts of the Asal Series,  
529 with only pyritization processes occurring (up to 90 mmol/kg rock). Conversely, H<sub>2</sub> concentrations are much  
530 higher in the Stratoïd Basalts. Pyritization of magnetite (up to 486 mmol/kg rock) and oxidation of chlorite (up  
531 to 1332 mmol/kg rock) are the two processes leading to the highest H<sub>2</sub> production. It can be seen that olivine  
532 alteration and hematization do not offer high hydrogen generation potential in this setting, with olivine  
533 content being very low in these basalts. The presence of iron-rich chlorite at depth also offers interesting  
534 potential for the production of H<sub>2</sub>, if of course all of the Fe<sup>2+</sup> becomes Fe<sup>3+</sup>. To investigate this possibility  
535 further, we assumed the maximum point at 1332 mmol/kg of rock to be equivalent to approximately 32.04  
536 L/kg of H<sub>2</sub> (at 20°C and 1 atm). If we consider a redox cycle where iron is both reduced and oxidized under  
537 optimal conditions, where all iron reacts to form H<sub>2</sub>, the remnant H<sub>2</sub> production of these basalts from the F1  
538 and Glc1 wells is, respectively 211.5 and 197 mmol/kg for the Asal Series basalts and 1192 and 304.2 mmol/kg  
539 for the Stratoïd Series basalts.

540 This difference between the two series can be explained by the high Fe<sup>3+</sup> content of the basalts of the Asal  
541 Series, even though the alteration index is lower. The concentrations of magnetite and hematite (maghemite  
542 and ferrihydrite, intermediate iron oxides), where Fe<sup>3+</sup> is contained, are lower than Fe<sup>2+</sup>-minerals in basalts;  
543 accordingly, the reduction reactions of this iron that can generate H<sub>2</sub> are lower than the oxidation reactions. It  
544 can be argued that the latter basaltic units were formed in a more oxidizing environment in direct contact with  
545 the atmosphere. However, in the Asal Series, the remaining Fe<sup>2+</sup> is mainly concentrated in Fe-clinopyroxene,  
546 which has much slower H<sub>2</sub> formation kinetics than olivine or oxides and does not easily integrate Fe<sup>3+</sup> in its  
547 structure.

#### 548 4.4. H<sub>2</sub> system

549 A hydrogen system, as in a petroleum system, is defined by the source rock, reservoir, a seal and the migration  
550 pathways between these elements. Here, we discuss likely candidates for each of these components.



#### 551 4.4.1. Source

552 There is not a single source; we were able to distinguish a primary volcanic source produced by degassing of  
553 the magma chamber under the Fiale Caldera, with a summit identified at 3–5 km depth in the rift axis (Doubré  
554 et al., 2007). In volcanic areas, the major gases present are H<sub>2</sub>O, CO<sub>2</sub>, and S phases (Giggenbach, 1996). Thus,  
555 during degassing, H<sub>2</sub> is controlled by the SO<sub>2</sub>–H<sub>2</sub>S equilibrium and formed mainly via the reaction H<sub>2</sub>O + H<sub>2</sub>S =  
556 SO<sub>2</sub> + H<sub>2</sub> (Klein et al., 2020). Little H<sub>2</sub>S has been observed at the surface in fumaroles (Pasquet et al., 2021),  
557 suggesting that it has interacted with water to form H<sub>2</sub> and SO<sub>2</sub> or sulfides. Pyrite is observed in our sample 30  
558 and in all other Asal wells (Zan et al., 1990). Otherwise, because SO<sub>2</sub> and H<sub>2</sub>S are extremely soluble in the  
559 aqueous phase, SO<sub>4</sub> may have been formed.

560 The two other possible sources are related to rock–fluid interactions. The remnant potential of these sources  
561 has been calculated for an ideal case where the whole iron-rich mineral undergoes a redox reaction. This  
562 provides an indication of the maximum potential remaining for H<sub>2</sub> generation. Fe<sup>3+</sup> reduction (or pyritization),  
563 as described in the previous section, involves iron minerals such as hematite (and maghemite) and magnetite  
564 reacting with H<sub>2</sub>S partly from degassing to form pyrite and H<sub>2</sub>. The presence of pyrite as revealed by XRD and  
565 Mössbauer analyses (Figure 9) supports this hypothesis, although the small quantities measured suggest that  
566 this is not the major source of H<sub>2</sub> (or the source with the greatest potential). In sample 30 from well Fiale 1,  
567 Fe<sup>2+</sup>-pyrite represents 17% of the iron content (Table 2), with a total iron concentration of 8.62 wt% in the  
568 sample, pyrites represent 1.47 wt% of the sample.

569 Secondly, hydrothermal reactions involving olivine, magnetite, or chlorite alteration by water reduction are  
570 associated with the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>. Although not measured (H<sub>2</sub> content) at depth in the rift axis wells  
571 during drilling, this source (and particularly the oxidation of Fe-chlorite in the Stratoïd Basalts deeper than 552  
572 m) has the greatest hydrogen generation potential (with an average of 1192 mmol H<sub>2</sub>/kg rock in the Stratoïd  
573 Series basalts) (Figure 15). Dehydrogenation chlorite processes occur systematically and differ based on the  
574 chlorite type, one oxidize Fe<sup>2+</sup> gives one H<sup>+</sup> (Steudel et al., 2016). Optimum dehydrogenation for Fe<sup>2+</sup>-rich  
575 chlorite, like our case, were calculated on a range between 390°C and 410°C (Lempart et al., 2018). This zone  
576 corresponds to the geothermal propylitic zone (chlorite–epidote assemblage). Olivine does not play a major  
577 role here, in contrast to what has been observed at the Mid Atlantic Ridge or in other ophiolitic contexts  
578 (Vacquand et al., 2018). In the Asal Series, according to the cuttings, olivine represents 0.1 to 0.5 wt% of the

579 rocks and 1.6 wt% for sample 30. However, in terms of volume, it should be noted that the volume of H<sub>2</sub> that  
580 could be generated in this area is considerable. Based on an average value of 500 mmol H<sub>2</sub>/kg, i.e. 1 g H<sub>2</sub>/kg of  
581 rock (by averaging the values obtained from the reactions in Figure 15) over a thickness of 500 m (according to  
582 the occurrence of chlorite by XRD in Figure 13, to be in the propylitic zone in well Fiale 1),. Even a “small” area,  
583 such as the Fiale Caldera between Ghoubbet Bay and Lake Asal (~25 km<sup>2</sup>), could produce up to 20 Mt of H<sub>2</sub>.  
584 Globally, one may then consider that the main focus of future exploration should be the detection of reservoirs  
585 and seals.

#### 586 4.4.2. Reservoir

587 A good reservoir must have a well-connected porosity and some permeability.  
588 As already noted, different volcanic units have been identified at depth, ranging from the Asal Series Basalts to  
589 the Stratoïd Basalts and Dahla Basalts (Varet, 1978). Although mineralogically similar, these transitional fissural  
590 basalts have a rather high primary porosity of approximately 10% (Aquater, 1989). This porosity can be  
591 explained by degassing during the emplacement of the lava flow but it does not imply that it is connected.  
592 Pasquet et al. (2021) also showed that there was porosity in the vicinity of the phenocrysts in the microlithic  
593 texture, through which the primary gases could flow forming these flames like hematite bodies in olivines.  
594 Physical parameters including porosity and large scale permeability were measured during the various drilling  
595 campaigns. In the rift axis, at wells A4, A5, F1, F2, and F3, permeability was found to be rather low (Houssein  
596 and Axelsson, 2010), with values <1.5 mD in well A5 (Elmi, 2005). Nevertheless, cold fluid circulation (~60°C)  
597 has been observed at depths between 600 and 1200 m in the Stratoïd Basalts, in the axis wells (Zan et al.,  
598 1990), and has been interpreted as marine intrusion. Greater permeability has been measured at the outer  
599 margins, in wells A3 and A6 (Abdillahi, 2014): between 10 and 50 mD in well A3 (near well Glc1) at depths of  
600 1016–1316 m which corresponds to the propylitic zone according to the XRD (Elmi, 2005; Houssein and  
601 Axelsson, 2010), and thus within the Dahla Series (D’Amore et al., 1997). This permeability originated from the  
602 fractures and the interbeds between the lava flows (Zan et al., 1990). Temperatures measured in these  
603 permeable zones are approximately 260°C (Zan et al., 1990; Elmi, 2005). Furthermore, the extensional activity  
604 of the rift induces local high vertical permeability, as evidenced by the surface fumaroles on the major rift  
605 faults (Pasquet et al., 2021).

#### 606 4.4.3. Seal

607 The various wells studied to date, both in the rift axis and along the margins, exhibit a strong increase in  
608 temperature associated with low resistivity (1.9  $\Omega \cdot m$ ) at depths between 240 and 600 m (Zan et al., 1990;  
609 Varet, 2014). This layer is interpreted as a relatively continuous clay-rich layer that may represent the seal of a  
610 geothermal reservoir (Varet, 2014). Figure 13 highlights the sharp increase in temperature from 30°C to 210°C  
611 over these 360 meters, that means a low thermal conductivity zone. It is in agreement with the rheology since  
612 the basalts have a conductivity around 3  $W \cdot m^{-1}K^{-1}$  and the shales around 1.7  $W \cdot m^{-1}K^{-1}$ . In the likely hypothesis  
613 of a thermal field mainly due to the fluid advection, cold as hot, this sharp increase suggests, as the low  
614 resistivity, a low permeability zone. This thermal field is not in steady state as confirmed by the fact that the  
615 cold zone is a consequence of the Ardoukoba event (1978-1987 period), also recent magmatic injections  
616 between 1991 and 2001, resulted in some heating events (Varet, 2014). The XRD and bulk analysis results  
617 reported in this study indicate the presence of smectite at these depths. The LOI results confirm this smectite-  
618 rich horizon in well F1 along the rift axis, at depths between 0 and 500m ( $LOI_{smectite} < LOI_{chlorite}$  (Sun et al., 2009)).  
619 In Glc1, a very altered layer dominated by hyaloclastites was observed at the top of the well with smectites  
620 below, with LOI decreasing progressively to 500 m depth (the limit of the well). With a thermal cap, a very low  
621 gradient zone is observed, at 130°C (Figure 13). In the literature the geothermal argillic zones are characterized  
622 by a dominant smectite composition with associated minerals such as calcite, zeolites or hematite, marked by  
623 temperatures below 180°C and resistivities below 10  $\Omega \cdot m$  (Henley and Ellis, 1983; Stimac et al., 2008). It  
624 corresponds to the geothermal reservoir seal.

625 Thus, despite the notable contribution of argillization to decreasing porosity and permeability, we cannot  
626 confirm that a seal for a geothermal reservoir is also a seal for a  $H_2$  reservoir. But if so, such a seal would be  
627 more likely present in well Glc1, along the outer margin, over 450 m deep ( $LOI > 11\%$ ) than in well F1 and  
628 therefore in the rift axis.

629 Resistivity and temperature analyses have indicated a potential seal between 0 and 500 m. The main issues yet  
630 to be resolved include the definition of the minimum clay content required to form an  $H_2$  seal and the  
631 confirmation of whether a geothermal reservoir seal can be considered equivalent to an  $H_2$  seal. So far 3 types  
632 of hydrogen reservoir seal have been described, namely the dolerite in the Mali wells (Prinzhofer et al., 2018),

633 the clays of the Mid-Rift system in Kansas (Coveney et al., 1987; Guélard et al., 2017) and the salt layer in the  
634 Amadeus basin (Leila et al., 2022).

#### 635 4.4.4. Migration

636 The poorly connected porosity and low permeability of basalts makes the circulation of gases complex. Gases  
637 will typically seek preferential paths along major or minor active faults (i.e., rather vertical permeability) (Figure  
638 16) or along the strata boundaries of basalt flows (i.e., horizontal permeability). The presence of vertical fast  
639 migration pathways is evidenced by the fumaroles on the surface along the faults and the absence of H<sub>2</sub> in the  
640 basaltic floor of the rift axis (Figure 2) (Pasquet et al., 2021).

### 641 Conclusions

#### 642 *Hydrothermal system in a young spreading center*

643 Many authors working on MORs have highlighted the differences between the basalts and the olivine-rich  
644 upper mantle in terms of H<sub>2</sub> generation and have shown that hydrothermal vent fluid composition is largely  
645 controlled by oceanic lithosphere composition (see, for instance, Wetzell and Shock (2000) and references  
646 therein). Studies of the evolution of fresh basalts with depth at MORs are less numerous and the one presented  
647 here both allows a closer view of alteration over the first few million years and discusses the influence of deep  
648 fluids versus those arising from water/rock interactions within the final gases.

649 Our data proves that the gases in the Asal–Ghoubbet rift are still mainly volcanic in origin, corresponding to the  
650 degassing of the magmatic chamber (Holloway and O’Day, 2000); CO<sub>2</sub> makes up the majority, but H<sub>2</sub>S reduction  
651 is likely to generate some H<sub>2</sub> in that process. The elevated heat flows in the rift induce rapid circulation of  
652 water and steam, which enhances basalt weathering. The resulting water/rock interactions will result in water  
653 reduction, although low quantities of olivine are present in the basaltic series of the Asal Rift. However, the  
654 alteration of basalt leads to the formation of clay; the resulting Fe-rich chlorite may then be oxidized and  
655 generate additional H<sub>2</sub>.

656 The alteration profile of the basalt of the Asal–Ghoubbet Rift is consistent with typical alteration in high-  
657 temperature geothermal fields. Furthermore, the first hundred meters of rock below the surface are already  
658 altered at the rift margins, with LOI reaching 17% for basalts with ages of less than 1 Ma, and slightly

659 weathered along the axis. This indicates that seawater was present and then removed during the accretion of  
660 the subsequent basalt flows. In this context, we have provided an overview of underwater, meteoric, and  
661 atmospheric alteration/oxidation over depths of a few kilometers. Here, the contacts between the basalt and  
662 the air and the oxygen-rich seawater have exerted a strong influence over this evolution.

### 663 ***Representativeness of the surface data***

664 The data recorded from Site 4, an emitting fracture related to the major faults that border the rift to the  
665 southwest, indicate the presence of H<sub>2</sub>. The concentration of H<sub>2</sub> here varies from 400 to 1000 ppm, although  
666 our sensor saturated at 1000 ppm; after air correction, our data indicate 0.5 to 3% H<sub>2</sub>. This value is not uniform;  
667 however, global variations in the value are smaller than the variations detected in soil affected by  
668 microseepage of H<sub>2</sub> in the continental domain (Prinzhofer et al., 2019; Moretti et al., 2021, 2022). This is  
669 coherent with the differences between micro- and macro-seepages observed for the natural gas, which reflect  
670 differences in the mode of transport of hydrogen through soils and fractures (Schumacher, 1996). The velocity  
671 of the fluid within fractures is greater than that in soil; faster fluid flow reduces the potential for interaction  
672 and, in our case, reduces the rate of H<sub>2</sub> consumption by chemical or microbiological reactions. This means that  
673 a few measurements may be sufficient to determine if a fracture emits H<sub>2</sub> and that long-term monitoring is not  
674 mandatory, as it is for the H<sub>2</sub>-emitting fairy circles in the cratons.

675 In this case study, microorganisms can be considered to have an indirect impact on H<sub>2</sub>. Indeed, it is known that  
676 NH<sub>3</sub> and NH<sub>4</sub> are present in volcanic gases and that, *via* interaction with water and/or iron, redox reactions  
677 occur and can form both N<sub>2</sub> and H<sub>2</sub>. The presence of these gases in fumaroles may explain the presence of  
678 ammonia-oxidizing archaea; further investigation could confirm the mechanisms underlying the high N<sub>2</sub>  
679 content of the emission zone at Site 4 (if we assume that the balance consists primarily of N<sub>2</sub>).

### 680 ***H<sub>2</sub> potential in the Fiale area***

681 The gas data demonstrates the presence of H<sub>2</sub> in the well on the margin of the rift. However, although the  
682 fumaroles at the center of the rift contain H<sub>2</sub>, no H<sub>2</sub> was detected at depth in this area (i.e., in the A5 and F1  
683 wells) during drilling, because of the absence of measurements. At the opposite, on the margin near Glc1, H<sub>2</sub>  
684 concentrations were very low at the surface. The other difference between the central axis and the margins  
685 relates to the presence of a geothermal gradient inversion due to the flow of seawater from Ghoubbet Bay to

686 Lake Asal. In addition, alteration of the basalts along the rift margins led to the formation of hyaloclastites and  
687 smectites, which may constitute a potential seal for both geothermal reservoirs and H<sub>2</sub>. Although diffuse, the  
688 H<sub>2</sub> potential (in terms of theoretical volume) is large: more than 500 mmol H<sub>2</sub>/kg rock. The majority of this H<sub>2</sub>  
689 may have been lost by continuous leakage to the surface. However, accumulations (even temporary ones) may  
690 still occur in cases where a reservoir and seal are present. Such a reservoir would be preferentially located at  
691 depths of 1000–1300 m on the southwestern rift margin, in the Dahla Basalts, zone with the best permeability  
692 (10 to 50 mD). This zone is located in the propylitic geothermal zone (chlorite–epidote assemblage) and it's also  
693 a potential source of H<sub>2</sub> through Fe<sup>2+</sup> oxidation and chlorite dehydrogenation (Figure 16). The outer margins of  
694 North Ghoubbet can also be considered prospective in this context but data are still scarce in this area without  
695 well.

696 Thermodynamic calculations must now be carried out to better constrain the reaction kinetics in these ferrous  
697 chlorites. Furthermore, despite the surface and well data on H<sub>2</sub> in the margins, can this poorly connected  
698 porosity make these basalts a good reservoir. Further experimental studies are also needed to improve the  
699 documentation of H<sub>2</sub> seals.

## 700 **Acknowledgements**

701 We thank Isotope Editing for editing a draft of this manuscript. We thank ODDEG for sharing with us their  
702 knowledge of Djibouti geology and for allowing us access to the cuttings from the two studied wells. This  
703 collaboration, ODDEG-UPPA, was initiated by K Moussad, J Varet, and I Moretti.

704 I would like to thank Alain Prinzhofer, Yves Geraud and an anonymous reviewer for their constructive  
705 comments which helped to clarify this article.

706 **Funding:** GP's PhD was funded by the Isite E2S; the fieldwork was funded by the Carnot ISIFOR. Amin

707 Mohamed Idriss is now studying in UPPA thanks to Campus France.

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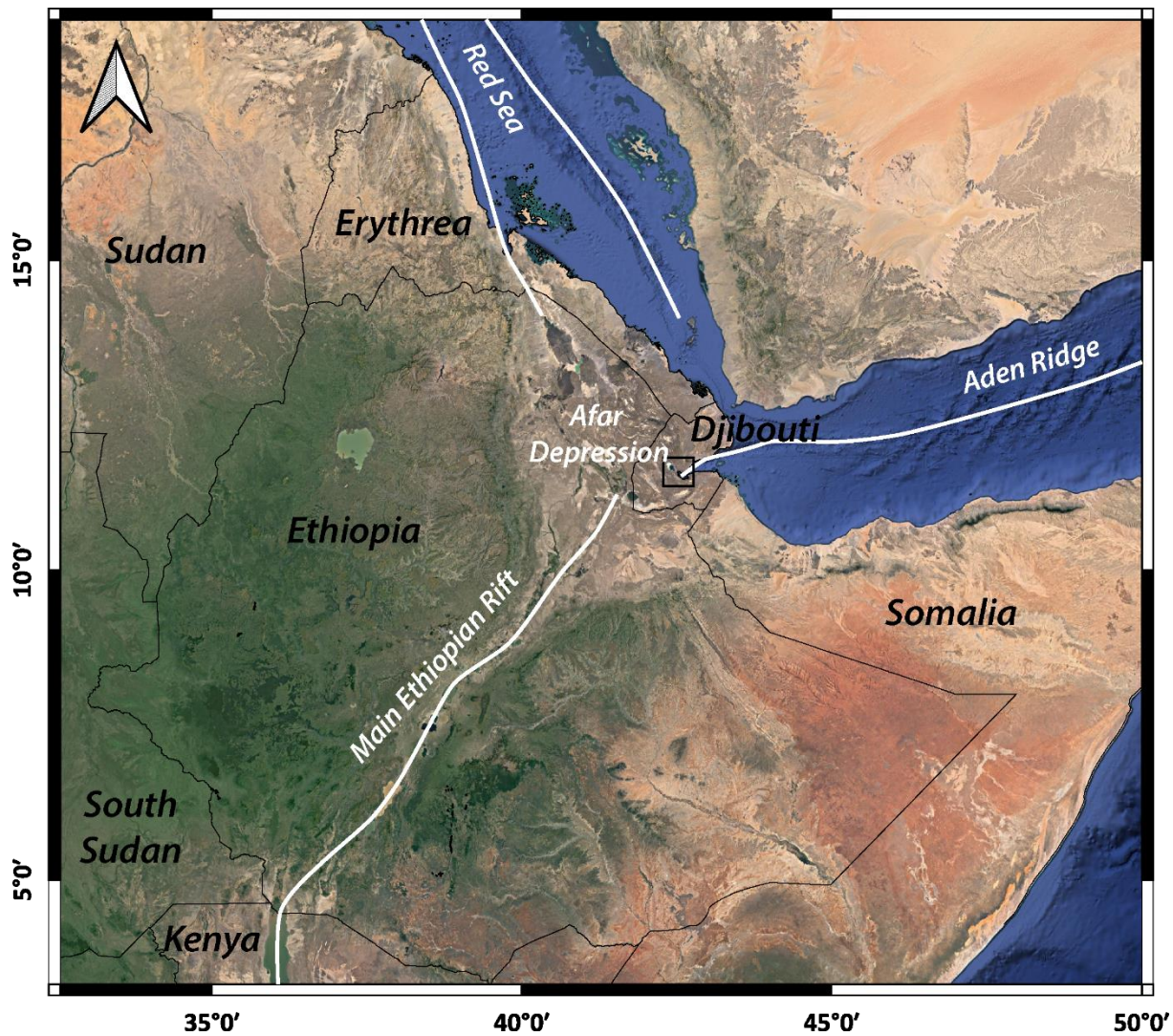
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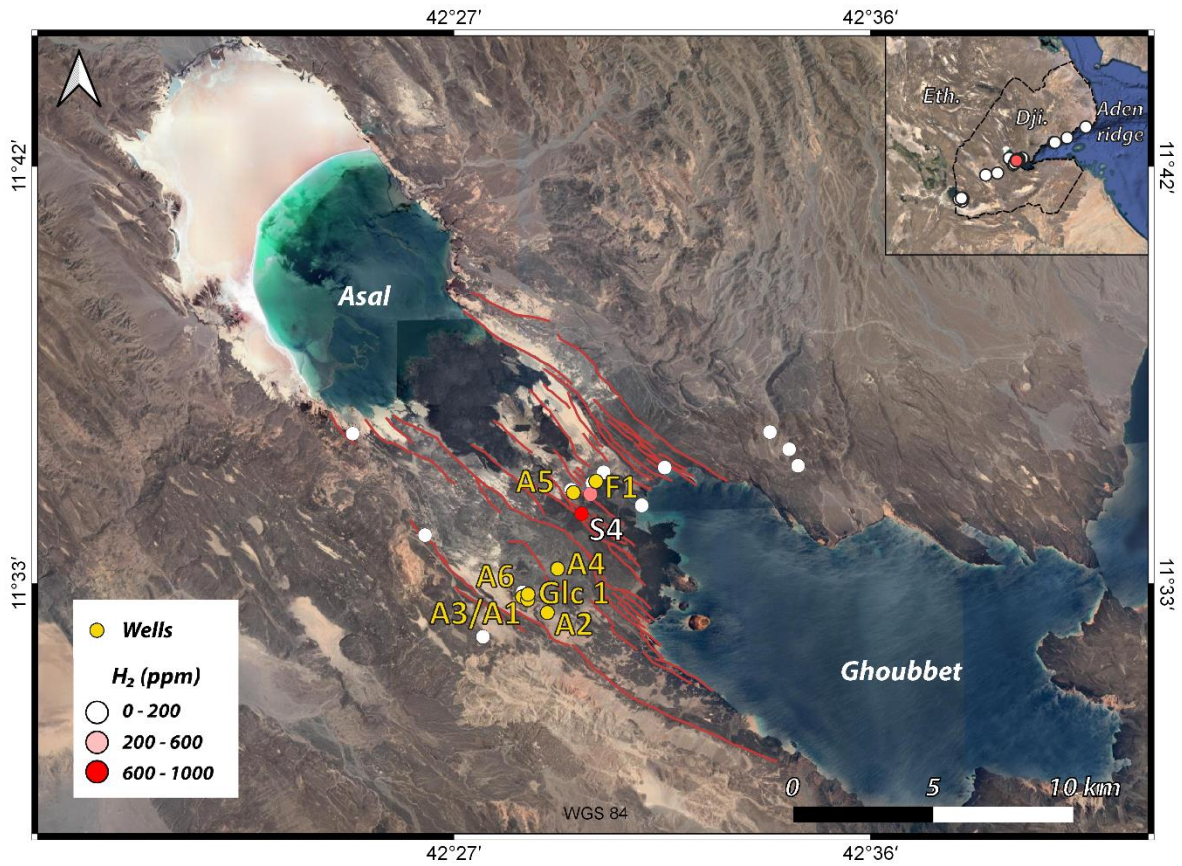
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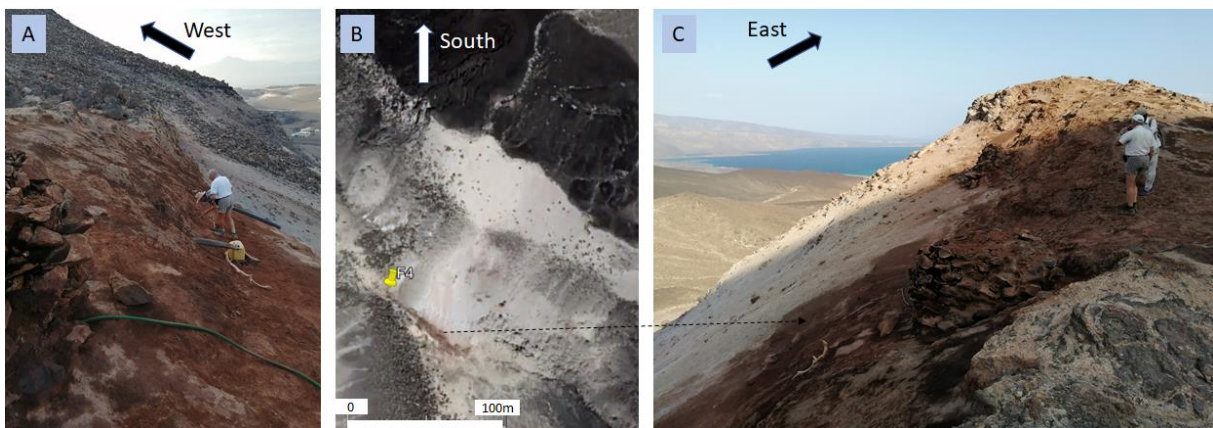
983 Figure 1 - Map representing the major opening axes of the EARS, with the Asal–Ghoubbet rift (study area)  
 984 indicated by black box.



985

986 Figure 2 - Map of the Asal-Ghoubbet rift showing major rift faults, geothermal wells, and surface H<sub>2</sub>  
 987 measurement points. The color scale from white to red indicates increasing H<sub>2</sub> contents in fumaroles at the site.

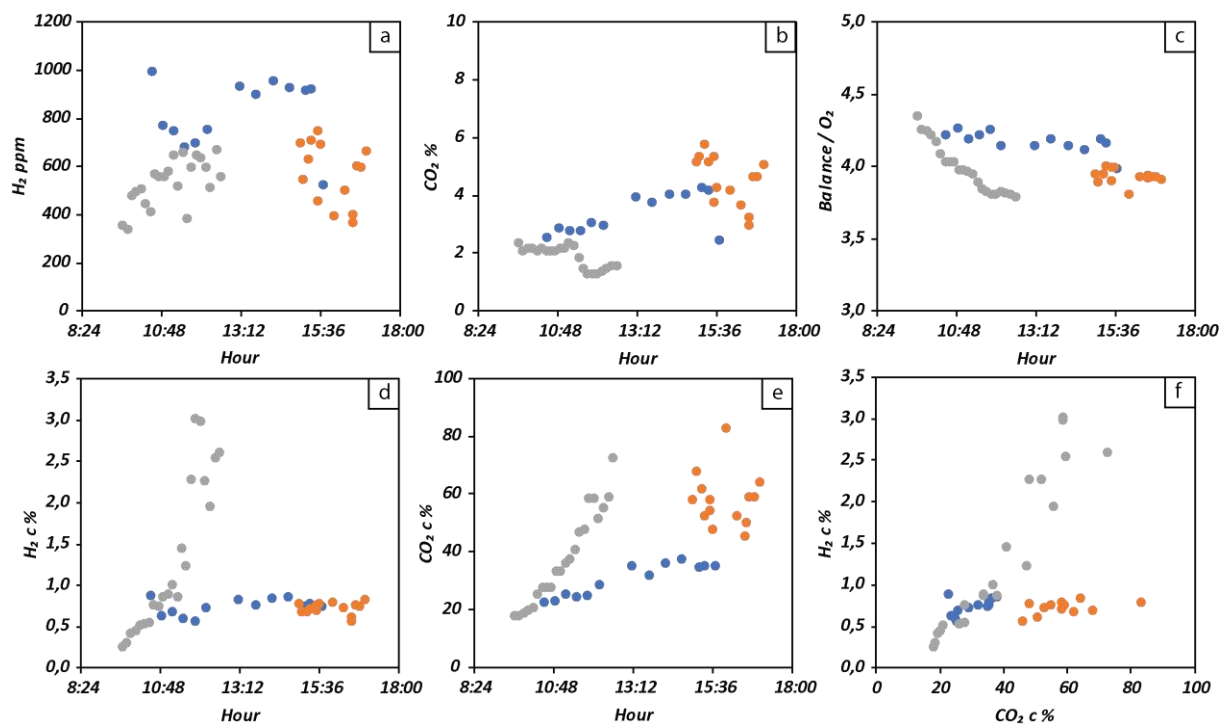
988 The red dot corresponds to site no. 4, presented in Figure 3.



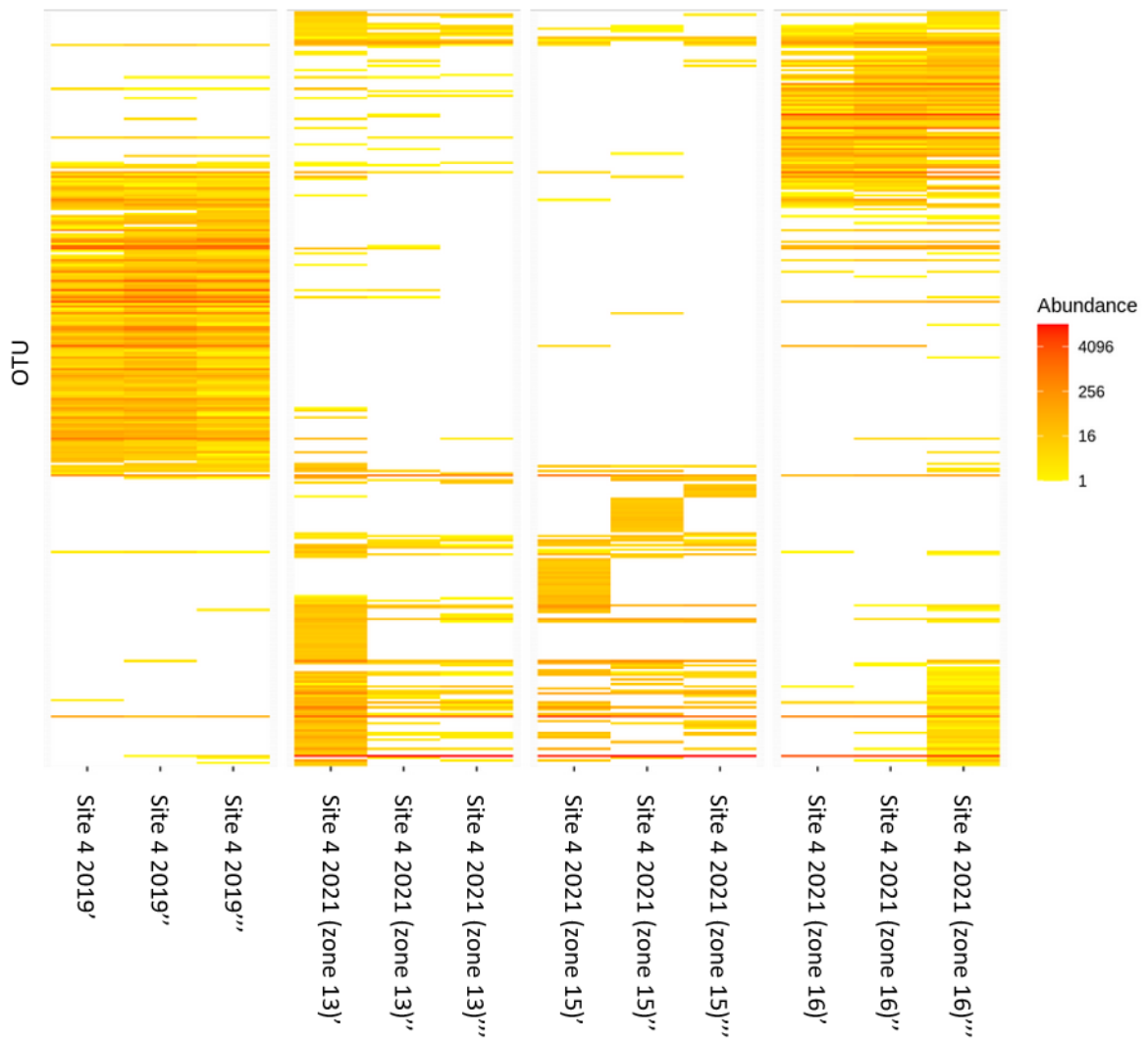
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990 Figure 3 - Site 4 of the Asal-Ghoubbet rift. A: View towards the west and Lake Asal, showing plastic tubes installed  
 991 by local inhabitants to collect fresh water. B: Satellite view, showing the area affected by the fumaroles with  
 992 visible surface alteration in brown. C: View to Ghoubbet Bay, showing the eastern hydrothermal zone with

993 numerous fumaroles and Afar condensation wells. The scarp of the N140°-oriented north-dipping normal fault  
 994 clearly demonstrates the tectonic activity of this central part of the rift.



995  
 996 Figure 4 - Evolution of gas content with time for the fumaroles of Site 4 within the Asal–Ghoubbet rift. Orange  
 997 points 21/11/2019; blue points 12/08/2020; gray points 13/08/2020. (a) H<sub>2</sub> (ppm) in situ as a function of time.  
 998 (b) CO<sub>2</sub> (%) in situ as a function of time. (d) Diurnal variation in H<sub>2</sub>, after correction. (e) Diurnal variation in CO<sub>2</sub>,  
 999 after correction. (f) Corrected H<sub>2</sub> as a function of corrected CO<sub>2</sub> (Pasquet et al., 2021).

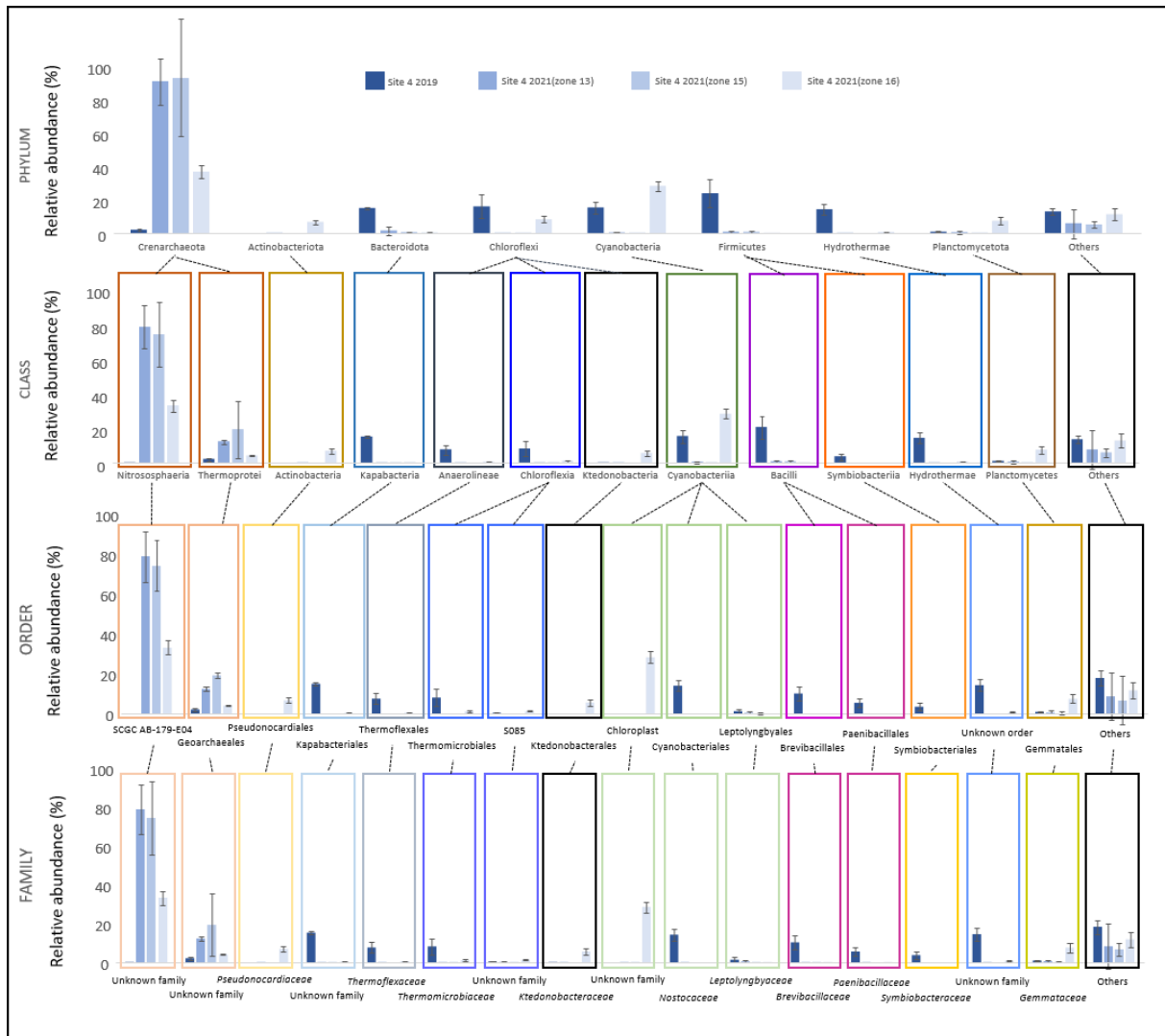


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1001 Figure 5 - Heat map showing the distribution of 326 microbial OTUs (Operational Taxonomic Units) at Site 4 based

1002 on two sampling campaigns (2019 and 2021 for zones 13, 15 and 16). High-throughput sequencing was

1003 performed using 16S rRNA gene amplicon (v3–v4).



1004

1005 Figure 6 - Representation of the taxonomic diversity of microbial communities at Site 4 during the two sampling  
 1006 campaigns (and for several zones, in the case of the 2021 campaign). High-throughput sequencing was performed  
 1007 using 16S rRNA gene amplicon (v3-v4).

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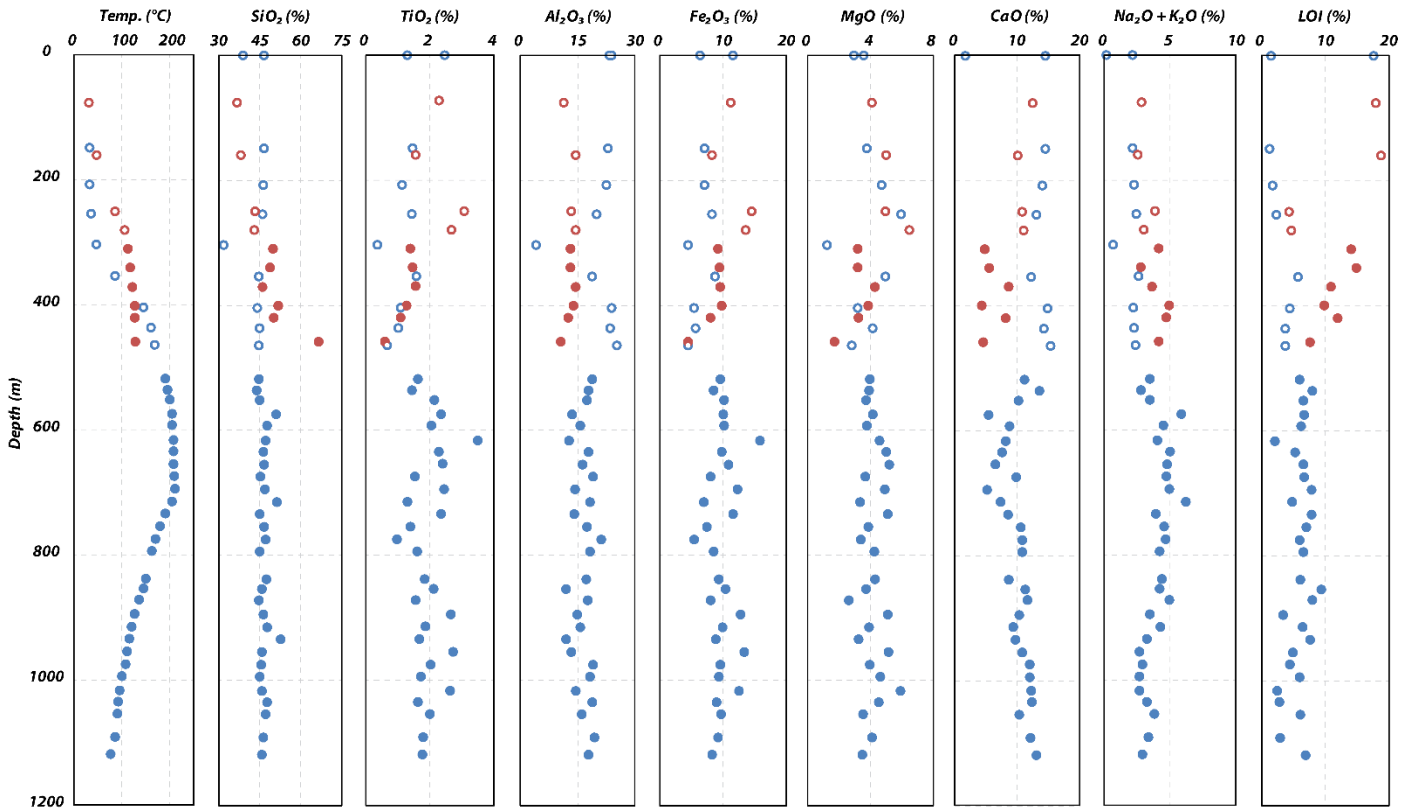
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1016 Figure 7 - Chemical evolution (Ox%) with depth for the cuttings from the Fiale 1 (blue dots) and Gale le Goma 1

1017 (red dots) wells. Asal series samples are represented by empty circles and Stratoïd series by solid circles.

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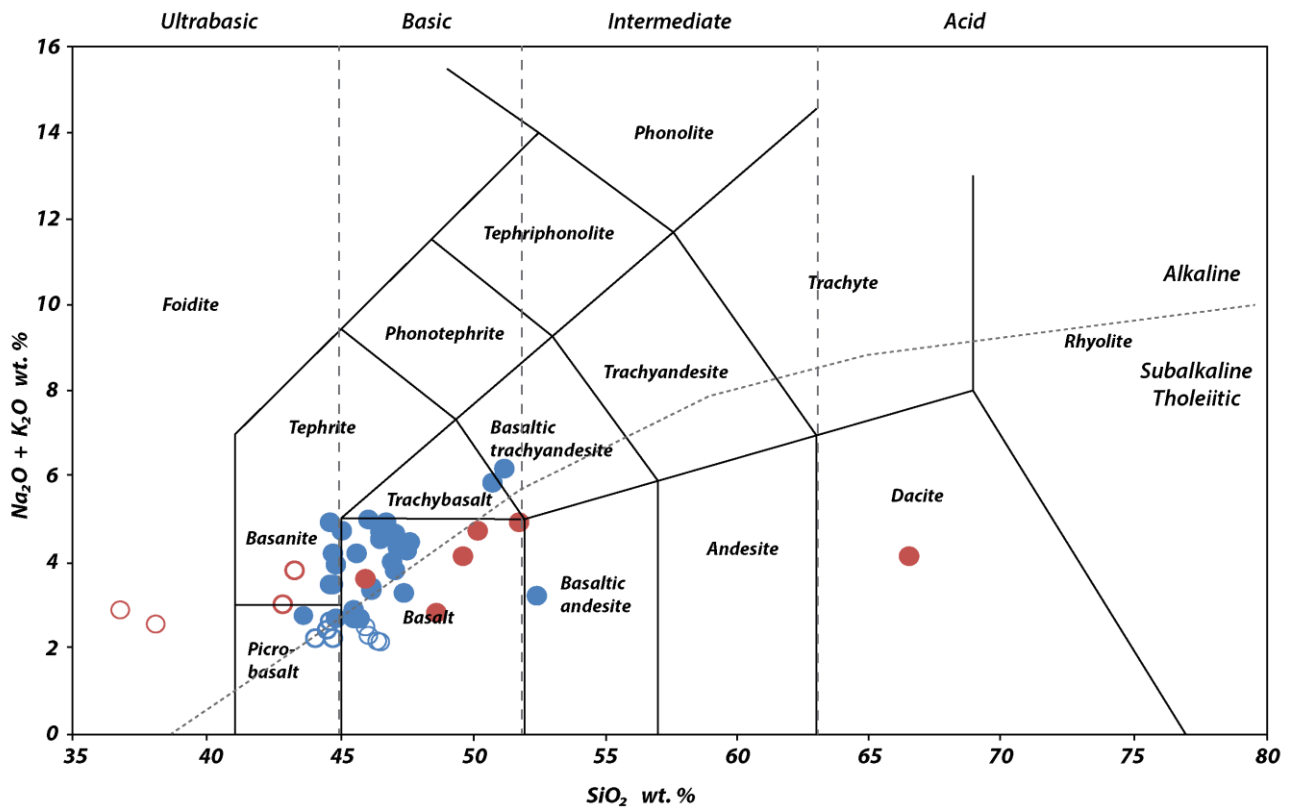
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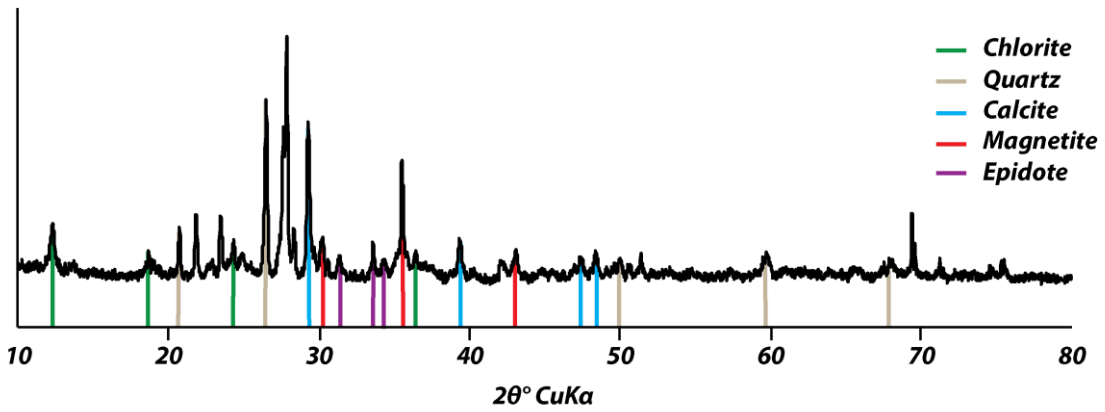
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1027 Figure 8 - TAS diagram representing the compositions of F1 (blue dots) and Glc1 (red dots) cuttings. Asal series  
 1028 samples are represented by empty circles and Stratoïd series by solid circles.



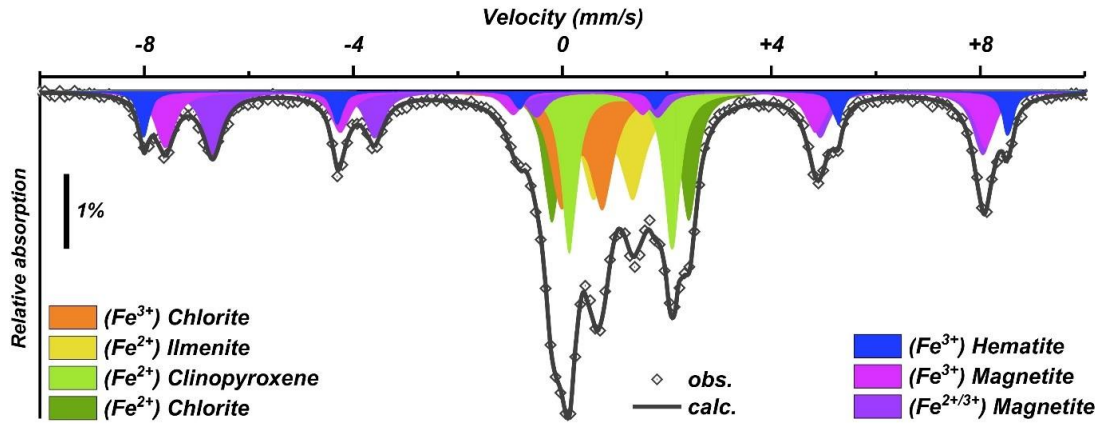
1029 Figure 9 - Example of one of the XRD interpretations of secondary minerals on the F1-51 cuttings (1118 m depth).  
 1030 Ordinate in number of counts and abscissa in  $2\theta^\circ$ . Primary minerals peaks are not shown.

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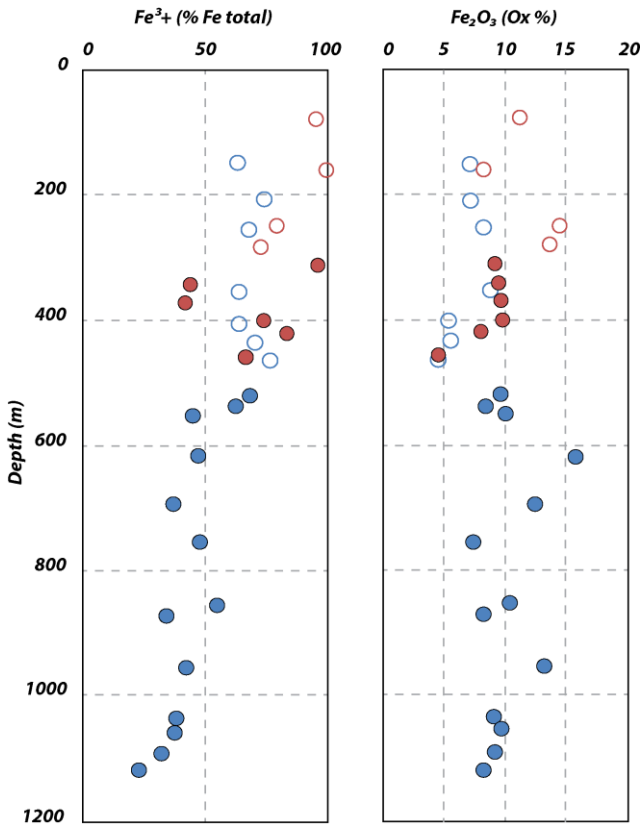
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1036 Figure 10 - Example of <sup>57</sup>Fe Mössbauer spectrum analysis (F1-26 sample).

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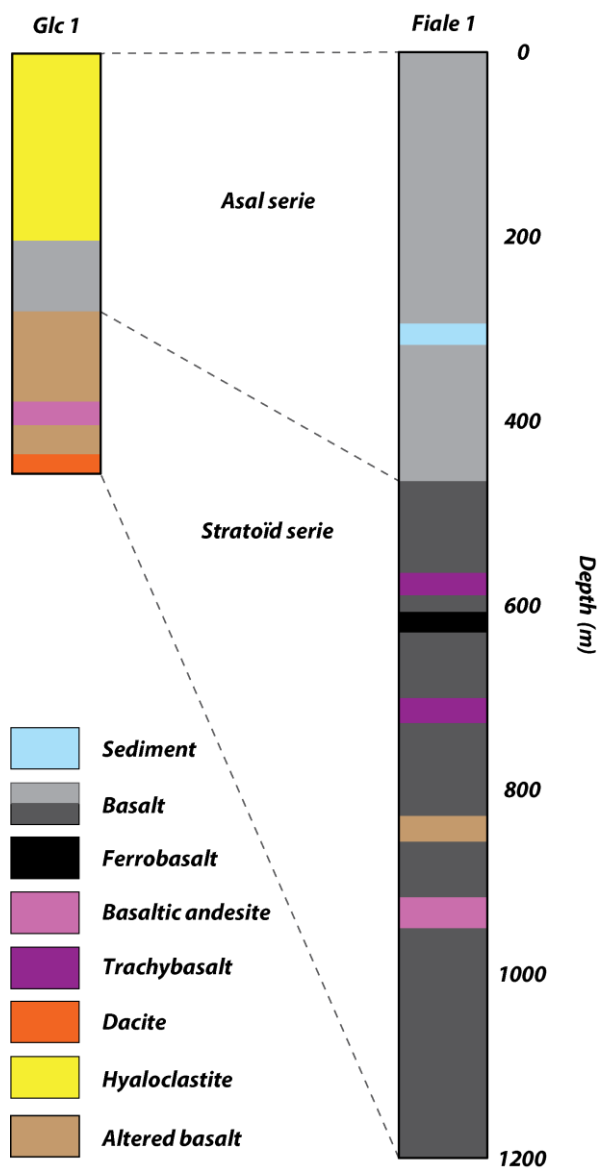


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1039 Figure 11 – Variation with depth in the F1 and Glc1 cuttings of (a) Fe<sup>3+</sup> content (%) and (b) total iron.

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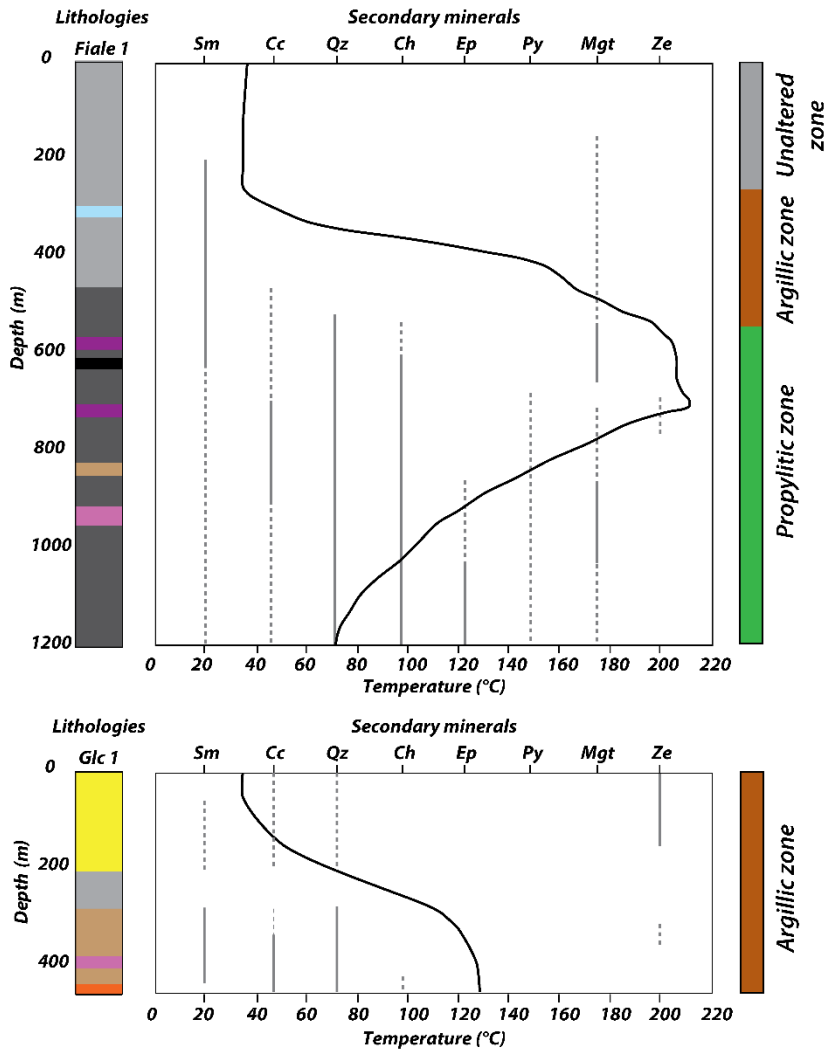
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1044 Figure 12 - Simplified lithological log of wells F1 and Glc1 from total rock and XRD analyses.

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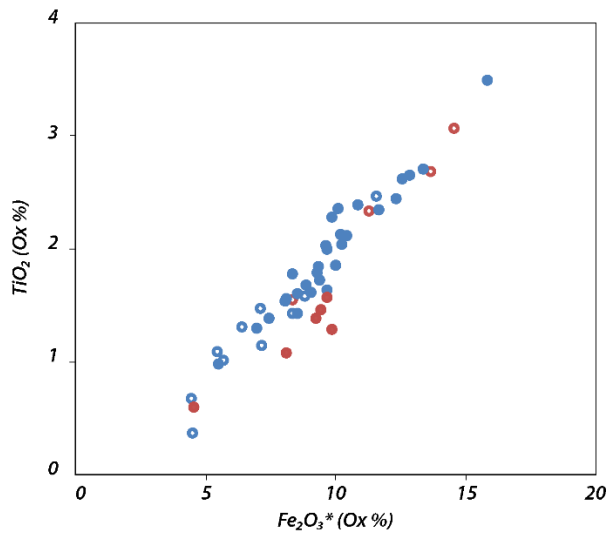
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1047 Figure 13 - Depth variation of secondary minerals in F1 and Glc1 wells from XRD and Mössbauer data (dashed

1048 lines) and temperature change with depth in the well (black line). Secondary minerals: Sm = smectite; Cc = calcite;

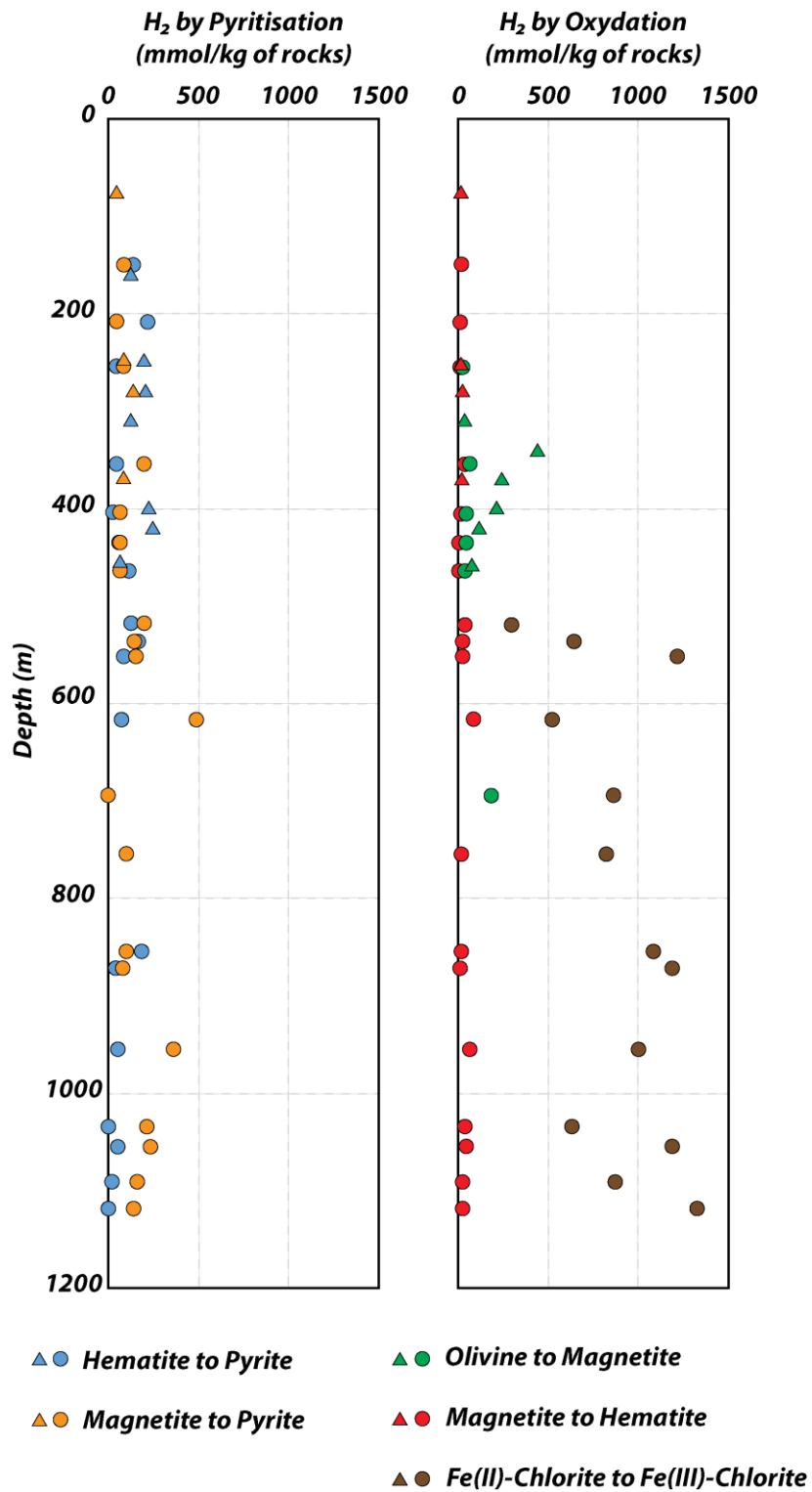
1049 Qz = quartz; Ch = chlorite; Ep = Epidote; Py = pyrite; Mgt = magnetite; Ze = Zeolite.

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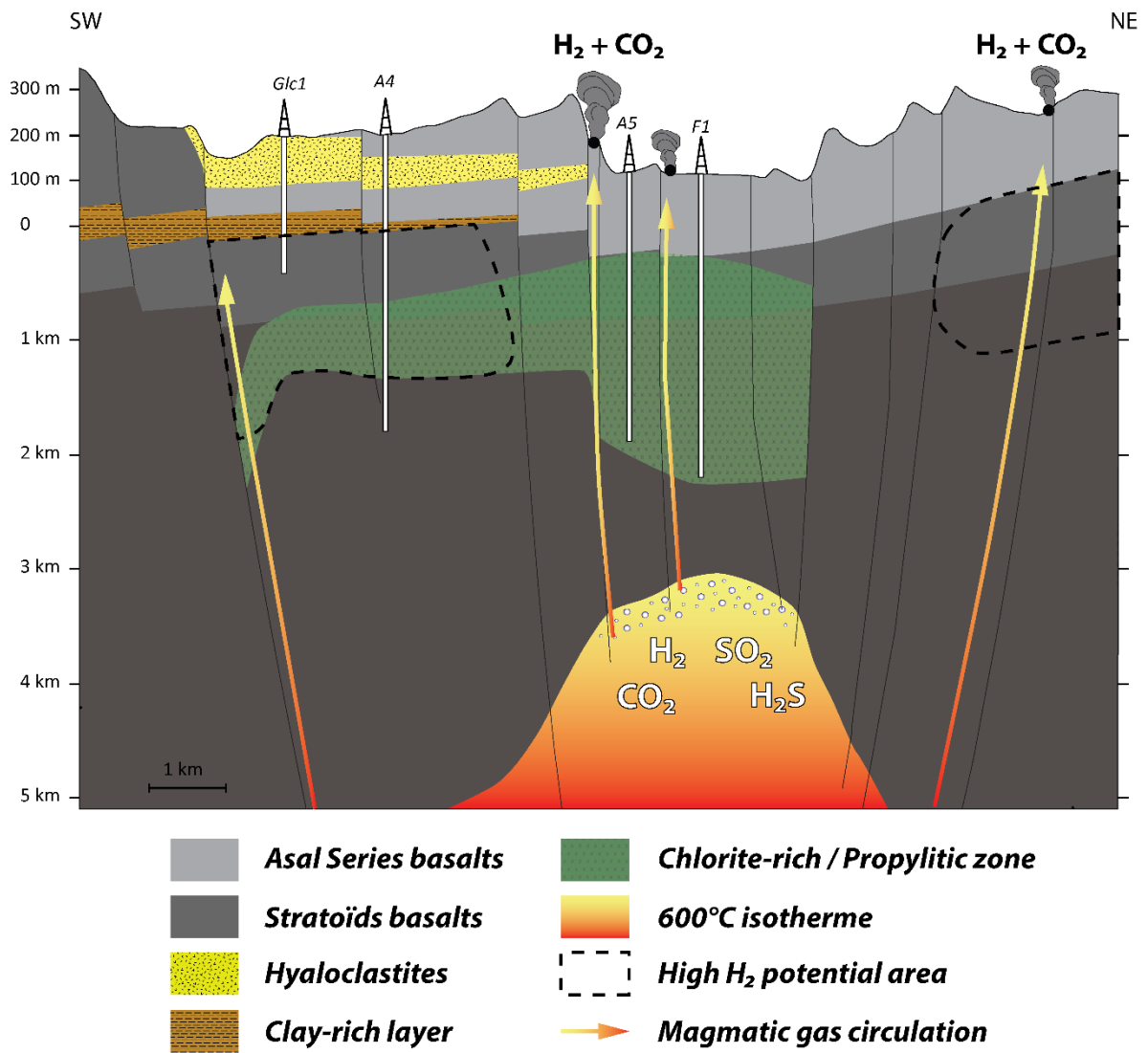
1052 Figure 14 - Evolution of  $TiO_2$  as a function of total iron in the cuttings of F1 and Glc1.



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1054 Figure 15 - Remnant potential of rocks as a function of depth according to different redox reactions and based

1055 on Mössbauer analyses. Glc1 (triangles) and F1 (dots).



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1057 Figure 16 - Schematic diagram of the geothermal and potential H<sub>2</sub> zones of the Asal-Ghoubbet rift.

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