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1 **Preserved organic matter in a fossil Ocean Continent Transition in the Alps: the**
2 **example of Totalp, SE Switzerland**

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11 Key words: serpentinitization, organic matter, Totalp unit, biogeochemistry, ocean continent
12 transition (OCT),

13 **Abstract:**

14 Evidence from ultraslow spreading mid-ocean ridges and both fossil and present-day Ocean-
15 Continent Transitions (OCT) demonstrates that mantle serpentinitization resulting from the
16 interaction of mantle rock and water during tectonic exhumation is widespread. Observations
17 at white smokers in modern ocean settings suggest that methane produced by serpentinitization
18 can support methanotrophic bio-systems, which use methane as the only source of carbon. An
19 important question is whether such bio-systems are more generally pervasive in their
20 association with serpentinitized mantle in the subsurface. In this study, we examined whether
21 there is evidence for such a methanotrophic system in exhumed serpentinitized mantle at a
22 magma-poor rifted continental margin, by probing for characteristic biological markers in these
23 and associated sedimentary rocks in the Totalp unit of SE Switzerland. This unit represents a
24 remnant of the former OCT of the southern Alpine Tethyan margin and was chosen because of
25 its mild Alpine tectonic and low-grade metamorphic overprint during Alpine orogeny, hence
26 giving potential for the preservation of indigenous organic matter (OM).

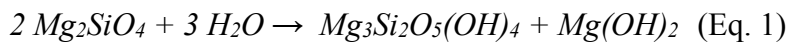
27 Totalp samples are characterized by low organic carbon contents of 11 to 647ppm. The majority
28 of the samples contain hydrocarbons in the form of *n*-alkanes in the range C₁₇ - C₃₆. Some

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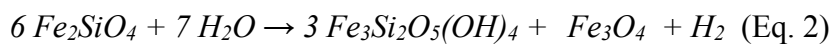
sediments contain isoprenoids, for example pristane and phytane and a suite of steranes that are consistent with a marine origin for the OM preserved in the rocks. Traces of marine planktonic and bacterial OM are preserved in the serpentinized mantle and overlying sediments of this ancient Tethyan OCT, but there is no evidence that the OM has been generated from methanotrophic bio-systems.

1. Introduction

Serpentinization is an important metamorphic exothermic hydration process potentially contributing chemical energy for anaerobic life, as well as thermal energy at oceanic hydrothermal vents (*e.g.* Shock et al. 2002; Jamtveit and Hammer 2012). Serpentinization converts olivine and pyroxene to serpentine, other Fe-Mg minerals (magnetite, brucite, talc) and free molecular hydrogen (Eq. 1). The Mg component of olivine may hydrate as follows:



The Fe component of olivine contributes to forming Fe-Mg serpentine by an analogous reaction and/or by reducing water



It has been proposed (*e.g.* McCollom 2013) that molecular hydrogen can then reduce CO_2 derived from carbonate and hydrogen carbonate in sea-derived pore waters to methane (CH_4) at high pressure and temperature, via a Fischer-Tropsch-like reaction (Eq. 3).



Serpentinized mantle rocks exposed along slow to ultraslow-spreading Mid-Ocean Ridges (MOR) show positive anomalies of methane and hydrogen in the overlying water column above active tectonic zones (Rona et al. 1987; Charlou et al. 1988; Rona et al. 1992; Bougault et al. 1993; Charlou and Donval 1993; Charlou et al. 1998; Gràcia et al. 2000; Kelley and Shank

53 2010). The abiotically produced methane can be anaerobically oxidised by methanotrophic
54 bacteria using sulphate as the electron acceptor (Eq. 4).



56 Sulphate reducers are one of the dominant bacterial populations at hydrothermal vents
57 (McCollom and Shock 1997). Furthermore, methanotrophic bacteria have been identified at
58 Lost City (mid-Atlantic Ocean), a low-temperature alkaline hydrothermal vent supported by
59 energy derived from the formation of serpentinite (Hinrichs et al. 2000; Kelley et al. 2001;
60 Orphan et al. 2001; Kelley et al. 2005). Recently, bacterial anaerobic nitrate oxidation of
61 methane has been demonstrated in the laboratory (Haroon et al. 2013; Arshad et al. 2015), using
62 two different microorganisms (Raghoebarsing et al. 2006); this may also occur at the MOR
63 methane sources, but is likely to be a minor pathway as nitrate concentrations in seawater are
64 significantly lower than sulphate (μM vs. mM , respectively).

65 Recent studies have focussed on the relationship between serpentinization and organic
66 compounds, mainly methane in the laboratory (*e.g.* McCollom and Seewald 2013; Etiope and
67 Ionescu 2014), at present-day serpentinite-hosted hydrothermal vents (*e.g.* Kelley et al. 2005;
68 Delacour et al. 2008; Proskurowski et al. 2008), mud volcanoes (*e.g.* Mottl et al. 2003; Holm
69 et al. 2006), and exhumed serpentinite mantle domains with high H_2 concentrations and high
70 pH (*e.g.* Cardace et al. 2013). High concentrations of OM found at the Mid-Atlantic Ridge
71 (MAR; 4-6°N) were associated with serpentinized peridotite rather than with the hydrothermal
72 vents (Ménez et al. 2012).

73 Hence, the present study uses an organic geochemical approach to quantify OM in the exhumed
74 mantle from an OCT in order to better understand the relationship between OM and mantle
75 serpentinization. We selected the Totalp unit exposed in the Eastern Swiss Alps, which
76 represents a remnant of the fossil Tethyan OCT emplaced during the Alpine orogeny (Fig. 1a)

77 (Bernoulli *et al.* 1985, Manatschal *et al.* 2003, Picazo *et al.* 2013). We searched for biomarkers
78 or molecular remains of former living organisms, specifically hydrocarbons with an origin
79 consistent with anaerobic methane oxidation (*e.g.* crocetane; Blumenberg *et al.* 2004). A wider
80 suite of biomarkers was used to determine source and thermal maturity of OM preserved in the
81 rocks.

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83 **2. Regional geological setting of the Totalp unit**

84 The Totalp unit is located north of Davos in SE Switzerland. It is part of the Tethyan OCT (Fig.
85 1b). The peculiarity of the Totalp unit is that it experienced little Alpine deformation and only
86 a low grade Alpine metamorphic overprint, not exceeding 100-150°C, *i.e.* prehnite-pumpellyite
87 grade (Peters 1968; Früh-Green *et al.* 1990). The Totalp unit consists of two Alpine tectonic
88 units namely the Upper and Lower Ultramafic Totalp sub-units (*e.g.* Picazo *et al.* 2013). These
89 are mainly composed of serpentized peridotite exhumed at the seafloor during Jurassic times
90 and ophicalcites that occur at the top basement; they can be found re-worked into the overlying
91 Jurassic marine sediments (Fig. 1c). In addition, the primary contacts between the exhumed
92 serpentized mantle, the ophicalcites and the oceanic sediments are well-preserved (Weissert
93 and Bernoulli 1985).

94 **2.1 Pre-Alpine and Alpine geological and thermal history**

95 The serpentized peridotites of the Totalp unit were exhumed to the Jurassic seafloor during
96 final late Middle Jurassic rifting (Peters and Stettler 1987; Bernoulli *et al.* 2003). Later, during
97 the Alpine orogeny, the exhumed mantle rocks were first tectonically emplaced within a Late
98 Cretaceous E-W directed nappe stack before being thrust during the Tertiary collision over
99 the European units forming the present-day Alpine orogen (Weissert and Bernoulli 1985; Früh-
100 Green *et al.* 1990; Manatschal *et al.* 2003). The serpentized peridotites in Totalp are

101 interpreted as derived from fertile subcontinental lithospheric mantle (Manatschal et al. 2001;
102 Müntener et al. 2010; van Acken et al. 2010), similar to other described remnants of fossil OCTs
103 from the Alps (*e.g.* Platta; Desmurs et al. 2002; Malenco in the Italian Alps; Müntener et al.
104 2004). Extensional faults and unroofing of their footwalls are responsible for the mantle
105 exposure at the seafloor (Picazo et al. 2013).

107 2.2 Lithologies

108 The Totalp unit consists mainly of serpentized peridotites, ophicalcites and post-rift
109 sediments (Figs. 1 and 2; Table 1). This association is typical of an OCT across magma-poor
110 margins where magmatic rocks are often either very rare or absent. Three types of serpentized
111 mantle rocks were identified:

- 112 i. Massive serpentized peridotites, which preserve mantle textures and mainly
113 consist of serpentized spinel-lherzolite. Locally these rocks also contain
114 pyroxenite and amphibole- and chlorite-rich layers (Picazo et al. 2013).
- 115 ii. During exhumation, the serpentized peridotites are affected by localization of the
116 deformation and intensive fluid circulation leading to complete serpentization of
117 fault-rocks, including serpentinite gouges, serpentinite cataclasites and foliated
118 cataclasites (Picazo et al. 2013). These rocks are best exposed in the Obersasställi
119 area, and they occur in the uppermost 150 m of the exhumed mantle in the footwall
120 of a Jurassic extensional detachment fault (Figs. 1 and 2; Picazo et al. 2013).
- 121 iii. Veins of serpentine that have been interpreted to result from later serpentization
122 during low-grade Alpine metamorphism, as suggested by the oxygen isotopes (Früh-
123 Green et al. 1990). Some serpentine veins may result from the percolation of
124 meteoric water associated with regional metamorphism (Burkhard and O'Neil
125 1988).

126 Ophicalcites are complex rocks that are made of serpentinite and calcite and represent the result
127 of different processes (Bernoulli and Weissert 1985; Lemoine et al. 1987). They either result
128 from the total to partial *in-situ* replacement of serpentine by carbonate, tectonic processes
129 related to exhumation and hydrothermal systems, and/or cementation and filling of fractures by
130 sediments (*e.g.* neptunian dykes of Bernoulli and Jenkyns 2009). These processes occur at or
131 near the seafloor and are often associated with hydrothermal fluid circulation at temperatures
132 of 100-150°C (Früh-Green et al. 1990; Picazo et al. 2013). Most ophicalcites are formed under
133 static (non tectonic) conditions within 20 m of the paleo-seafloor (Picazo et al. 2013).

134 Sedimentary ophicalcites at Totalp include neptunian dykes and debris-flows (Fig. 2). The
135 neptunian dykes are carbonate veins filled with pink or grey carbonate (pelagic sediments or
136 mechanically reworked cements), filling fractures in the exhumed mantle. These dykes are
137 typically located in the tectonized, serpentinitized peridotites forming the uppermost few meters
138 of the exhumed mantle (Bernoulli and Weissert 1985; Picazo et al. 2013). The second main
139 type, the tectono-sedimentary ophicalcites, include cemented clasts of serpentinite, gabbro and
140 continental basement (Manatschal and Bernoulli 1999; Bernoulli et al. 2003; Picazo et al. 2013).
141 The sediments overlying the ophicalcite are mainly pelagic deposits of Late Jurassic to Early
142 Cretaceous age, some of which have been reworked (most likely by ocean bottom currents)
143 (Weissert and Bernoulli 1985). Red shales are overlain by radiolarian cherts and grey micritic
144 limestones intercalated with claystones (*e.g.* Radiolarite Formation and Calpionella or
145 Aptychus limestone Formation of Weissert and Bernoulli 1985). The top of the sequence is
146 formed by black siliceous shales that are characteristic of poorly oxygenated bottom waters
147 during the Early Cretaceous (Weissert et al. 1985; Weissert and Bernoulli 1985).

148 North east of Totalp, exposed on a topographic cliff near Gotschnagrat (Figs. 1 and 2), is a
149 weathered outcrop with visible pyrite on the top of the radiolarian cherts and siliceous
150 claystones (Fig. 3; Weissert and Bernoulli 1985). This outcrop has been described by Früh-

151 Green *et al.* (1990) as a zone of pyrite mineralization associated with radiolarian cherts. The
152 radiolarites contain quartz, illite, hematite and chlorite (Weissert and Bernoulli 1985). The
153 sulphidized outcrop has a bulk chemistry different from its surrounding and could have been
154 formed during early diagenesis or metasomatism of amorphous silica or limestone (Berner
155 1984; Williams *et al.* 1985). Alternatively, the sulphide could be related to a fossil
156 hydrothermal system (*e.g.* Styrk *et al.* 1981, Beard and Hopkinson 2000; Zeng *et al.* 2015). Early
157 diagenetic reactions producing pyrite depend *inter alia* on a source of OM as electron donor
158 (Fig. 3b); the high present-day porosity of the rock (Fig. 3c) could be produced by weathering
159 of calcite (Berner 1984). Hydrothermal vent systems are characterized by pelagic sediment
160 accumulation alongside ferrous oxides (*i.e.* radiolarian chert) of hydrothermal origin which can
161 potentially be preserved (Haymon 1989; Montgomery and Kerr 2009). The second most
162 common mineral in the sulphide bearing samples is quartz that may have originated from
163 amorphous silica or opal, which are common in hydrothermal vents (*e.g.* MAR- mount Saldanha
164 36.30N; Dias and Barriga 2006; 25°48'N Rona 1984, 24°21'N; Rona 1984 ; Kane 23°35'N
165 Fracture zone; Kelley and Delaney 1987) reflecting a large input of hydrothermal silica (Dias
166 and Barriga 2006). There is no evidence of fossilized worm tubes associated with the zone of
167 pyrite mineralization; these are characteristic of inactive white smokers (Haymon 1983) and so
168 the origin of this formation remains unclear.

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170 **3. Sample Collection, Preparation and Analysis**

171 3.1 Sample collection

172 A total of 47 samples were selected from the Totalp unit for geological and organic
173 geochemical studies (Table 1). We collected samples from the three main lithologies:
174 serpentized mantle rock (lizardite, serpentinite gouge and cataclasite), opicalcites (neptunian
175 dykes and tectono-sedimentary breccias) and associated sediments (Figs. 1 and 2; Table 1).

176 Samples were oriented, geo-referenced and collected using a geological hammer or a hand drill
177 using water as lubricant. On collection the samples were wrapped in pre-combusted foil
178 (400°C) for return to the laboratory.

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180 3.2. Sample preparation

181 In order to avoid contamination with modern material the samples were cleaned with de-ionised
182 water (18 MΩ cm⁻¹ resistivity; Milli-Q) and rinsed with re-distilled dichloromethane (DCM).
183 The outer edges were removed from each sample, which was then cut into smaller pieces using
184 a small rock saw lubricated with water. The aim was to get fresh, un-weathered samples for
185 laboratory analysis. These were then used for preparing thin sections and for stable isotope
186 analyses of carbonate veins, with 90 - 110 µg of calcite being extracted from using a small
187 electrical hand drill. For organic geochemistry selected pieces were washed with Milli-Q water
188 and DCM, then crushed (to particles <50µm) using a tungsten Tema Mill, which was previously
189 thoroughly cleaned (Decon-90 solution 2% v/v, milli-Q water, methanol and finally DCM). In
190 order to assess lab contamination, blanks composed of pre-combusted silica gel (600°C) were
191 subjected to the same procedures as the samples.

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193 3.3 Mineralogical analyses

194 Optical microscopy, cathodoluminescence microscopy (CL; CITL Mk5-2) and X-Ray
195 Diffraction (XRD) were used to identify the mineralogy, chemistry, texture and textural
196 relations within the samples and to associate the mineralogy with the OM. A Panalytical X'Pert
197 PRO XRD system (CuK^{-α} radiation, 45 kV, 40 mA) was used to identify the volume proportions
198 of the minerals associated with serpentinization and the polytypes of the serpentine minerals.

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200 3.4 Geochemical analyses

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201 Analyses of total carbon (TC) and total organic carbon (TOC) were performed before and after
202 decarbonation (10% HCL, 25°C), respectively, using a Carlo Erba Instrument NC2500
203 elemental analyser.

204 Stable isotopic analyses of organic carbon were carried out on five samples of four different
205 lithologies, prepared using a “sealed tube” method and injecting the resulting CO₂ into a VG
206 Sira 10 dual-inlet mass spectrometer (Craig 1957; Frazer and Crawford 1963; Sofer 1980). The
207 standard error for analysis is ± 0.1‰. The isotope data was normalized to IAEA-CH7
208 calibration material and reported using the VPDB scale. Carbon and oxygen isotope
209 measurements on calcite were performed on material extracted from veins by conversion to
210 CO₂ using a VG SIRA 10 MS Isocarb (common acid bath). The carbon and the oxygen isotope
211 analyses are referenced to the VPDB standard with a standard error for each analysis of ± 0.1‰
212 (McCrea 1950; Craig 1957; Friedman and O'Neil 1977; Swart et al. 1991).

213 Soxhlet extraction was used to extract the bitumen from the powdered rocks using DCM:
214 methanol (24 h) (modified after Wolff et al. 1995). Full blank extractions were conducted in
215 parallel to identify any possible contamination. After evaporation of the solvent, the extracts
216 were re-dissolved and passed through short columns of alumina and sodium sulphate using
217 hexane as solvent to isolate the hydrocarbons. The eluent from the alumina column was re-
218 dissolved in hexane (50 µL) and analysed by gas chromatography (GC) and GC- mass
219 spectrometry (GC-MS).

220 For GC-MS we used a GC Trace 1300 and Thermoquest ISQMS single quadrupole fitted with
221 a split-splitless injector, GC column (DB-5MS non-polar 5% phenyl and 95% methyl silicone
222 stationary phase, 60m x 0.25mm i.d., film thickness 0.1µm) using helium as a carrier gas (2mL
223 min⁻¹). The GC oven temperature was programmed from 60°C to 170°C after 1 min at 6°C min⁻¹
224 ¹, then from 170°C to 315°C at 2.5°C min⁻¹ and finally held at 315°C for 15 min. GC-MS was

225 carried out in full data acquisition mode, providing mass spectra of compounds eluting from 20
226 to 90 minutes; these were identified by comparison with the literature and with authentic
227 standards where available (PAHs - polynuclear aromatic hydrocarbons). 5 α (H)-Cholestane was
228 used as an external standard for quantification; response factors were assumed to be 1, hence
229 data are semi-quantitative. Data were processed using XCalibur 1.2 software
230 (ThermoScientific).

231 The mean carbon numbers, MC# (Peltzer and Gagosian 1989) and the carbon preference index
232 (CPI) of *n*-alkanes (Peters et al. 2005a) were calculated over the carbon number range C₁₆- C₄₀
233 (Eq. 5 and 6; Table 2).

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$$235 \quad MC\# = \frac{\sum ([C_i] \times C_i)}{\sum [C_i]} \quad (\text{Eq 5})$$

236 where [C_i] = concentration of the *n*-alkane with C_i carbon number

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$$238 \quad CPI = 0.5 \times \frac{\sum ([\text{odd } C_{21} - C_{35}])}{\sum ([\text{even } C_{20} - C_{34}]) + \sum ([\text{odd } C_{23} - C_{37}])} \quad (\text{Eq 6})$$

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241 **4 Carbon and hydrocarbon distributions in the analysed lithologies**

242 The TOC and TC results are summarized in Table 2 and vary considerably. The TOC values
243 are low, while TC reflect carbonate contents. The stable isotopic composition of carbonate
244 varied from -0.78 to 1.86‰VPDB and -11.7 to -6.2‰VPDB for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively
245 (Table 2; Fig. 4). Five decarbonated samples (sample 1: neptunian dyke; samples 9 and 39:
246 reworked tectono-sedimentary opicalcite; sample 19: limestone; sample 69: specimen from
247 the sulphide- rich outcrop) have similar values for $\delta^{13}\text{C}_{\text{VPDB organic}}$ of between -27.4 and -26.2
248 ‰ (Table 2).

249 Hydrocarbons (HCs) identified in Totalp samples include *n*-alkanes, steranes, polynuclear
1 aromatic hydrocarbons (PAHs), hopanes and isoprenoids, namely pristane and phytane.
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5 251 Samples of the same lithology do not necessarily have similar distributions of HCs (Table 2).
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7 252 This may reflect the heterogeneity of the samples collected, for example in the relative amount
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9 253 of carbonate, calcite veins and serpentinite clasts.

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12 254 Aliphatic compounds (> C₁₅), mainly in the form of *n*-alkanes dominate (Fig. 5a). The CPI
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15 255 (carbon preference index) for the *n*-alkanes are in the range 1 ± 0.3 , except for two samples that
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17 256 were visibly weathered, having CPI = 2.6 - 2.87, i.e. an odd over even ratio for the *n*-alkanes
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20 257 confirming contamination from modern material, such as soil (e.g. Villanueva et al. 1997).
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22 258 Steranes included 20R and 20S $\alpha\beta\beta$ isomers from C₂₇ to C₂₉, as well as 20 R and S diacholestane
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25 259 and pseudohomologues (Fig. 5 b). The steranes were dominated by C₂₇ compounds with a lower
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27 260 abundance of C₂₈ and C₂₉ pseudo-homologues (Fig. 5 b). The ranges of values for the thermal
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30 261 maturity parameters of the C₂₇ steranes are between 0.41 and 0.69 for ST1 = $\alpha\alpha\alpha$ 20S/ $\alpha\alpha\alpha$ 20S+
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32 262 $\alpha\alpha\alpha$ 20R and 0.37 and 0.59 for ST2 = $\alpha\beta\beta$ / $\alpha\alpha\alpha$ + $\alpha\beta\beta$ (Fig. 6; Seifert and Moldowan 1980; Peters
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35 263 et al. 2005b). PAHs having molecular masses ≤ 276 were identified in some of the bitumen
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37 264 extracts (Table 2; Fig. 5 c).

40 265 41 42 266 4.1. Serpentinite

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45 267 All serpentinite samples contain *n*-alkanes, and several PAHs in the form of phenanthrene (P)
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47 268 and fluoranthene (Fluo); steranes and hopanes were largely absent (Table 2).

49 269 50 51 52 270 4.1.1 Upper ultramafic sub-unit

53 54 55 271 *Massive serpentinite*

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57 272 The massive serpentinites collected from the Weissfluhjoch (samples 77, 78; Fig. 1c; Table 1)
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60 273 area have HC concentrations between 0.05 to 4 ppm while the C₂₉ *n*-alkane dominates their

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274 distribution ($C_{\max}=29$; Table 2). Total carbon (454 ppm) and total organic carbon (TOC) (≈ 180
275 ppm) concentrations are both very low.

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277 *4.1.2 Lower ultramafic sub-unit*

278 *Massive serpentinite*

279 XRD analysis shows a lizardite polytype 1 (Bailey 1969) (87%), garnet (andradite) (7%) and
280 pyroxene (clinopyroxene) (5%). In thin section olivine is completely replaced by serpentine
281 minerals, with phantoms of pyroxene, euhedral magnetite, spinel and several calcite and
282 carbonate veins not visible to the naked eye (Table 1).

283 HC concentrations vary from 23 ppm for the serpentinite from Parsenfurrga (sample 5) to 900
284 ppm from an outcrop with ophicalcite in Obersasställi (sample 16; Fig. 1c; Table 2). The TOC
285 values range from 102-176 ppm and TC from 395-3134 ppm; steranes and hopanes are below
286 detection limits (BDL) (Table 2). Serpentinite samples showing numerous calcite veins (sample
287 24, 26, 44 and 47) have higher amounts of TC (20400 to 42500 ppm). They show variable TOC
288 (19 to 135 ppm) and low HC concentrations (1- 124 ppm). In the lower ultramafic sub-unit a
289 red coloured serpentinite was identified by XRD to contain hematite (4%) (Table 1). The
290 serpentine mineral is a lizardite polytype 1 (59%), also containing talc (18%) and calcite (19%).
291 The isotopic composition of the calcite in the veins is 0.03‰ and -11.75‰ for $\delta^{13}C_{VPDB}$ and
292 $\delta^{18}O_{VPDB}$, respectively (Fig. 4).

293 *Serpentinite cataclasite and gouges*

294 The serpentine cataclasites and gouges have TC of 540-875 ppm, *n*-alkanes with a carbon
295 number range of C_{17} - C_{36} and no detectable steranes or hopanes (Table 1 and 2). The serpentine
296 cataclasites (sample 70), which are less deformed than the serpentine gouge (sample 69),
297 contain more hydrocarbons (46 ppm and 3 ppm, respectively Table 2) but similar TOC contents
298 (284 and 269 ppm, respectively).

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2 300 4.2. Ophicalcrite
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5 301 The ophicalcrites from the Totalp unit all contain *n*-alkanes and the PAHs (P, Fluo and Pyr, see
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7 302 glossary; Table 2). Steranes and hopanes are also present in the majority of samples.

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12 304 *4.2.1. Neptunian dykes*

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14 305 Samples of neptunian dykes have a red micritic limestone matrix with millimetre-scale
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16 306 serpentinite clasts and calcite veins (samples 1, 23) (Fig. 1c, Table 1). The $\delta^{13}\text{C}_{\text{VPDB organic}}$ of
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18 307 one of the samples (sample 1) was - 27.1‰ (Table 2). There are high amounts of TC with
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20 308 variable TOC (15 to 103 ppm) and HC concentrations (0.3 – 121 ppm) (Table 2).

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26 310 *4.2.2 Tectono-sedimentary ophicalcrites*

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29 311 The tectono-sedimentary ophicalcrite has various sub-lithologies from a reworked tectono-
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31 312 sedimentary breccia with folded serpentinitized and carbonate clasts in a red carbonate matrix
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33 313 crosscut by calcite veins (sample 9) to centimetre scale serpentinite clasts in a carbonate vein
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35 314 (sample 72) (Fig. 1c) (Table 1). The stable isotopic composition $\delta^{13}\text{C}_{\text{VPDB organic}}$ of one of the
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37 315 samples was -26.1‰ (sample 9) (Table 2). A second type of ophicalcrite, a serpentinite breccia
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39 316 composed only of serpentinite clasts fragmented by calcite veins has low TOC (30 ppm) and
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41 317 HCs concentrations (124 ppm) including only *n*-alkanes (sample 72) (Table 2). The isotopic
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43 318 compositions of the calcite veins surrounding the serpentinite clast are 1.60‰ and -
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45 319 10.6‰VPDB for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively. The third most common ophicalcrite is composed
46
47 320 of anhedral serpentinite clasts, carbonate veins, calcite veinlets in a reddish pelagic matrix and
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49 321 has a low amount of TOC (11-116 ppm), but high concentrations of HCs (2-2470 ppm) (samples
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51 322 21, 25, 39, 41, 42, 44, 66; Fig. 1c; Tables 1 and 2). The isotopic composition of the samples
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53 323 varies from $\delta^{13}\text{C}_{\text{VPDB}} = 0.32\text{‰}$, 0.42‰ and 0.58‰ with $\delta^{18}\text{O}_{\text{VPDB}} = -11.75\text{‰}$, -10.28‰ and -
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10.9‰ (for samples 25, 42 and 39 respectively) to $\delta^{13}\text{C}_{\text{VPDB}} = 1.07$ and 1.78‰ with $\delta^{18}\text{O}_{\text{VPDB}} =$
-11.7 to -7 ‰ for samples 42 (second generation calcite vein) and 41 (Fig. 4, Table 1). Isotopic
analysis of organic carbon (sample 39) gave $\delta^{13}\text{C}_{\text{VPDB organic}} = -27.4\text{‰}$ (Table 2). The ophicalcite
outcrop near the Gotschnagrat NE Totalp has isotopic values for calcite veins of 1.86‰ for
 $\delta^{13}\text{C}_{\text{VPDB}}$ and -6.2‰ for $\delta^{18}\text{O}_{\text{VPDB}}$ (sample 66).

4.3. Sediments

Limestones are, together with radiolarian cherts, the most common sediments in the Totalp
unit. All of the sediment samples contain detectable levels of HCs including PAHs.

4.3.1 Radiolarian cherts

The radiolarian cherts are situated mostly around the Gotschnagrat NE Totalp (samples 62, 68)
and along small distributed outcrops some of which are 1-2 m in length and located between
Parsennfurgga and Parsenhütte (sample 6; Fig. 1c). Except for the weathered sample, they have
very low concentrations of HCs (1 -17 ppm) and low TOC values (66-187 ppm) (Table 2). The
radiolarian cherts are hard, fine grained siliceous sediments that are transected by post-
depositional quartz and calcite veins, the latter having isotopic compositions of $\delta^{13}\text{C}_{\text{VPDB}} = -$
 0.79‰ and $\delta^{18}\text{O}_{\text{VPDB}} = -6.4\text{‰}$ (Sample 62; Table 1; Fig. 4).

4.3.2 Siliceous shales

The siliceous shales are located mostly above Parsennhütte and around the Gotschnagrat
(samples 15, 18, 60, 61; Fig. 1c). XRD analysis of the siliceous shales (sample 61) above the
pyrite rich area revealed a mineralogical composition consisting of quartz (83%), albite (10%),
pyrite (2%), illite/muscovite (4%), chlorite and hematite. This composition is similar to the
siliceous shale (samples 15, 18) found nearby, which consists of quartz (89%), plagioclases

349 (6%), illite/muscovite (4%), chlorite and trace of hematite (Fig. 1c; Table 1). They have low
350 concentrations of HCs (13 – 144 ppm) and variable amounts of TOC (194-433 ppm) (Table 2).

351 4.3.3 Limestone

352 Samples (53 to 57) are pelagic grey limestones that contain visible calcite veinlets and fine
353 greyish veinlets (serpentinite) from the syncline in the Parsennhütte (Fig.1c) (Table 1). They
354 contain a low amount of TOC (14-92 ppm) and variable concentrations of HCs (Table 2).

355 The pelagic limestones with higher amount of calcite veins (samples 10, 19) are also poor in
356 TOC (74- 82ppm) and contain HCs from 79 to 171 ppm (Fig. 1c; Tables 1 and 2). Isotopic
357 analyses of the first generation of calcite veins in sample 19 show $\delta^{13}\text{C}_{\text{VPDB}} = 0.56\text{‰}$ and
358 $\delta^{18}\text{O}_{\text{VPDB}} = -6.5\text{‰}$ and $\delta^{13}\text{C}_{\text{VPDB organic}} = -26.6\text{‰}$ (Fig. 4; Table 1).

360 4.4 Silica – rich carbonate (sulphide-rich outcrop)

361 The mineralogy of the pyrite rich rocks is dominated by calcite (53%) with quartz (24%),
362 chlorite (12%) and pyrite (6%) being the other main minerals (sample 63, 64, 65; Figs. 1c and
363 3; Table 1). The samples were on the top of the radiolarian chert and red shale sequences where
364 the contact between these rocks are weathered and not affected by deformation (Fig. 3). Isotopic
365 composition of organic carbon is $\delta^{13}\text{C}_{\text{VPDB organic}} = -26.02\text{‰}$ (sample 64) and that of the calcite
366 veins in the same sample 1.4‰ for $\delta^{13}\text{C}_{\text{VPDB}}$ and -6.6‰ for $\delta^{18}\text{O}_{\text{VPDB}}$ (Table 1). The samples
367 are characterized by a TOC contents from 153 to 647ppm and low HC concentrations (1 – 24
368 ppm) (Table 2); bitumen extracts are dominated by elemental sulphur, but HCs include *n*-
369 alkanes, PAHs (P, Fluo, MPs) and steranes (Table 2).

371 5 Interpretation and discussion

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372 Traces of OM with a composition consistent with a marine origin were found in serpentized
373 exhumed mantle. The generally low and variable amounts of TOC reflects the large lithological
374 diversity of the Totalp area, and the distributions of hydrocarbons are consistent with the
375 temperature history of the Totalp unit (*i.e.* no metamorphic overprint) (Table 2; Fig. 5).

376 5.1 Source of OM

377 A cross-plot of Pristane (Pr) to *n*-C₁₇ versus phytane (Ph) to *n*-C₁₈ is commonly used to
378 determine the depositional environment of OM in sedimentary rocks (Peters et al. 2005b). For
379 the Totalp samples (Fig. 7), this cross-plot implies a reducing (anoxic) depositional
380 environment for the OM, with a marine source of planktonic algal/bacterial OM consistent with
381 a marine mixed transitional environment that might be expected at this fossil OCT. Sterane
382 ternary diagrams are also commonly used to provide information on the source of OM in
383 sedimentary rocks (Peters et al. 2005a). Comparison of Totalp steranes with predicted
384 distributions of source materials (Fig. 8) are consistent with a mixed marine source of
385 planktonic algal and bacterial OM (Gonçalves et al. 2013; Wójcik-Tabol and Ślącza 2015) and
386 are similar to OM deposited in marine settings during and since the Jurassic (Grantham and
387 Wakefield 1988; Wójcik-Tabol and Ślącza 2015). Such a source for OM in the radiolarian
388 cherts reflects the dominant planktonic signature of coccoliths and nanoconids (Manatschal et
389 al. 2003). The variability in the sterane distributions most likely reflects spatial and temporal
390 variability in environmental conditions during OM deposition.

391 In five samples (ophicalcite, limestone and samples from the sulphide bearing outcrop) with
392 enough TOC to allow measurement of its stable isotopic composition, the determined values of
393 $\delta^{13}\text{C}_{\text{VPDB organic}}$ of *ca.* -26.2 to -27.4‰ (Table 2) are again consistent with an origin from marine
394 OM (-26‰ ± 7‰) (Schidlowski 1988; Hayes et al. 1990) and are similar to those found in
395 hydrothermal systems from the Galapagos ($\delta^{13}\text{C} = -27.4\text{‰}$) and the Guaymas Basin ($\delta^{13}\text{C} = -$

396 25‰ to - 21‰) (Orem et al. 1990). Orem et al. (1990) argued that the OM in these
397 hydrothermal systems derived from chemoautolithotrophic bacterial production. The carbon
398 isotopic composition of methane in modern hydrothermal vents ranges from -8.8 to -19.6‰ (
399 e.g. TAG 26°N -8/-9.5‰, Rainbow 36°14'N -15.8‰, see Charlou et al. 2002; Lost City 30°N
400 -13.6 to -8.8‰, Kelley et al. 2005; Bradley and Summons 2010). Fixation of hydrothermal
401 methane by methanotrophs would be expected to lead to OM more depleted in ¹³C by 15 - 30‰
402 (Summons et al. 1994; Schidlowski 2001; Templeton et al. 2006), i.e. in the range -23.8 to -
403 34.6‰ assuming the most conservative fractionation. Hence, isotopic data from the Totalp
404 samples suggests that there could be a contribution from methanotrophic biomass; however the
405 values are also consistent with marine-derived OM. Taken together with the molecular data and
406 in the absence of specific methanotrophic biomarkers (e.g. crocetane), we consider that the
407 Totalp hydrocarbons derive from marine OM.

5.1.1 Thermal history of OM

408 The distributions of PAHs are in part consistent with a high temperature origin (e.g. Killops
409 and Massoud 1992), for example with pyrolytic residues (e.g. Geissman et al. 1967) arising
410 from OM alteration by hydrothermal activity (Kawka and Simoneit 1990) or low-grade
411 metamorphism (Heymann et al. 2003). Hence, the methyl-PAH/PAH ratios of ≤0.8 observed
412 in our samples are consistent with a pyrogenic source (Saha et al. 2009). However, the Fluo/Pyr
413 ratio <0.6 of all the samples is lower than what would be expected of an exclusively pyrolytic
414 source and indicates that lower temperature pathways of PAH formation also contribute to the
415 HCs (Fabiańska et al. 2016). The biomarker maturation parameters of C₂₇ steranes fall within
416 values that might be expected within a temperature envelope consistent with a moderate thermal
417 history (Fig. 6; ca. 80 - 150°C; Mackenzie et al. 1980; Peters et al. 2005a) and are therefore
418 consistent with the temperature history of the basin (Früh-Green et al. 1990; Peters et al. 2005b).
419 This suggests that where steranes are present, their degree of isomerisation reflects gradual

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2 420 maturation over time, rather than the pyrogenic process that may have yielded PAHs at the
3 421 contact of hot rock with seawater OM.
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5 422 *5.1.2 Origin of calcite veins*

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8 423 The measured carbon and oxygen isotopic composition of carbonates are 0 to 2‰ and - 11.7
9 424 to - 6.2‰, for $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB}}$, respectively and are similar to values previously reported
10 425 for calcite veins in ophicalcite and late calcite veins collected in the Davos-Parsenn and Arosa
11 426 areas (Fig. 4; Früh-Green et al. 1990). The $\delta^{13}\text{C}_{\text{VPDB}}$ values are consistent with seawater-
12 427 derived early diagenetic calcite (Fig. 4a) (Hudson 1977; Coleman et al. 1993; Heydari 1997).
13 428 The $\delta^{18}\text{O}_{\text{VPDB}}$ values of the calcite veins for the majority of samples vary between -11.7 to -
14 429 6.2‰ and indicate calcite precipitation during shallow burial (<250m), not influenced by
15 430 organic carbon derived CO_2 but typical of Cretaceous calcite (Dix and Mullins 1992; Heydari
16 431 1997). One sample (radiolarian chert) has a negative calcite carbon isotope value perhaps
17 432 indicating the influence of CO_2 delivered from diagenesis of OM (Heydari 1997).
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34 434 *5.1.3 OM in serpentinite – mechanism of emplacement*

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40 435 The occurrence of HC's in the serpentinite rocks of Totalp is at first sight surprising.
41 436 Schwarzenbach et al. (2013) listed the five main sources of organic carbon (OC) that can be
42 437 preserved in basement rocks, namely: seawater, mantle, Fischer-Tropsh-like reactions (F-T),
43 438 *in-situ* production from microbial activity in the basement rock, and, thermogenic
44 439 decomposition of OM. The hydrocarbons recovered from the Totalp serpentinites and the OC
45 440 have isotopic compositions consistent with an origin from marine OM, *i.e.* from a seawater
46 441 source rather than from *in-situ* production or abiotic F-T reactions. Therefore, the probable
47 442 origin of the OC preserved in the rocks is from dissolved and particulate organic carbon (DOC
48 443 and POC) derived from seawater or thermal alteration of OM in sediments that then migrated
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2 445 to the basement rock within fluids (Fig. 9a). However, there could be different pathways of
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5 446 emplacement of OM in the serpentinites.
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8 447 The OM could have been deposited within the two types of precipitated carbonate found in the
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10 448 serpentinite, namely the mechanically deposited carbonate that fills fractures, or *via* pore fluids
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12 449 fuelling the formation of calcite veins (Fig. 9b; Bernoulli and Weissert 1985; Früh-Green et al.
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14 450 1990). The latter has an isotopic composition consistent with seawater carbonate and any DOM
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16 451 transported with the pore fluids would be trapped within the calcite matrix on precipitation
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18 452 (Figs. 4 and 9b). The presence of ophicalcite and the numerous calcite veins from the time of
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20 453 exhumation indicates a high supply of dissolved inorganic carbon (Ménez et al. 2012). As the
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22 454 OM clearly has a marine origin, it could have been emplaced by the first main phase of fluid-
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24 455 rock interactions at the ocean floor and the tectono-sedimentary and hydrothermal processes
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26 456 described by Früh-Green et al. (1990). The OM may have migrated with seawater through
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28 457 fractures in the sediment into the basement rock (Fig. 9c; Delacour et al. 2008). These fractures
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30 458 formed by tectonic and crystallization stresses, which are not reliant on matrix permeability
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32 459 (Farough et al. 2016). Where initial contact between DOM-containing fluid and rock was at
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39 relatively high temperature, this could have led to the formation of the “pyrolytic” PAHs.

40 460 With respect to the sedimentary facies, organic carbon preservation is linked to grain size (or
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42 461 mineral surface area) and oxygen exposure after deposition (Fig. 9d; Hartnett et al. 1998;
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44 462 Kennedy et al. 2002). Clay minerals, one of the constituents of shale sediments found in the
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46 463 Totalp unit, strongly retain DOM both on the external surfaces and interlayer spaces of clay
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48 464 particles (Kennedy et al. 2002). However the Totalp sediments have low TOC values and could
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50 465 been highly oxidised during deposition or diagenesis. During deposition of shales, OM is also
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52 466 deposited as discrete biogenic particles, but largely these are not preserved; rather clays,
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54 467 particularly smectites, facilitate the absorption of DOM and POM from seawater and pore-
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56 468 fluids, and preserve it during burial (Kennedy et al. 2002).
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469 In summary, OM in the exhumed mantle rocks at Totalp is of marine origin that migrated into
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2 470 the serpentinite most likely from the overlying seawater or sediment cover (Simoneit et al.
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4 471 1978; Simoneit and Philp 1982). Our results are consistent with previous studies that show a
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7 472 lack of, or only minor formation of the CH₄ and H₂ needed for the production of OM involving
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9 473 serpentinization at low-temperature (McCollom and Donaldson 2016) and that the molecules
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12 474 necessary for life at hydrothermal systems are formed during the abiotic degradation of existing
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14 475 OM at low temperatures on the ocean floor (Reeves et al. 2014).
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19 477 **6 Conclusions**

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25 479 We provide evidence for the preservation of traces of OM originally deposited in a reducing
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27 480 marine environment in serpentinitized mantle rocks and overlying sediments, but with no
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29 481 indication that the OM was generated from methanotrophic bio-systems. The presence of OM
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32 482 within serpentinitized mantle raises two questions; how much is there and how is this OM
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34 483 distributed in depth? Drilling to recover rock cores from the Totalp area would allow sampling
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37 484 of serpentinitized mantle deeper than surface outcrops and would shed light on the depth
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39 485 distribution of OM and its composition.
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44 487 **Acknowledgments**

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54 491 that improved the manuscript.
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60 493 **Figure and Table Legends**

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Fig. 1 Maps showing location and geology of the Totalp area. **a** Location of the Totalp area

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in the tectonic map of the Alps (from Schmid *et al.* 2004; modified by Mohn *et al.* 2010).

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b Location of Totalp as a part of the South Penninic units in Grisons (Manatschal *et al.*

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2003). **c** Geological map of Totalp (modified from Picazo *et al.* 2013) showing location of

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the analysed samples as well as the distribution of the major lithologies and samples

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described in this study (for description of samples see Table 1).

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Fig. 2 Sketch showing the lithologies and the stratigraphy of the Totalp area (Weissert and

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Bernoulli 1985; Früh-Green *et al.* 1990; Manatschal *et al.* 2003; Picazo *et al.* 2013).

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Fig. 3 The sulphide bearing outcrop in the Totalp area showing weathered lithology. Red

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circles are the sampling location in this outcrop. In the line-drawing on the right, light red

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identifies radiolarian cherts, dark red siliceous shale and yellow sulphate rich carbonate,

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rich in silica. **A** Zoom of outcrop. **b** Sample 65 is composed by calcite 50%. 25% quartz

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and is highly weathered. **c** Sample shows visible hematite crystals and calcite as the major

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mineral. **d** Sample 60 shows a siliceous rock with 3 different colours composed by 83%

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quartz, 10% albite and pyrite, illite and chlorite.

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Fig. 4 **a** Global range of carbon isotopic composition of carbonates precipitated during early

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diagenetic processes (modified after Coleman *et al.* 1993; Kiriakoulakis 1996; Heydari

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1997). **b** Carbon and oxygen isotopic composition of calcite veins in Totalp samples. **c**

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Limestone (sample 19) showing two generation of calcite veins.

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519 Fig. 5 Representative mass chromatograms of the HCs of a typical sample of limestone
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2 520 (sample 10) and a siliceous rock from the sulphide rich outcrop of Totalp (sample 60). **a** *n*-
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4 521 alkanes (m/z 85) of sample 10 (limestone) **b** sterane distribution (m/z 217, 218) of sample
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7 522 60 **c** PAH distribution (m/z 178, 192, 202, 228) of sample 60. For abbreviations see
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9 523 appendix
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14 525 Fig. 6 Thermal maturity parameters of C₂₇ steranes for Totalp samples. The classification
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16 is from Peters et al., 2005. The brown shaded area represents the range of complete
17 526 isomerization for the 20S/(20S + 20R) aaa C₂₇ steranes (ca. 55%) and αββ/(ααα + αββ) C₂₇
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19 527 steranes (ca. 68%).
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26 530 Fig. 7 Plot of pristane/*n*-C₁₇ vs phytane/*n*-C₁₈ for Totalp samples used to identify
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28 depositional environment and OM type (after Peters et al. 1999).
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34 533 Fig. 8 Sterane ternary distribution of the analysed samples for the αββ steranes of Totalp
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36 534 samples. The interpretation of depositional environment is from Patrycja Wójcik-Tabol &
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38 Ślęczka (2015).
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43 537 Fig. 9 Conceptual model explaining origin and migration of OM from the seawater into
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45 different lithologies in the Totalp unit. **a** The OM is represented by particulate and dissolved
46 538 organic matter (POM and DOM, respectively). The OM infiltrates the basement rock by
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48 539 rock-fluid circulation. **b** Some OM may be deposited within the carbonate veins (e.g. calcite
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50 veins). **c** OM circulates with fluids through fractures and porosity of sediments to migrate
51 540 into the basement rock. **d** OM is preserved at the surfaces and in the interlayer surfaces of
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53 541 clay minerals in the sediments.
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2 545 Table 1. Results by lithology including mineralogy and texture observed in hand specimens
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5 546 and the texture on the calcites used for the isotopic analyses ($\delta^{13}\text{C}_{\text{VPDB}}$, $\delta^{18}\text{O}_{\text{VPDB}}$). The vein
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7 547 generation is defined from the specific example and may not correlate across all samples. ¹
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9 548 Thin section of the lithology is observed. • All lithology are from the lower sub-unit with
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11 549 the exception of the massive serpentinite (samples 77, 78).
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17 551 Table 2. Results by lithology including TC, TOC and total HC concentration in ppm (parts
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19 552 per million) and organic carbon isotopic composition of bulk rock $\delta^{13}\text{C}_{\text{organic}}$. For the *n*-
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21 553 alkanes: the carbon number range (*n*-alkane range), the maximum carbon number (Cmax),
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23 554 carbon preference index (CPI values) and mean carbon number (MC#) are shown. For the
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25 555 steranes, hopanes and PAHs the concentrations are in ppm and are represented in intervals
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27 556 by star symbol *, where * = [0 - 0.1), ** = [0.1 - 1) and *** = [1 - 10) and BDL = below
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29 557 detection limit. a: identified PAHs in the samples were: Phenanthrene, P; Fluoranthene,
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31 558 Fluo; Pyrene, Pyr; Chrysene, Chry; Benzo(a)anthracene, BaA; Benzo(b)fluoranthene,
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33 559 BbF; Benzo(a)pyrene, BaP; Indeno(1,2,3-cd)pyrene, IndPy; Benzo(ghi)perylene, BghiP;
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35 560 Dibenzothiophene (DBT), methylP (3,2,1 and 9 MPs) and 2-methyl naphthalene; not all
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37 561 were present in every sample. ¹ All lithology are from lower sub-unit except the massive
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39 562 serpentinite (samples 77, 78) which is from upper sub-unit
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46 563 **References**

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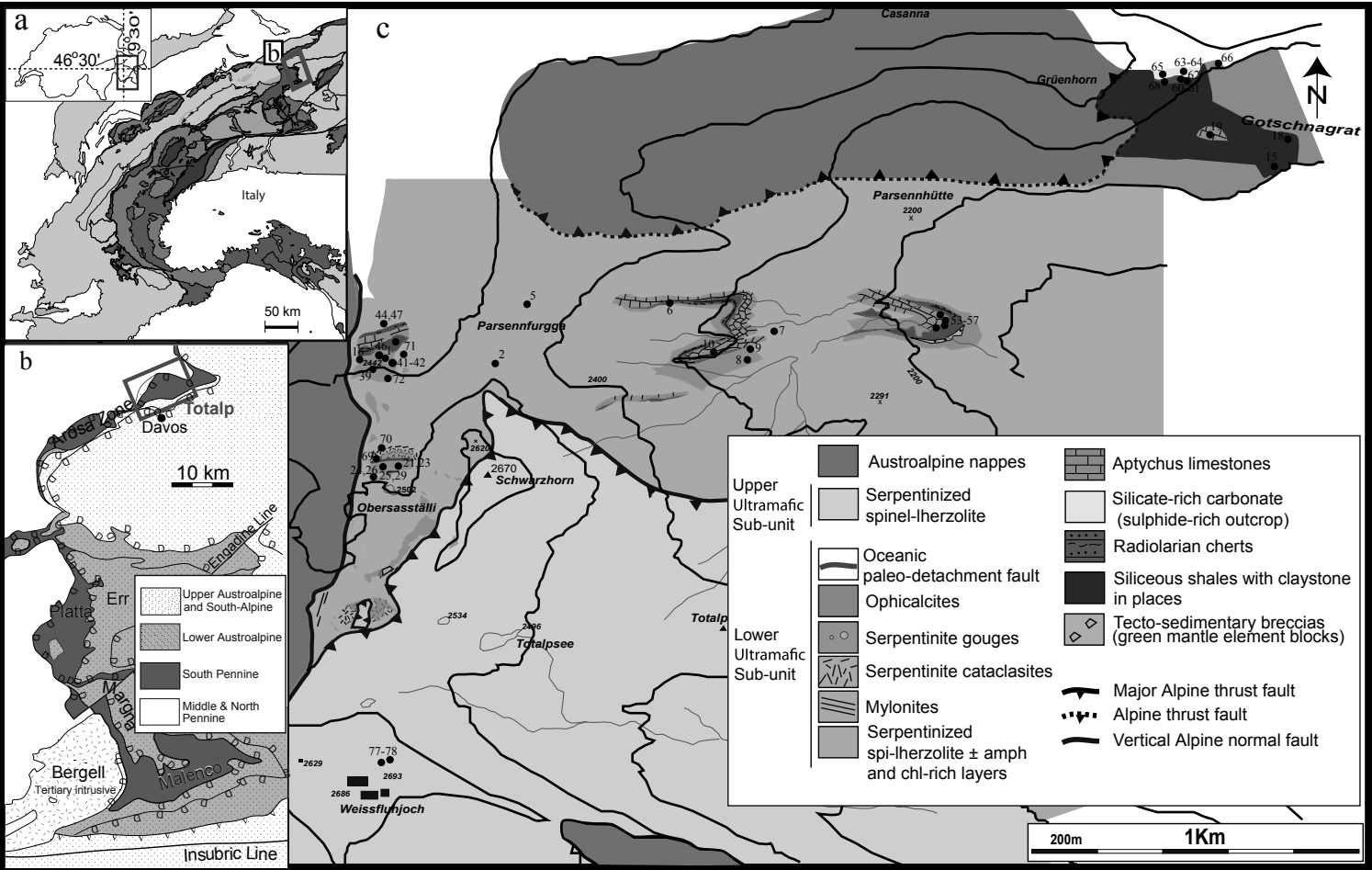


Fig 1. Maps showing location and geology of the Totalp area. **a** Location of the Totalp area in the tectonic map of the Alps (from Schmid *et al.* 2004, modified by Mohn *et al.* 2010). **b** Location of Totalp as a part of the South Penninic units in Grisons (Manatschal *et al.* 2003). **c** Geological map of Totalp (modified from Picazo *et al.* 2013) showing location of the analysed samples as well as the distribution of the major lithologies and samples described in this study (for description of samples see Table 1).

Log of Totalp exhumed mantle and sedimentary cover

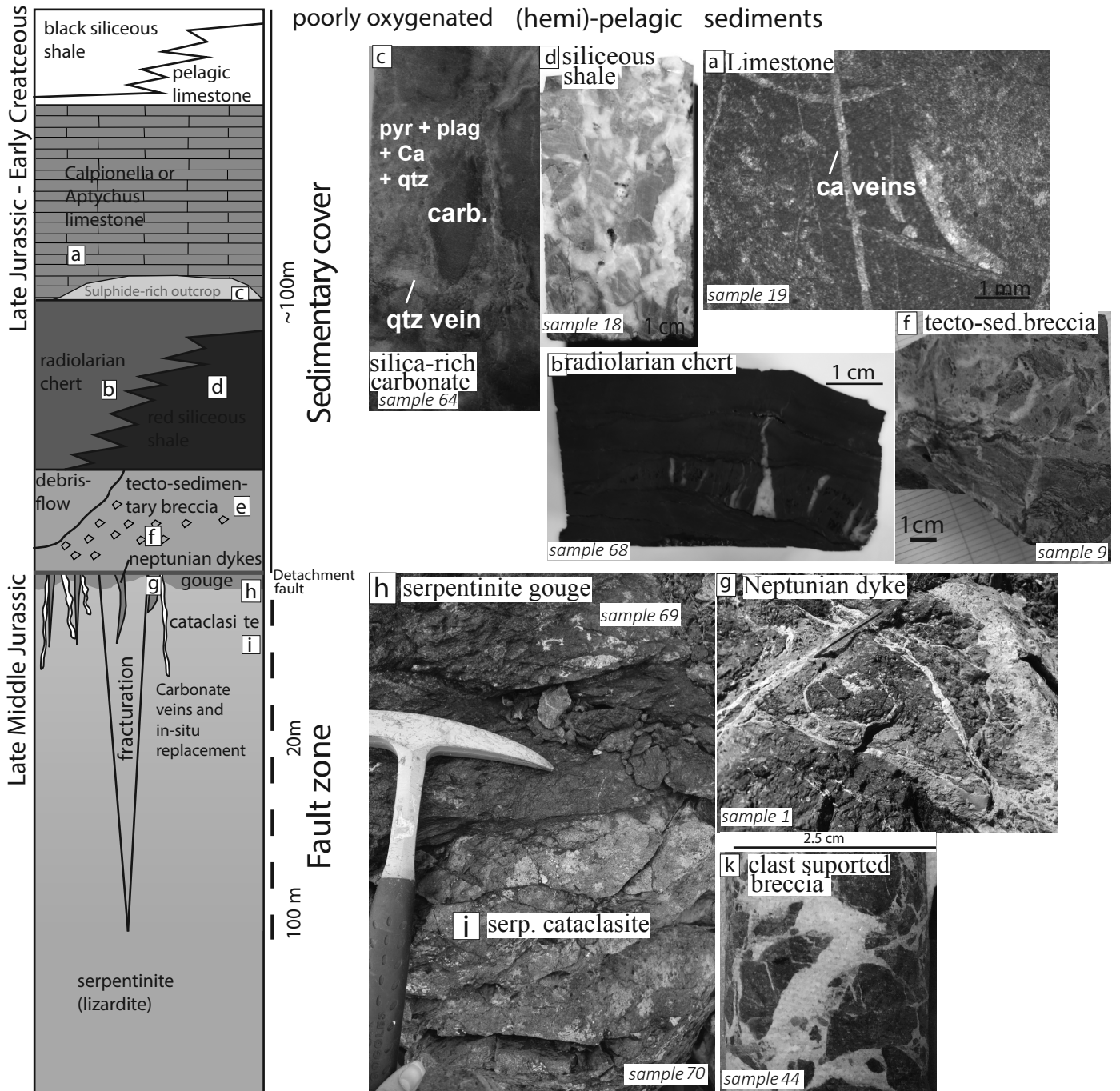


Fig. 2 Sketch showing the lithologies and the stratigraphy of the Totalp area (Weissert and Bernoulli 1985; Früh-Green et al. 1990; Manatschal et al. 2003; Picazo et al. 2013).

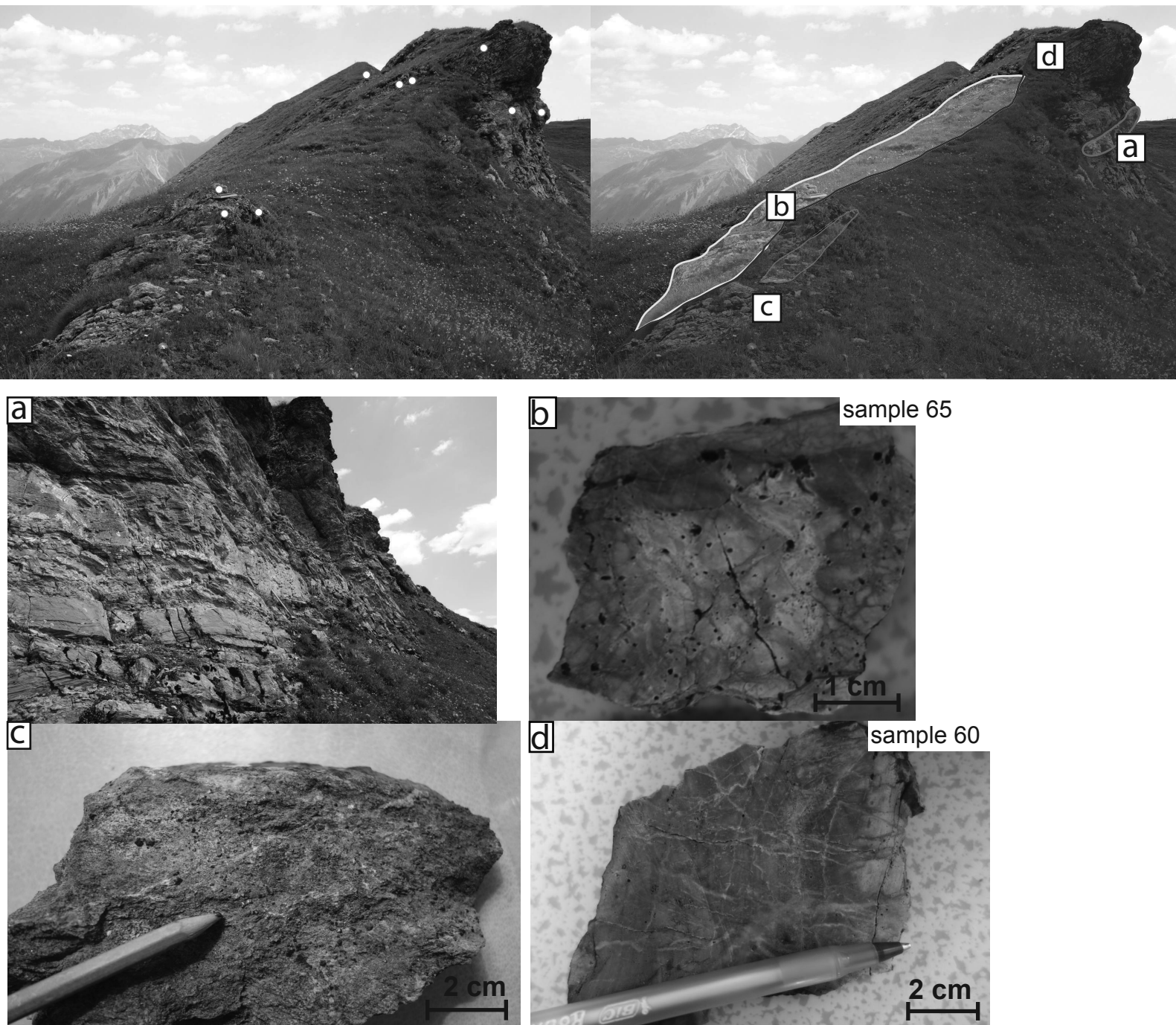


Fig 3. The sulphide bearing outcrop in the Totalp area showing weathered lithology. Circles show the sampling location for this outcrop. In the line-drawing on the right, light red identifies radiolarian cherts, dark red siliceous shale and yellow sulfite rich carbonate, rich in silica. **a** Zoom of outcrop. **b** Sample 65 is composed by calcite 50%, 25% quartz and is highly weathered. **c** Sample shows visible hematite crystals and calcite as the major mineral. **d** Sample 60 shows a siliceous rock with 3 different colours composed by 83% quartz, 10% albite and pyrite, illite and chlorite.

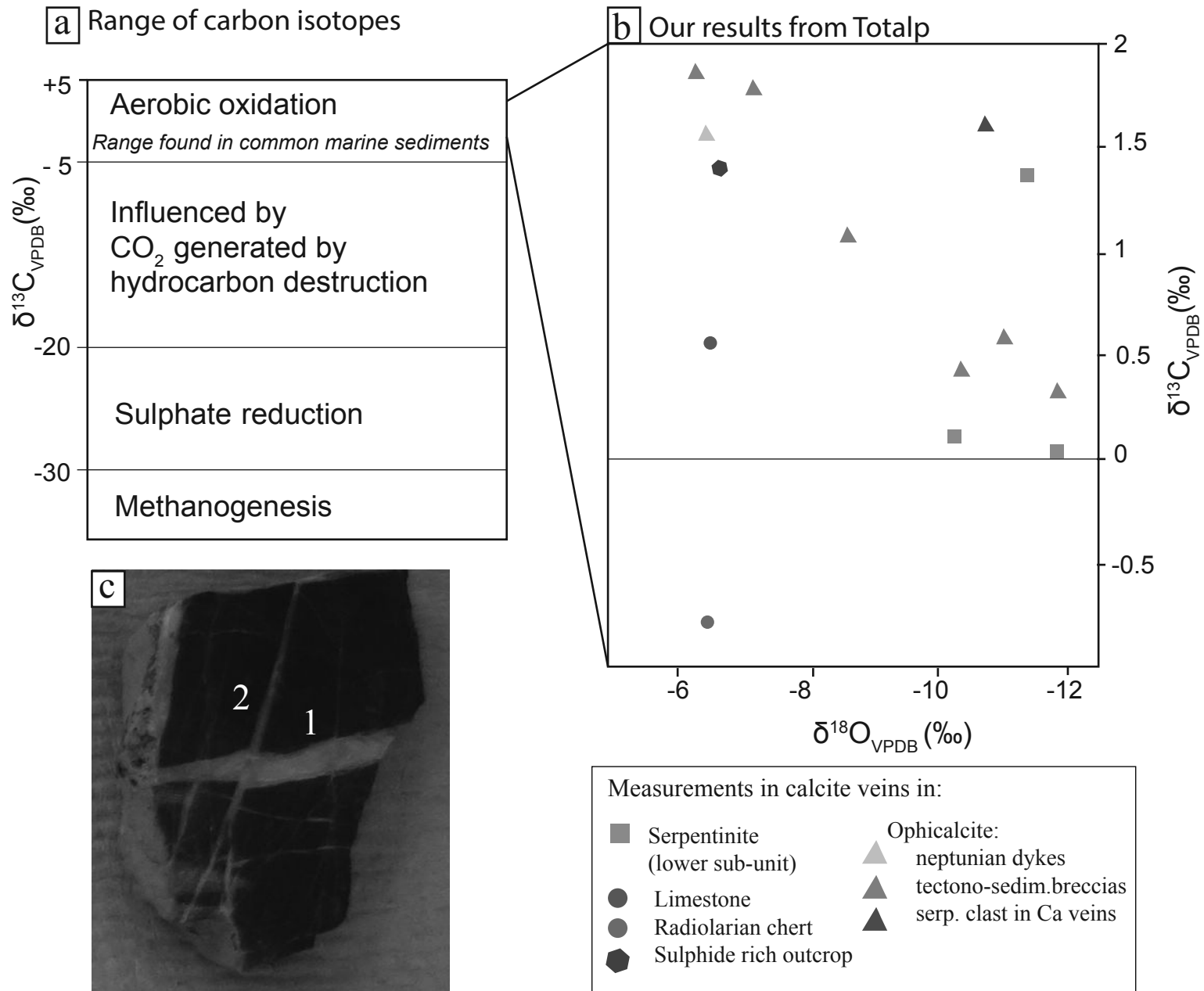


Fig. 4 **a** Global range of carbon isotopic composition of carbonates precipitated during early diagenetic processes (modified after Coleman *et al.* 1993; Kiriakoulakis 1996; Heydari 1997). **b** Carbon and oxygen isotopic composition of calcite veins in Totalp samples. **c** Limestone (sample 19) showing two generations of calcite veins.

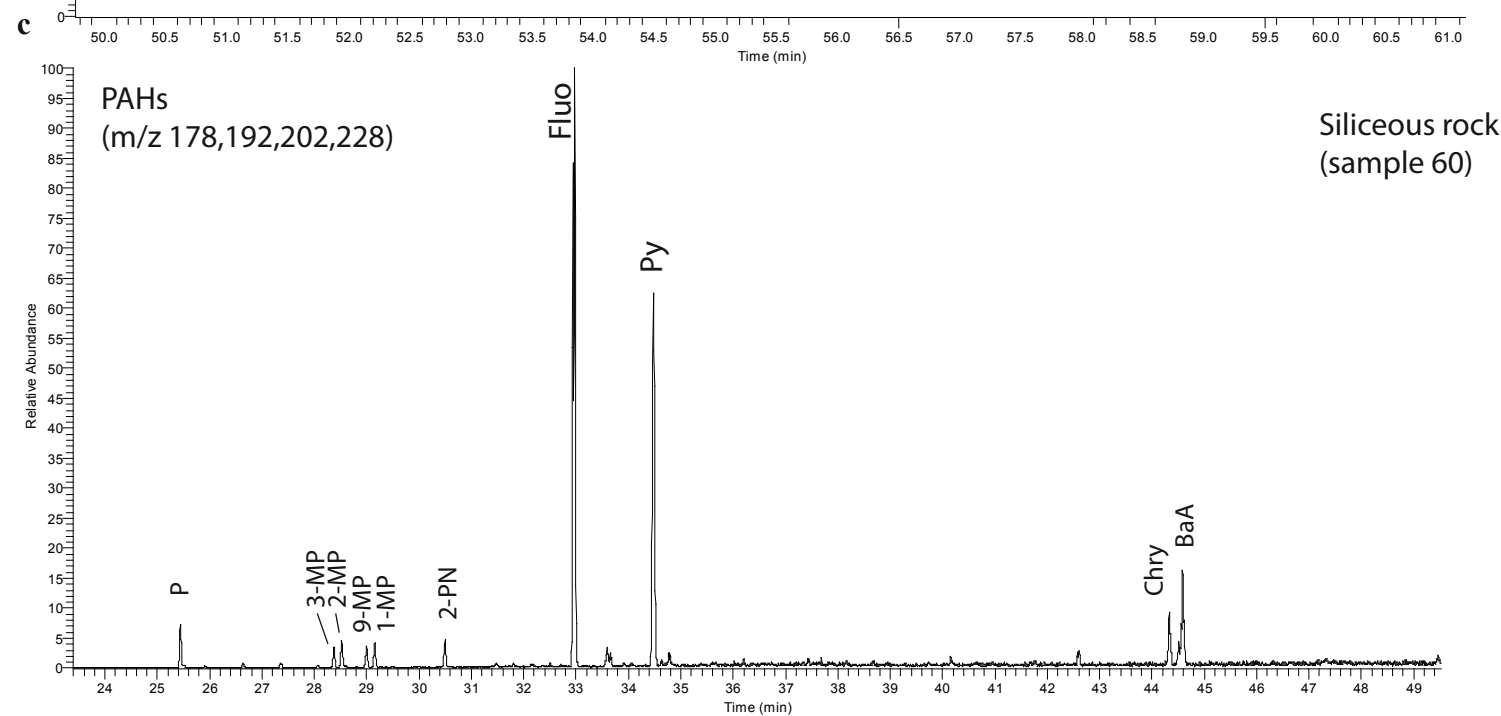
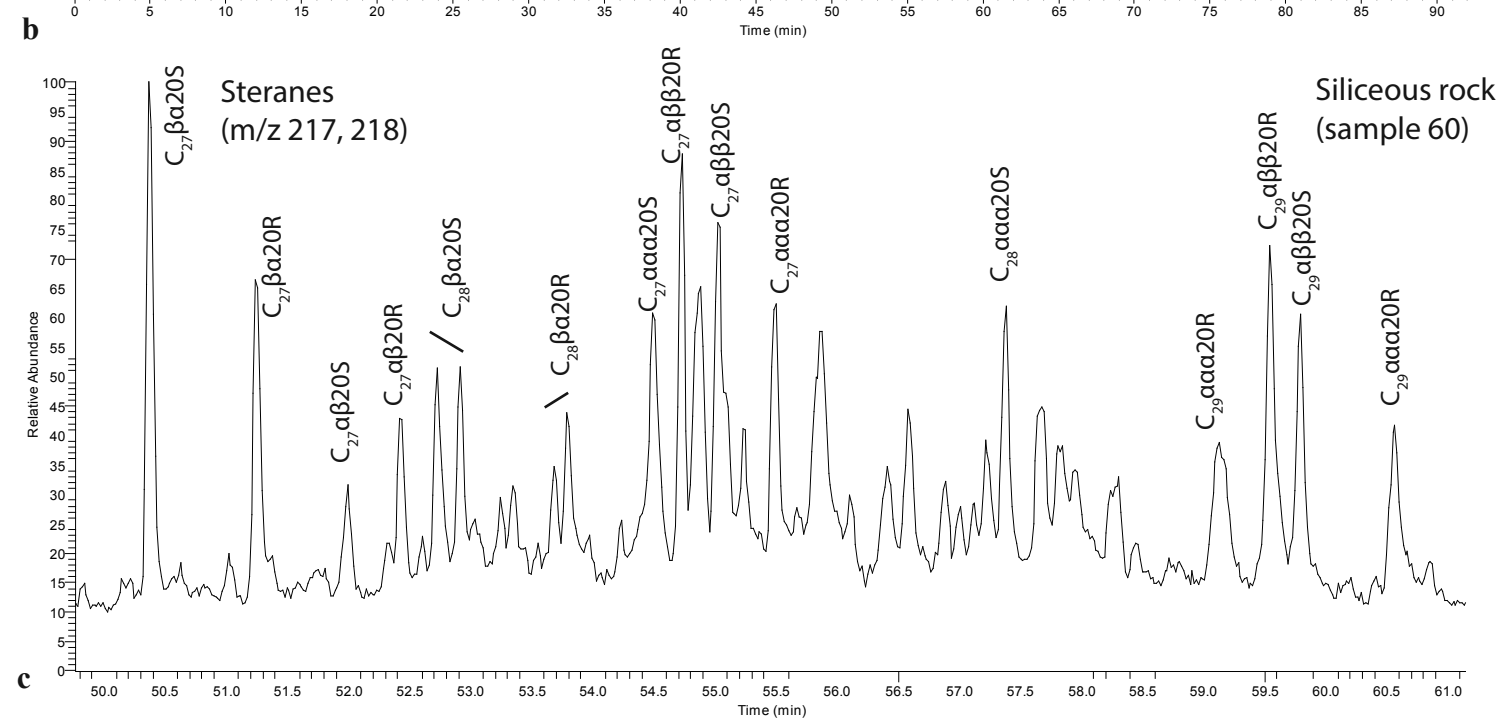
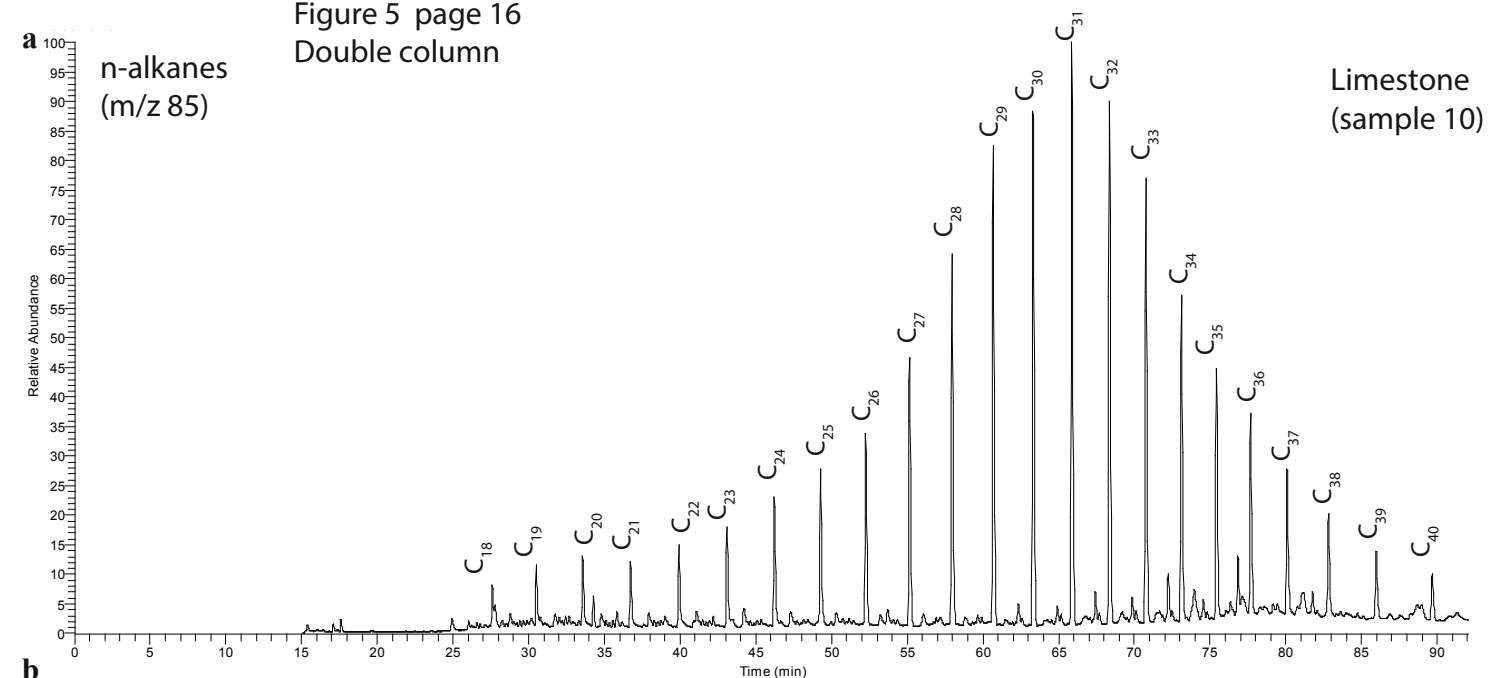


Fig. 5 Representative mass chromatograms of the HCs of a typical sample of limestone (sample 10) and a siliceous rock from the sulphide rich outcrop of Totalp (sample 60). **a** n-alkanes distribution (m/z 85) of sample 10 (limestone) **b** sterane distribution (m/z 217, 218) of sample 60 **c** PAH distribution (m/z 178, 192, 202, 228) of sample 60. For abbreviations see appendix

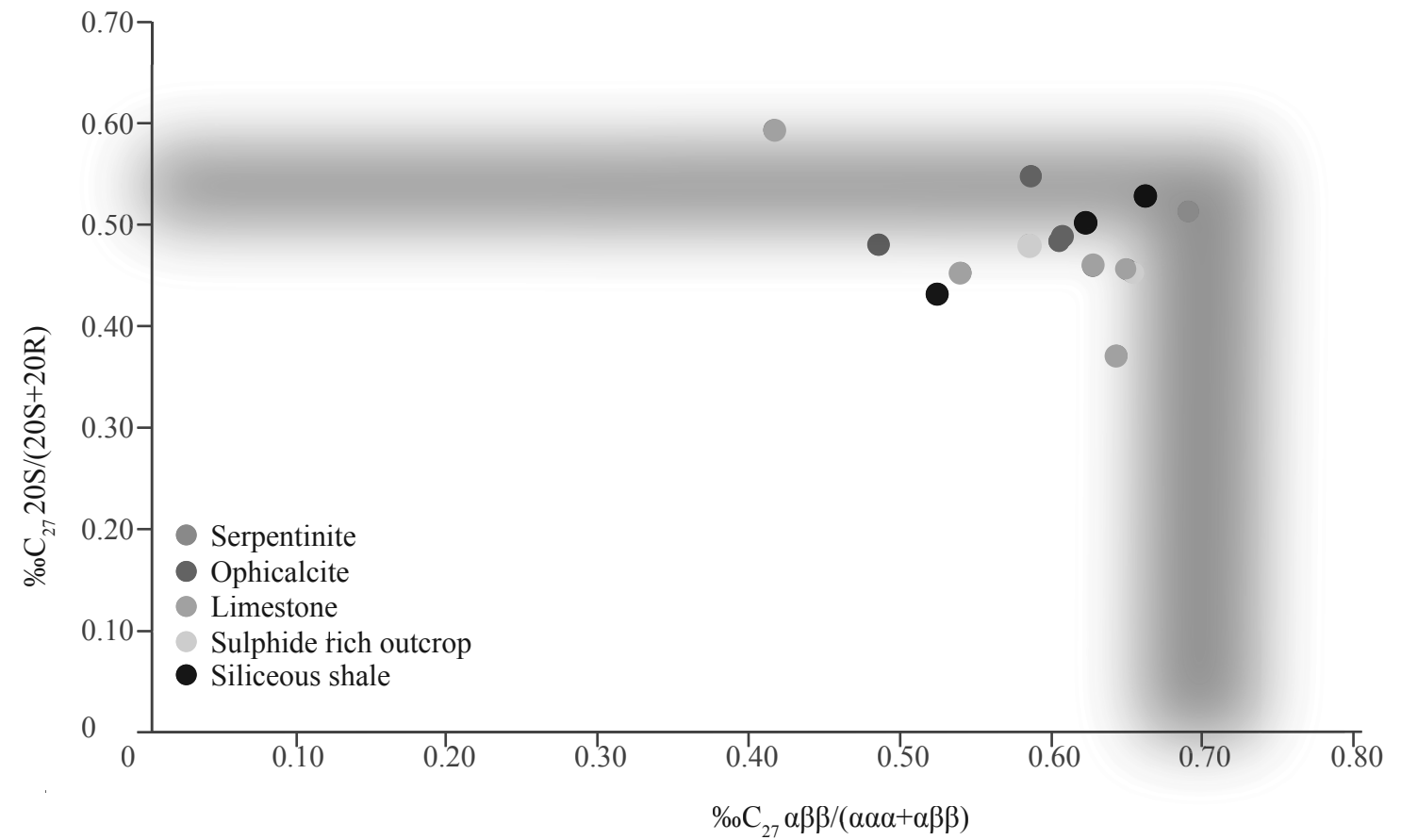


Fig. 6 Thermal maturity parameters of C_{27} steranes for Totalp samples. The classification is from Peters et al. 2005. The brown shaded area represents the range of complete isomerization for the 20S/(20S + 20R) $\alpha\alpha\alpha$ C_{27} steranes (ca. 55%) and $\alpha\beta\beta/(\alpha\alpha\alpha+\alpha\beta\beta)$ C_{27} steranes (ca. 68%).

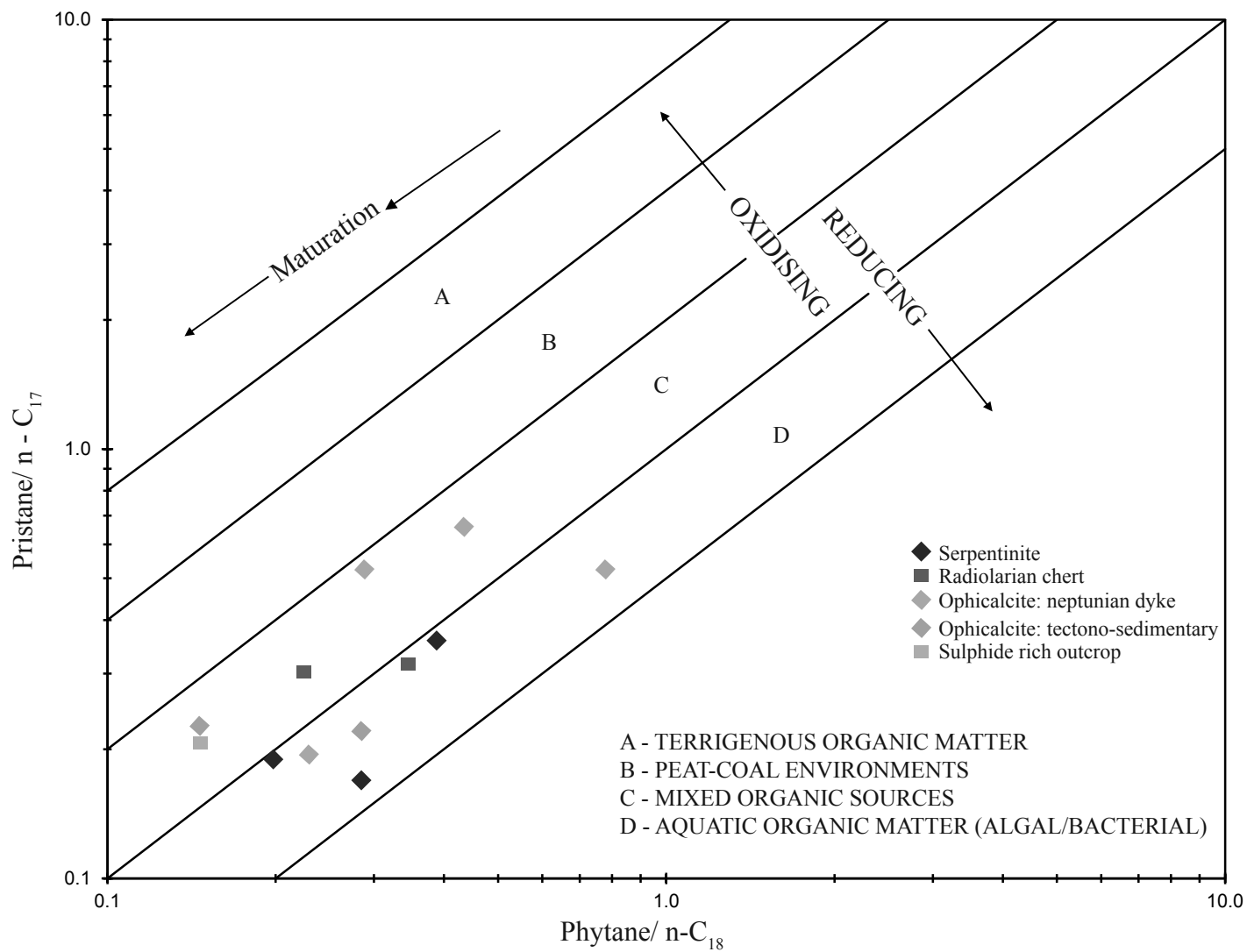


Fig. 7 Plot of pristane/n-C₁₇ vs phytane/n-C₁₈ for Totalp samples used to identify depositional environment and OM type (after Peters et al. 1999).

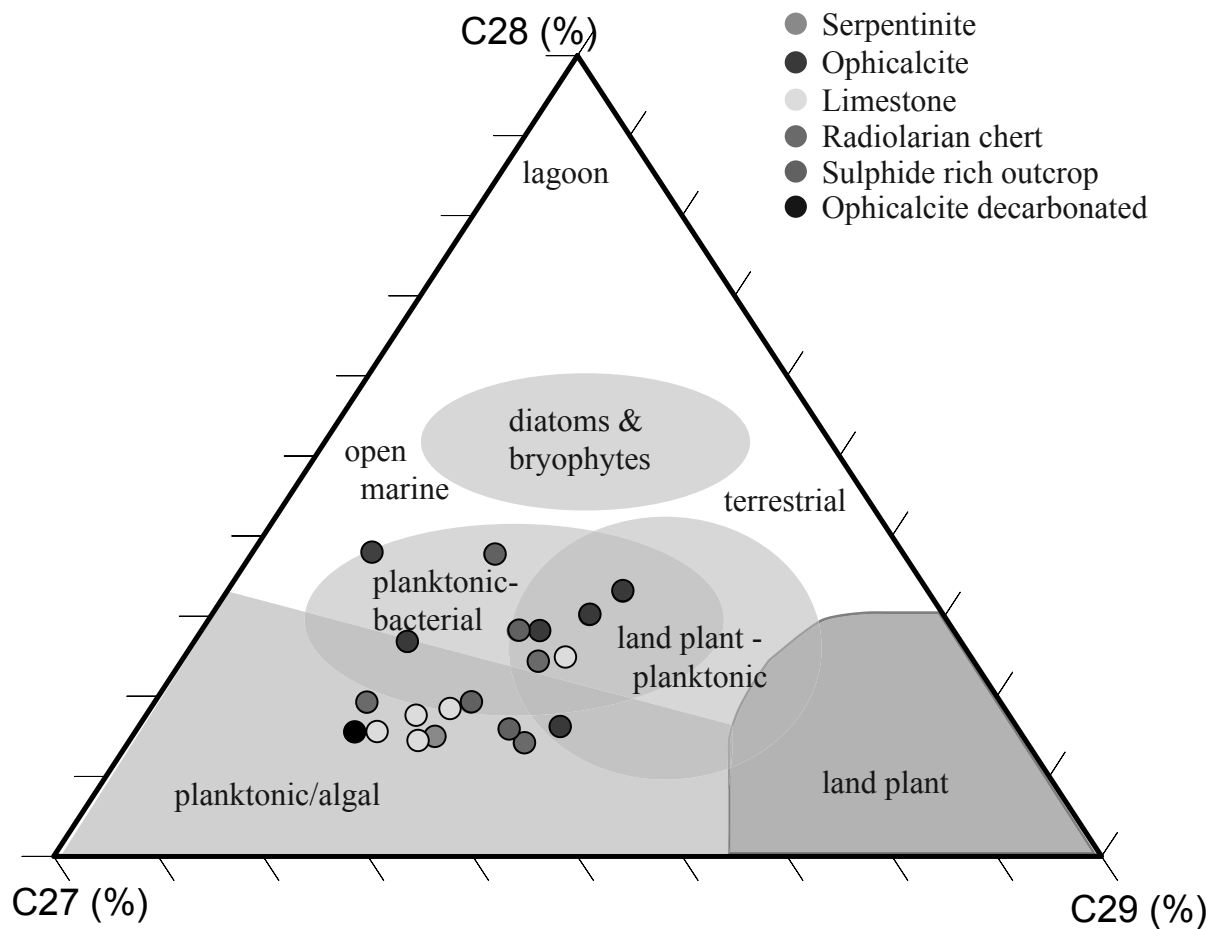


Fig. 8 Sterane ternary distribution of the analysed samples for the $\alpha\beta\beta$ steranes of Totalp samples. The interpretation of depositional environment is from Patrycja Wójcik-Tabol & Ślaczka (2015).

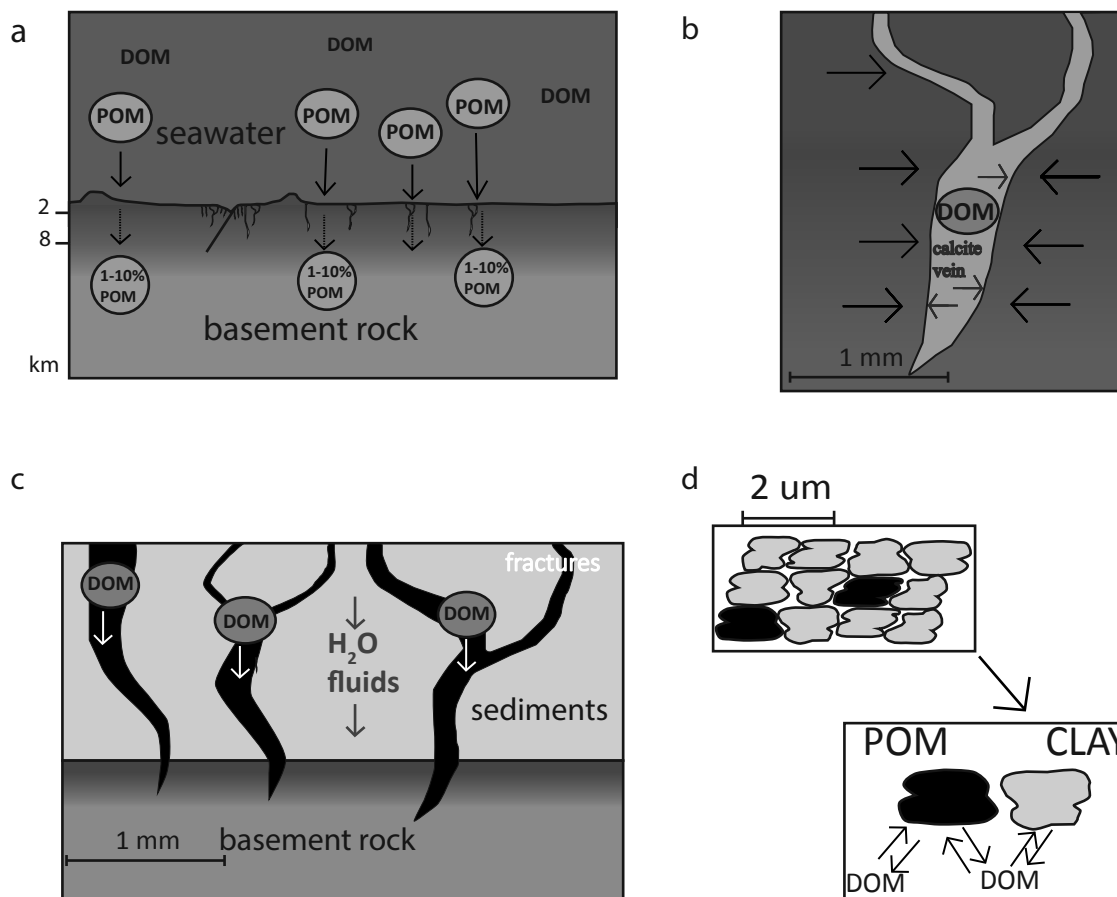


Fig. 9 Conceptual model explaining origin and migration of OM from the seawater into different lithologies in the Totalp unit. **a** The OM is represented by particulate and dissolved organic matter (POM and DOM, respectively). The OM infiltrates the basement rock by rock-fluid circulation. **b** Some OM may be deposited within the carbonate veins (e.g. calcite veins). **c** OM circulates with fluids through fractures and porosity of sediments to migrate into the basement rock. **d** OM is preserved at the surfaces and in the interlayer surfaces of clay minerals in the sedimentary rocks.

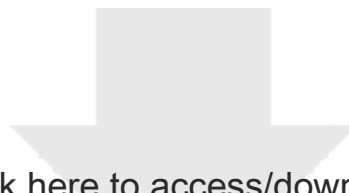
| rock type | sample number | coordinates (UTM) | | locality | macroscopic description | mineralogical description | texture | Carbonate texture | $\delta^{13}\text{C}_{\text{VPDB}}$ (‰) Ca veins | $\delta^{18}\text{O}_{\text{VPDB}}$ (‰) Ca veins | |
|---|---------------|-------------------|---------------|--------------------------------------|--|---|--|--|--|--|--|
| | | X (m) | Y (m) | | | | | | | | |
| Serpentinite | | | | | | | | | | | |
| Massive serpentinite | 5 | 561895 | 5188662 | Parsennfurgga | massive black serpentinite with white angular borders defining the ex-serpentine minerals, phantoms of peridotite minerals, small green pyroxene, magnetite, later chrysotile veinlets and white carbonate veins | Olivine completely replace by ex-serpentine minerals, phantoms of peridotite minerals, magnetite, later chrysotile veinlets and white carbonate veins; calcite veins with only one stage of crystal growing | <i>mesh</i> ¹ | | | | |
| | 16 | 561522 | 5188399 | 2442m. Obersasställi - Parsennfurgga | | | | calcite vein, 1 st generation | 0.11 | -10.2 | |
| | 24 | 561514 | 5188009 | Obersasställi | Broken serpentinite clasts from a first mainly mesh texture with rare generation of greyish deformed calcite ribbon texture; randomly dispersed anhedral magnetite by a second generation of white calcite veins | | <i>clast supported breccia</i> ¹ | calcite vein, 1 st generation | 0.03 | -11.75 | |
| | 26 | 561504 | 5188010 | | | | | | | | |
| | 44 | 561518 | 5188415 | 2442m. Obersasställi - Parsennfurgga | | | | | | | |
| 47 | 561540 | 5188427 | | | | | | | | | |
| Red serpentinite | 71 | 561588 | 5188095 | 2442m. Obersasställi - Parsennfurgga | red matrix with dark-black deformed the clasts/veins with numerous calcite veins, also contain dark green serpentinite. | serpentinite is lizardite containing also talc and calcite; the red colour is due to hematite (4%). | <i>red</i> | calcite vein, 2 nd generation | 1.37 | -11.3 | |
| Serpentinite gouge | 69 | 561929 | 5187152 | Obersasställi | black fine-grained deformed serpentinite with equant serpentine grain following and distributed systematically and fine short veinlets (chrysotile; calcite) | no thin section or XRD | <i>fine grained</i> | | | | |
| Serpentinite catadaseite | 70 | 561929 | 5187152 | Obersasställi | black serpentinite with subangular serpentine clasts showing no preferred orientation | no thin section or XRD | <i>fine grained</i> | | | | |
| Massive serpentinite • | 77 | 561482 | 5187004 | Weissfluhjoch | black serpentinite with sub-rounded anhedral white-grayish peridotite mineral (pyroxene) and small chrysotile veins | no thin section or XRD | <i>mesh</i> | | | | |
| | 78 | 561482 | 5187004 | | | | | | | | |
| Sedimentary ophicalcite | | | | | | | | | | | |
| Limestone (Neptunian dykes) | 1 | 561543 | 5188408 | 2442m. Obersasställi - Parsennfurgga | fine micritic pink and red pelagic limestone; serpentine minerals as clasts and veins | three types of carbonate crystal growing; the matrix composed of rounded to angular coarse grains with hornblend floating randomly in the matrix | <i>porphyro-clastic</i> ¹ | calcite vein, 2 nd generation | 1.56 | -6.4 | |
| | 23 | 561514 | 5188009 | Obersasställi | | | | | | | |
| Tectono- sedimentary ophicalcite | | | | | | | | | | | |
| Tectono- sedimentary ophicalcite | 21 | 561520 | 5188015 | Obersasställi | red fine carbonate matrix with black serpentinite clasts broken by anhedral serpentinite | serpentinite clasts broken by several stage of crystal growing for the carbobnates; | <i>fine grained with clasts</i> ¹ | calcite vein, 1 st generation | 0.32 | -11.7 | |
| | 25 | 561511 | 5188009 | | | | | calcite vein, 1 st generation | 0.58 | -10.9 | |
| | 39 | 561515 | 5188439 | 2442m. Obersasställi - Parsennfurgga | crosscutted by calcite veins | | | calcite vein, 2 nd generation | 1.78 | -7.1 | |
| | 41 | 561572 | 5188406 | | | | | calcite vein, 1 st and 2 nd gener. | 0.42; 1.07 | -10.3; -8.6 | |
| | 42 | 561572 | 5188406 | | | | | | | | |
| | 46 | 561540 | 5188418 | | | | | | | | |
| 66 | 564260 | 5190402 | near Grünhorn | | | | | calcite vein, undetermined generation | 1.86 | -6.2 | |

| rock type | sample number | coordinates (UTM) | | locality | macroscopic description | mineralogical description | texture | Carbonate texture | $\delta^{13}\text{C}_{\text{VPDB}}$ (‰) Ca veins | $\delta^{18}\text{O}_{\text{VPDB}}$ (‰) Ca veins |
|-----------------------------------|---------------|-------------------|---------|--|---|---|-------------------------------|--|--|--|
| | | X (m) | Y (m) | | | | | | | |
| Reworked tec-sed. ophicalcite | 9 | 562586 | 5188578 | Parsennfurga-Parsennhütte | pink carbonate with randomly orientated elongated clast of ophicalcite (serpentinite+carbonate); numerous calcite veins | no thin section or XRD | <i>reworked</i> ¹ | | | |
| | 72 | 561929 | 5187152 | 2442m. Obersasställi - Parsennfurga | centimetric angular clasts of green serpentinite tectonically broken by calcite veins | no thin section or XRD | <i>vein supported breccia</i> | calcite vein, undetermined generation | 1.60 | -10.6 |
| Sediments | | | | | | | | | | |
| Radiolarite | 62 | 564212 | 5190386 | near Grünhorn from sulphide rich outcrop | hard fine grained red siliceous rock ; post deposition quartz vein perpendicular to the geometry of deposition | no thin section or XRD | <i>fine grained</i> | post-deposit calcite vein | - 0.79 | -6.4 |
| | 68 | 564252 | 5190393 | | | | | | | |
| Siliceous shale | 60 | 564212 | 5190386 | near Grünhorn from sulphide rich outcrop | greyish - reddish fine grained siliceous rock, great porosity and numerous fractures | composed mainly by quartz (46%), plagioclase (30%), chlorite, muscovite and hematite | <i>fine grained</i> | | | |
| | 61 | 564212 | 5190386 | | | | | | | |
| Limestone | 15 | 564049 | 5189517 | Gotschnagrat | red and grey fine grained intercalated siliceous shale with deformed quartz veins | dominated by quartz (89%) with plagioclase, muscovite, chlorite and trace of hematite | <i>fine grained</i> | | | |
| | 18 | 564213 | 5189544 | | | | | | | |
| Limestone | 10 | 562494 | 5188558 | Parsennfurga-Parsennhütte | grey limestone with numerous calcite veins of two generation almost perpendicular to each other | pelagic limestone, evidence of fossil organisms filled by sparry calcite | <i>fine grained</i> | calcite vein, 1 st generation | 0.56 | -6.5 |
| | 19 | 563790 | 5189694 | Gotschnagrat | | | <i>fine grained</i> | | | |
| Limestone | 53 | 563144 | 5188716 | south from Parsennhütte | grey limestone with fine greyish veinlets and rare short calcite veins with pink pelagic limestone (hematite) in places | no thin section or XRD | | | | |
| | 54 | 563140 | 5188707 | | | | | | | |
| | 56 | 563140 | 5188707 | | | | | | | |
| | 57 | 563144 | 5188716 | | | | | | | |
| | 58 | 563144 | 5188716 | | | | | | | |
| Carbonate (Sulphide rich outcrop) | 63 | 564212 | 5190386 | near Grünhorn | carbonate rock with deformed quartz veins; microscopic grain everywhere except in the quartz and calcite veins | dominated by calcite (53%) with quartz, chlorite (12%) and pyrite. | <i>porphyro - clastic</i> | calcite vein, 2 nd generation | 1.4 | -6.6 |
| | 64 | 564212 | 5190386 | | | | | | | |
| | 65 | 564252 | 5190393 | | very fractured sample with greater porosity | | | | | |

Table 1. Results by lithology including mineralogy and texture observed in hand specimens and the texture on the calcites used for the isotopic analyses ($\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB}}$). The vein generation is defined from the specific example and may not correlate across all samples. ¹ Thin section of the lithology is observed. * All lithology are from the lower sub-unit with the exception of the massive serpentinite (samples 77, 78).

| | sample number | Total Carbon ppm | Total C _{organic} ppm | Hydrocarbons (HC) ppm | n-alkanes | | | δ ¹³ C _{VPDB} (‰) on TOC | Steranes | Hopanes | PAHs* | |
|--|----------------------------|------------------|--------------------------------|-----------------------|-----------|------------------------------------|-------------|--|----------|---------|-------|--------------------|
| | | | | | Range | C _{max} | CPI | | | | | Mean Carbon number |
| | | | | | | | | | | | | |
| Serpentinite | | | | | | | | | | | | |
| Massive serpentinite | 5, 16 | 395- 3135 | 102- 176 | 23-900 | 16-39 | C ₂₀ , C ₂₉ | 0.76 - 1.29 | | BDL | BDL | * | |
| Serpentinite with numerous Ca veins | 24, 26, 44, 47 | 20400-42500 | 19-135 | 1 - 124 | 16 - 35 | C ₂₀ , C ₂₆ | 0.8 - 1.05 | | BDL | * | * | |
| Red serpentinite (with hematite) | 71 | 88205 | 268 | 1 | 17-35 | C ₂₆ | 1.17 | | BDL | BDL | ** | |
| Serpentinite gouge | 69 | 539 | 284 | 3 | 17-33 | C ₂₉ | 0.94 | | BDL | * | BDL | |
| Serpentinite cataclasisite | 70 | 876 | 269 | 46 | 17-36 | C ₂₀ | 0.94 | | BDL | BDL | ** | |
| Massive serpentinite ¹ | 77, 78 | 454 | ≈ 190 | 0.05-4 | 17-40 | C ₂₉ | 0.84 - 0.97 | | BDL | * | BDL | |
| Ophicalcite | | | | | | | | | | | | |
| <i>Sedimentary ophicalcite</i> | | | | | | | | | | | | |
| Neptunian dykes | 1, 23 | 95600 - 107500 | 15- 103 | 0.03 - 121 | 17 - 35 | C ₂₉ | 1.05 | | ** | ** | ** | |
| <i>Tectono- sedimentary ophicalcite</i> | | | | | | | | | | | | |
| Red matrix, serp. claste and Ca veins | 21, 25, 39, 41, 42, 46, 66 | 33360 - 101700 | 11 - 116 | 2 - 2470 | 17-38 | C ₁₈ to C ₂₈ | 0.81 - 1.42 | | ** | ** | ** | |
| Reworked tec-sed. Ophicalcite | 9 | 106000 | 86 | 50 | 16-36 | C ₂₂ | 0.65 | | BDL | * | ** | |
| Serp. clasts in Ca veins | 72 | 69600 | 30 | 124 | 20-36 | C ₂₉ | 0.90 | | BDL | BDL | BDL | |
| Sediments | | | | | | | | | | | | |
| Radiolarite from sulphide rich outcrop | 62, 68 | 671 - 13200 | 66-187 | 1 - 17 | 17 - 34 | C ₂₀ C ₃₁ | 1.19-2.87 | | BDL | ** | * | |
| Siliceous shale from sulphide rich outcrop | 60, 61 | 384 - 672 | 194 - 433 | 22-144 | 16 - 37 | C ₂₀ C ₂₇ | 1.05 - 1.52 | | ** | ** | ** | |
| Siliceous shale near sulphide rich outcrop | 15, 18 | 285- 318 | 136- 145 | 13 - 27 | 16-33 | C ₁₈ , C ₂₀ | 0.95 - 1.19 | | * | * | BDL | |
| Limestones | 10,19 | 98200 - 129000 | 74- 82 | 79 - 171 | 16-35 | C ₂₂ , C ₂₇ | 0.92 - 0.94 | | BDL | *** | *** | |
| Limestone from Parsennhütte | 53, 54, 56, 57, 58 | 46500 - 94500 | 14 - 92 | 3 - 238 | 16 - 37 | C ₂₃ , C ₂₉ | 0.82 - 1.10 | | * | * | ** | |
| Sulphide rich outcrop | 63, 64, 65 | 442 - 90400 | 153 - 647 | 1 - 24 | 17-33 | C ₂₀ C ₂₇ | 0.93- 1.55 | | ** | ** | ** | |

Table 2. Results by lithology including TC, TOC and total HC concentration in ppm (parts per million) and organic carbon isotopic composition of bulk rock δ¹³C_{VPDB} organic. For the n-alkanes: the carbon number range (n-alkanes range), the maximum carbon number (Cmax), carbon preference index (CPI values) and mean carbon number (MC#) are shown. For the steranes, hopanes and PAHs the concentrations are in ppm and are represented in intervals by star symbol *, where * = [0 - 0.1), ** = [0.1 - 1) and *** = [1 - 10) and BDL = below detection limit. a: identified PAHs in the samples were: Phenanthrene, P; Fluoranthene, Fluo; Pyrene, Pyr; Chrysene, Chry; Benzo(a)anthracene, BaA; Benzo(b)fluoranthene, BbF; Benzo(a)pyrene, BaP; Indeno(1,2,3-cd)pyrene, IndIPy; Benzo(ghi)perylene, BghiP; Dibenzothiophene (DBT), methylP (3,2,1 and 9 MPs) and 2-methyl naphthalene; not all were present in every sample. ¹ All lithology are from lower sub-unit except the massive serpentinite (samples 77, 78) which is from upper sub-unit



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