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Thermal and exhumation histories of the northern subalpine chains (Bauges and Bornes-France): evidence from forward thermal modeling coupling clay mineral diagenesis, organic maturity and carbonate clumped isotope ($\Delta 47$) data.

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3 1 **Thermal and exhumation histories of the northern subalpine**
4 **chains (Bauges and Bornes – France): evidences from forward**
5 **thermal modeling coupling clay mineral diagenesis, organic**
6 **3 maturity and carbonate clumped isotope (Δ_{47}) data.**
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26 17 **ABSTRACT**
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29 19 **Assessing the thermal evolution of sedimentary basins over time is a major aspect of**
30 20 **modern integrated basin analysis. While the behavior of clay minerals and organic**
31 21 **matter with increasing burial is well documented in different geological and thermal**
32 22 **settings, these methods are often limited by the temperature ranges over which they can**
33 23 **be precisely applied and by the available material. Here, we explore the emergent Δ_{47}**
34 24 **clumped isotope thermometry (based on the diffusional redistribution of heavy carbon**
35 25 **and oxygen isotopes in the carbonate lattice at elevated temperatures) to refine time-**
36 26 **temperature paths of carbonate rocks during their burial evolution. This study provides**
37 27 **a reconstruction of the thermal and exhumation history of the Upper Cretaceous thrust**
38 28 **belt series in the western subalpine massifs (Bauges and Bornes, French Alps) by a new**
39 29 **approach combining available data from three independent geothermometers. The**
40 30 **investigated area presents two zones affected by contrasting thermal histories. The most**
41 31 **external zone has undergone a relatively mild thermal history ($T < 70^{\circ}\text{C}$) and does not**
42 32 **record any significant clay mineral diagenetic transformation. By contrast, the internal**
43 33 **zone has experienced tectonic burial (prealpine nappes) in response to thrusting,**
44 34 **resulting in overheating ($T > 160\text{-}180^{\circ}\text{C}$) that induced widespread clay mineral**
45 35 **diagenetic transformations (progressive illitization from R0 to R1 and R3 illite-smectite**
46 36 **mixed-layers), organic matter maturation (oil window) and Δ_{47} thermal resetting with**
47 37 **apparent equilibrium temperatures above 160°C . The three employed geothermal**
48 38 **indicators conjointly reveal that the investigated Upper Cretaceous rocks have suffered**
49 39 **a wide range of burial temperatures since their deposition, with a thermal maximum**
50 40 **locally up to $160\text{-}180^{\circ}\text{C}$. High temperatures are associated with the tectonic**
51 41 **emplacement of up to 4km of prealpine nappes in the northern part of the studied area.**
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3 42 **Finally, a forward thermal modeling using the kinetic algorithms for Δ_{47} , vitrinite**
4 43 **reflectance and clay mineral data, is attempted to precisely refine the time-temperature**
5 44 **evolution of these rocks during burial and exhumation.**
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8 45 **KEY-WORDS: subalpine massifs, Δ_{47} clumped isotope thermometry, Thermicity, Clay**
9 46 **diagenesis, Kinetic models.**

10 11 47 **INTRODUCTION**

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14 49 Assessing the thermal evolution of sedimentary basins over time is a major goal of
15 50 modern integrated basin analysis, especially in areas where major erosion occurred, such as
16 51 the fold and thrust belts. This requires looking for past thermal conditions recorded by the
17 52 modifications of minerals and organic matter. Among the numerous temperature dependent
18 53 transformations occurring during burial and uplift, vitrinite reflectance and apatite fission
19 54 track annealing are the most widely used for studying the evolution of low-temperature
20 55 systems (ie., 60-100°C). At higher temperatures (i.e., 80-200°C), other kinetically-dependent
21 56 indicators can be used to assess past thermal conditions, including the T_{\max} parameter from
22 57 kerogen Rock-Eval pyrolysis (Espitalié et al. 1985), the illite crystallinity index (otherwise
23 58 named “Kubler index” ; Kubler & Jaboyedoff, 2000) and the decrease in smectite content in
24 59 mixed-layered illite/smectite (I-S ; Inoue et al. 1987). In this context, coupling different
25 60 methods together may provide a more reliable dataset to refine paleo-thermicity
26 61 reconstructions, especially when each employed technique has its own kinetic dependence to
27 62 the burial and time-temperature histories.

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32 63 However, the kinetic response of clay mineral reactions, such as illitization of
33 64 smectite, can vary significantly from that of vitrinite, mainly due to strong inhibiting effects
34 65 of the Na^+ , Ca^{2+} and Mg^{2+} release on the illitization (Roberson & Lahann, 1981; Howard &
35 66 Roy, 1985). Lithology is an additional issue when correlating mineral and organic matter
36 67 thermal indicators. Generally, limestones and sandstones are not suitable, largely because they
37 68 do not contain sufficient clay. Moreover, these lithologies can either inhibit clay mineral
38 69 reactions, through early cementation or promote reactions through pore fluid movement,
39 70 which are not comparable with reaction conditions in pelitic rocks (Aldega et al. 2005; Honlet
40 71 et al. 2017). In this study, we present results of a correlation between vitrinite reflectance and
41 72 illite content in illite-smectite (I-S) mixed-layers in a clay-poor limestone unit, that we
42 73 combine here for the first time with carbonate clumped isotopes thermometry (Δ_{47}).
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47 75 The emergent carbonate clumped isotope Δ_{47} thermometry relies on an internal
48 76 equilibrium within the carbonate lattice with rare, heavy isotopes (notably ^{13}C and ^{18}O)
49 77 preferentially bonding to each other at low temperature. The abundance of $^{13}\text{C}^{18}\text{O}^{16}\text{O}_2$ groups
50 78 in carbonate lattices relative to its random distribution depends on temperature (Schauble et
51 79 al., 2006). This Δ_{47} dependence to temperature has been experimentally determined for
52 80 several types of carbonates (e.g., Dennis and Schrag, 2010; Henkes et al., 2013; Kele et al.,
53 81 2015; Bonifacie et al., 2017; Katz et al., 2017; Kelson et al., 2017) and can be applied to
54 82 virtually any (Ca, Fe, Mg) CO_3 carbonate in the 0-350°C geologically-relevant temperature
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3 83 range (Bonifacie et al., 2017). Over the last decade, the Δ_{47} thermometry has been mostly
4 84 applied for paleoclimatic reconstructions of fossil carbonates, with more recent application to
5 85 reconstruct mild diagenetic conditions (ie., below 100°C) as for example by reconstructing
6 86 paleotemperatures and fluid chemistries associated with cements and fractures (e.g., Bristow
7 87 et al., 2011; Huntington et al., 2011; Budd et al., 2013; Loyd et al., 2013; Mangenot et al.,
8 88 2018 and 2017; Pagel et al., 2018), faults (Swanson et al., 2012; Bergman et al., 2013; Fay-
9 89 Gomor et al., 2018), and concretions (Loyd et al., 2012; Dale et al., 2014) or identifying
10 90 cryptic recrystallization of carbonate fossils (Bennett et al., 2018). However, when carbonates
11 91 experience high temperatures, the initial abundance of $^{13}\text{C}^{18}\text{O}^{16}\text{O}_2$ groups (and thus the Δ_{47}
12 92 value acquired at the time of precipitation) might change due to diffusional reordering of
13 93 isotopes within the carbonate lattice. This process can happen on both the prograde and
14 94 retrograde paths during a geological heating event (e.g., Passey and Henkes, 2012), and
15 95 without any dissolution/recrystallization of the carbonate phase or imparting noticeable
16 96 changes to bulk isotopic compositions ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$), elemental concentrations, or mineral
17 97 textures. This has been first highlighted in metamorphic marbles that generally show apparent
18 98 equilibrium temperatures of about ~150-200°C for calcites (Ghosh et al., 2006; Bonifacie et
19 99 al., 2013) despite peak metamorphic temperatures far above 500°C. This apparent
20 100 temperature for marbles is thought to represent the “blocking” temperature with respect to
21 101 diffusional resetting of the carbonate clumped isotope thermometer – that is the temperature
22 102 at which the isotopes stop exchanging by solid state diffusion during gradual cooling (e.g.,
23 103 Passey and Henkes, 2012; Bonifacie et al., 2013). Later studies allowed to determine that for
24 104 calcites exposed to temperatures in excess of 75–100°C over hundreds of millions of years
25 105 this process can affect the Δ_{47} composition such as it wholly or partially reflects the
26 106 temperature experienced by the ambient rocks (Passey and Henkes 2012; Stolper and Eiler,
27 107 2015). Those experimental and theoretical studies also allowed to build a kinetic framework
28 108 describing the rates of solid state reordering during heating and cooling. Overall, this
29 109 phenomenon provides a way to use Δ_{47} as a geospeedometer and to reconstruct heating and
30 110 cooling path conditions (e.g., Bristow et al., 2011; Passey and Henkes, 2012 ; Bonifacie et al.,
31 111 2013 ; Henkes et al., 2014 ; Stolper and Eiler, 2015). Here, we exploit this kinetic behavior of
32 112 Δ_{47} as an emerging archive of basin thermal histories, as recently done for thermal history
33 113 evaluation of natural carbonates (Shenton et al. 2015 and Lawson et al., 2017). In this work,
34 114 we couple for the first time this kinetic behavior of Δ_{47} clumped isotopes thermometry with
35 115 clay mineralogy thermometry, and previously published vitrinite reflectance data, in order to
36 116 refine the current knowledge on the burial and exhumation evolution of an Upper Cretaceous
37 117 limestone unit cropping out in the subalpine chains of the western French Alps (Bauges and
38 118 Bornes massifs).

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120 GEOLOGICAL SETTING

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122 The northern subalpine chains of France, is a fold-dominated thrust belt consisting of
123 Mesozoic and Cenozoic sedimentary strata located between the Molasse foreland Basin to the
124 northwest and the External Crystalline Massifs (ECM) to the southeast (e.g., Bellahsen et al.,
125 2014, Fig. 1). The northern subalpine chains (Bauges and Bornes massifs) are structurally

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3 126 beneath the Prealps (Chablais nappe), which were emplaced by the Helvetic thrust that has
4 127 since been eroded, leaving Sulens and Annes klippen, as remnants of the Prealps nappes on
5 128 the Bauges and Bornes massifs (Fig. 1). These thrust sheets are made of various Mesozoic
6 129 and Cenozoic strata derived from the more internal domains of the Alps compared to the
7 130 ECM. The maximal geographical extent and the thicknesses of these thrusting units are
8 131 poorly defined because they were mainly eroded during Plio-Pleistocene times. Since the
9 132 1970's, several paleothermal proxies have been investigated to estimate the thermal,
10 133 diagenetic and structural histories of these chains, and to attempt to predict the thickness of
11 134 the tectonic belts emplaced onto the subalpine chains during the final stages of the alpine
12 135 compression. The pioneering works of Kübler et al. (1974) and Sawatzki (1975) revealed an
13 136 increasing low-grade metamorphism from the northern subalpine massifs in Haute-Savoie
14 137 towards the Swiss Alps in the Northeast. Then, Deconinck & Debrabant (1985) highlighted
15 138 important diagenetic transformations of clay mineral assemblages in Upper Cretaceous
16 139 carbonate deposits ("sublithographic limestones"), expressed by a systematic increase of illite
17 140 and chlorite at the expense of smectite in the more internal domain of the northern subalpine
18 141 chains. They interpreted the mineralogical evolution as the expression of the tectonic overload
19 142 (prealpine nappes) in the eastern part of the subalpine basin. Consistently, more recent data on
20 143 vitrinite reflectance revealed an increase of organic matter thermal maturation in the
21 144 northeastern part of the subalpine chains (Gorin & Monteil, 1990, Butler, 1991; Moss, 1992).
22 145 Such a combination of independent thermal indicators indicates that the northeastern part of
23 146 the chain suffered higher temperatures, due to the greater tectonic loads exerted onto the
24 147 subalpine chains. Thermal data and modeling results suggest that the eastern Bornes and
25 148 Bauges massifs have experienced a burial depth up to 5 km greater than their western areas
26 149 (Moss, 1992). Butler (1991) estimated maximal temperatures induced by this tectonic load
27 150 around 180°C in the eastern domain and 60-70°C in the western domain.
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152 MATERIAL AND METHODS:

153 Field samples collection

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155 This study focuses on a Late Cretaceous calcareous unit called the "sublithographic
156 limestones" ranging in age from the Turonian to the Campanian (Villard, 1991). The major
157 rock-forming constituents are micrite particles, calcareous ooze, and allochems fragments,
158 including planktonic and benthonic foraminifera and calcispheres (coccolithes fragments).
159 These limestones were chosen for the two following reasons: (1) the "sublithographic
160 limestones" consist of a fine grained and homogeneous micritic formation containing small
161 amounts of clay minerals (<5%), allowing for clay diagenesis and Δ_{47} composition to be
162 measured conjointly on the same samples, and (2) it is a well exposed unit across the fold and
163 thrust belt this allowing for collecting samples through a large range of low-grade
164 metamorphism domains. The "sublithographic limestones" are generally well-exposed to the
165 heart of the synclines of the Bauges and Bornes massifs. They superimpose condensed
166 horizons of glauconite and phosphate bearing green sandstones of Aptian/Albian age
167 (Delamette et al., 1997) and are unconformably overlain by Cenozoic deposits (Fig. 2). A
168 total of 110 samples were collected from 18 sites (Fig. 1) for XRD analyses, from which 8

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3 169 representative samples were targeted for petrophysical measurements and Δ_{47} thermometry
4 170 analyses.

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6 172 **X-ray diffraction analyses**

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8 174 Clay mineral assemblages were identified by XRD on oriented mounts of non-
9 175 calcareous clay sized particles ($<2\mu\text{m}$) following the procedure described by [Moore &](#)
10 176 [Reynolds \(1997\)](#). The XRD apparatus is composed of a Bruker D4 Endeavor diffractometer
11 177 with $\text{CuK}\alpha$ radiations with a Lynx-eye detector, Ni filter, and under 40kV voltage and 25 mA
12 178 intensity. Three preparations were analyzed for each sample: (1) a first after air-drying (AD),
13 179 (2) a second after ethylene-glycol (EG) solvation and (3) a third after heating at 490°C for 2h.
14 180 The goniometer scanned from 2.5° to 28.5° for each run. Identification and semi-quantitative
15 181 estimates of clay minerals were made according to the position of the (001) basal reflection
16 182 on the three XRD (AD, EG and heated). The quantification of smectite and illite layers (%S
17 183 and % I respectively) in illite-smectite mixed-layers minerals (I-S) is estimated on oriented
18 184 clay sized particles following two different methods: (1) the first one is based on the
19 185 measurement of the position of I-S (001/002) and (002/003) reflections ([Środoń, 1980](#)) before
20 186 and after glycolation. The second one is found on the morphology of I-S (001) reflection peak
21 187 ([Inoue et al., 1989](#)) after glycolation. Besides, semi-quantitative XRD bulk rock and insoluble
22 188 residue analyses were performed on few representative samples.

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24 190 **Scanning Electron Microscopy (SEM) and petrophysical properties**

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26 192 To ensure the homogeneity of the petrographic characteristics of all the samples studied, we
27 193 made SEM characterization of micrite microtexture on fresh surfaces, without acid attack, and
28 194 after gold plating, and we measured the petrophysical properties (porosity and permeability)
29 195 from plugs obtained from the same samples. Water porosimetry was performed to quantify
30 196 total porosity (connected porosity) using Archimedes method ([Richard et al., 2007](#), [Cavailles](#)
31 197 [et al., 2013](#)). Plugs were first dried in an oven at 60°C until they reached a stable mass (m_d)
32 198 and then put upright in an airtight enclosure for 24 hours. at room temperature under vacuum
33 199 at 2.6 Pa. They were progressively imbibed from their base with degassed deionized water,
34 200 under a dynamic vacuum. The total porosity ϕ (%) is given by: $\phi = [(m_1 - m_d) / (m_1 - m_2)] \times$
35 201 100, where m_1 is the mass of the sample saturated with water and m_2 is the mass of the
36 202 sample saturated with water weighed under water (hydrostatic underwater weighing).
37 203 Permeability measurements (K) were performed on the same plugs with a gas permeameter
38 204 equipped with a Hassler cell using nitrogen and the steady state flow method. They were
39 205 made under an effective pressure of 0.1 MPa and then corrected for the Klinkenberg effect
40 206 using a graphical method ([Zinsner & Pellerin, 2007](#); [Cavailles et al., 2013](#)). They are given
41 207 here in millidarcy (mD).

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43 209 **$\delta^{13}\text{C}$, $\delta^{18}\text{O}$, Δ_{47} measurements**

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3 211 Eight samples have been analyzed for their stable isotope composition. These samples
4 212 have been chosen as representative of each of the three studied areas (domain A, B and C of
5 213 figure 1), based on petrographic observations and clay mineralogy data that were acquired
6 214 prior to stable isotope measurements. The required amount of carbonate for replicate Δ_{47}
7 215 measurements of the same sample (between 2 and 4 replicate analyses here; i.e., ~ 20 mg)
8 216 was collected with a dental drill on the same plugs used for petrophysical measurements and
9 217 SEM characterization. Measurements of Δ_{47} composition of carbonate samples were
10 218 performed at Institut de Physique du Globe de Paris (IPGP, Stable Isotopes Team) using a
11 219 Thermo Scientific MAT 253 gas-source mass spectrometer. Carbon, oxygen and clumped
12 220 isotopes data were simultaneously acquired on gaseous CO_2 released after reaction of ~ 5 mg
13 221 of carbonate powder in 104% phosphoric acid at 90°C (20 min in a common acid bath). The
14 222 methods used for carbonate digestion, CO_2 purification, mass spectrometric measurements
15 223 and data correction and standardization follow the procedure detailed by [Bonifacie et al.](#)
16 224 ([2017](#)) and [Katz et al. \(2017\)](#), and includes two kinds of standards : i) gaseous CO_2
17 225 equilibrated at 25 and 1000°C and ii) homogenous carbonate powders (with a 1:1 ratio for
18 226 unknown samples/standards).

19 227 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of the carbonate samples are expressed in per mil with respect to the
20 228 VPDB standard. To guarantee the accuracy of the Δ_{47} data, we routinely analyzed two
21 229 carbonate reference materials (IPGP-Carrara marble and 102-GCAZ01b, also reported by
22 230 Dennis et al., 2011 and many other studies). The Δ_{47} values obtained for these carbonate
23 231 standards over the course of this study (July 2014–May 2016) are: $\Delta_{47} = 0.412 \pm 0.016\text{‰}$
24 232 (1SD, n = 28) for IPGP-Carrara marble; $\Delta_{47} = 0.721 \pm 0.020\text{‰}$ (1SD, n = 21) for 102-GC-
25 233 AZ01b. Finally, the corrected Δ_{47} values were converted into temperatures using the
26 234 composite Δ_{47} -T calibration determined for all carbonate minerals for the 0–300°C
27 235 temperature range (i.e., Eq. (3) from [Bonifacie et al., 2017](#) that compiles 103 mean Δ_{47} data
28 236 from seven different laboratories and with proper error propagation, which is $\Delta_{47} = 0.0422 * 10^6 / T + 0.2182$ in the 25 °C acid digestion frame).

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30 238 **Parameterization of the kinetic models**

31 239 Extracting thermal history information from kinetic paleothermometers is best treated
32 240 with a forward approach, meaning that from quantitative observations in a given sample, such
33 241 as a clumped isotope temperature or a vitrinite reflectance, we select preferred time-
34 242 temperature history that would best reproduce all the measured paleothermometric data.
35 243 These relationships can be simulated through a mathematical (forward) model representing
36 244 the time-temperature dependence of the employed paleothermometric technique over
37 245 geological time. This approach gains a particular interest when different paleothermometers
38 246 are simultaneously employed, because each method acts with its own kinetic response to the
39 247 inferred thermal history.

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41 249 In this study, two distinct prograde thermal history paths, previously proposed by
42 250 [Butler, \(1991\)](#) were used as an initial scenario to drive the different kinetic models.
43 251 Furthermore, in order to consider mid-temperature scenarios, we also integrated five

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3 252 additional time-temperature paths by adjusting the maximal burial temperature from 80 to
4 253 180°C. We computed the expected changes in vitrinite composition, Δ_{47} temperatures and %
5 254 illite in I-S with time and temperature, for comparison with the measured values. Three
6 255 empirical kinetic models were used with sequential time-temperature steps of 1Ma: (1)
7 256 Vitrinite maturation was predicted by the Easy% Ro kinetic model of [Sweeney & Burnham,](#)
8 257 [1990](#); (2) The extent of solid-state C-O bond reordering over time was simulated using the Δ_{47}
9 258 kinetic model of [Henkes et al. \(2013\)](#) (see [Shenton et al. 2015](#) for an application); and (3) the
10 259 extent of smectite to illite conversion in I-S was calculated following the kinetic model of
11 260 [Huang et al., 1993](#).
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14 262 The convergence criteria between measured data *versus* model predictions were
15 263 iteratively defined to minimize: (1) the discrepancy between the whole dataset obtained by the
16 264 mean of three independent paleothermometers (%illite in I-S, Ro% and $T\Delta_{47}$), and (2) the gap
17 265 between the measured data for each paleothermometer and the values computed
18 266 mathematically for each proxy (%illite in I-S, Ro% and $T\Delta_{47}$), given the different time-
19 267 temperature paths to evaluate. A good match between data and models was observed by
20 268 considering typical errors of $\pm 0.1\%$ for Ro%, $\pm 10\text{-}15^\circ\text{C}$ for $T\Delta_{47}$ and $\pm 10\%$ for %illite in I-S.
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23 270 **RESULTS**

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25 272 The semi-quantitative XRD bulk rock analyses showed that the studied limestone unit
26 273 is mostly composed by calcite (>95%) with a minor proportion of clay minerals (<5%)
27 274 including glauconite in some samples. XRD analyses on HCl-insoluble fraction revealed trace
28 275 concentration of quartz, opal CT and K-feldspars. Table 1 shows the results of the
29 276 mineralogical, petrographic, petrophysical and geochemical analyses of the clay and
30 277 carbonate components from the investigated limestone unit.
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33 279 **Clay mineralogy**

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35 281 Clay mineralogyl results are presented in figure 2, where the relative proportions of
36 282 the different minerals identified in the samples from the eighteen sampled sections are
37 283 reported. From top to base are presented the results from sections located respectively in the
38 284 external and internal domains (A, B, C) of the Bauges and Bornes massifs. In the studied area,
39 285 clay minerals include illite, illite/smectite mixed-layers (I-S), chlorite, chlorite/smectite
40 286 mixed-layers (C-S) and some kaolinite. Small quantities of quartz occur in the clay fraction of
41 287 all samples. Three types of clay mineral assemblages are distinguished, depending on the
42 288 geographical location of the samples (c.f. A, B and C domains). The first type (Sections A1
43 289 to A8) refers to clay mineral assemblages largely dominated by illite/smectite mixed-layers
44 290 expanding to 17 Å after glycolation and therefore corresponding to I-S R0 ordering scheme
45 291 (Fig. 3). They are associated with illite and occasionally with small amounts of C-S and
46 292 kaolinite. The second type of clay mineral assemblages (Sections B9 to B13) is characterized
47 293 by higher percentages of illite, a decreasing proportion of I-S, and the systematic occurrence
48 294 of chlorite and C-S. In samples from the B domain, the proportion of illitic sheets in I-S
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295 increases, and these I-S now mostly correspond to R1 ordering scheme. The last type
 296 (Sections C14 to C18) shows higher proportions of chlorite and illite, a lower amount of I-S
 297 with more than 90% illite layers, now corresponding to R3 ordering scheme (Fig. 3).

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299 **Micro-textural and petrophysical properties of the carbonate fraction**

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301 SEM characterization of micrites microtexture revealed very comparable and
 302 homogeneous properties among all samples (Fig. 5). The micritic particles are essentially
 303 anhedral, compact, with fully coalescent, though distinct, contacts (Deville de Periere et al.,
 304 2011, Régnét et al 2014). A relevant crystallography parameter, defined as the median of the
 305 maximum 2D particle lengths measured on SEM photomicrographs, varies between 1.30 and
 306 1.45 μm , and corresponds to fine micrites granulometry (0.5-2 μm). Porosity and permeability
 307 measurements out of 58 samples exhibit very homogeneous values; i.e. porosity between
 308 0.40% and 1.36% and permeability lower than 0.0001mD. No significant geographic
 309 variation was detected, both in term of petrographic texture and petrophysical properties
 310 (Table 1). These results suggest that the carbonate fraction from the investigated sections is
 311 not composed by differently sourced particles mixed together and did not experience
 312 distinctive recrystallization events.

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314 **Stable isotope composition of micrites ($\delta^{18}\text{O}_{\text{carb}}/\delta^{13}\text{C}_{\text{carb}}/\Delta_{47}$)**

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316 The stable isotopes data ($\delta^{18}\text{O}_{\text{carb}}/\delta^{13}\text{C}_{\text{carb}}/\Delta_{47}$) acquired on eight samples collected in
 317 the three different geographical domains (A, B and C) are reported in Table 1 and illustrated
 318 with different colors in the cross plots of Figure 5. Despite the fact that the samples were
 319 collected in different localities tens of kilometers apart, they all exhibit small ranges of
 320 variations in $\delta^{18}\text{O}_{\text{carb}}$ (between -3.15‰ and -3.89‰; n=8 samples) and $\delta^{13}\text{C}_{\text{carb}}$ (from 1.6‰ to
 321 2.90 ‰; n=7 – sample A1 is offset with a $\delta^{13}\text{C}_{\text{carb}} = 0.04‰$). This small range of variation
 322 likely reflects the fact that all samples precipitated (or recrystallized) in comparable
 323 environmental conditions (i.e., temperature, oxygen isotope composition of the parent fluid,
 324 water to rock ratios).

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326 The Δ_{47} values of the samples investigated here are varying between 0.634‰ and
 327 0.400‰. The external reproducibility out of 2 to 4 replicate analyses of the same micrite
 328 powder ranges between $\pm 0.010‰$ and $\pm 0.049‰$ (± 1 S.D., with one offset for sample B12
 329 $\pm 0.076‰$; Table 1). This is larger than the external reproducibility obtained in this study on
 330 homogeneous standards ($\pm 0.018‰$, n=49) and likely reflects the relative isotopic
 331 heterogeneity of the micrite samples investigated here (compared to homogeneous standards).
 332 In contrast with the regional-scale homogeneity on $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ compositions of the
 333 micrites from all investigated geographical domains, Δ_{47} values from carbonate samples from
 334 the C domain are significantly different from the two other domains. The Δ_{47} values of the C
 335 domain are averaging at $0.421 \pm 0.015‰$ (n=4 samples and 11 analyses in total), which is
 336 within the uncertainties on the Δ_{47} values found for calcite marbles (Bonifacie et al., 2013; see
 337 for example Carrara marble analyzed as a standard in this study with $\Delta_{47} = 0.412 \pm 0.016‰$,

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3 338 1SD, n = 28 analyses). On the other hand, the Δ_{47} values found for domain A and B are
4 339 indistinguishable from each other (respectively of $0.615 \pm 0.025\text{‰}$ and $0.623 \pm 0.015\text{‰}$, n=2
5 340 samples for each domain, 11 analyses in total). Given the fact that the four samples collected
6 341 from the A and B domains display $\delta^{18}\text{O}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{carb}}$ and Δ_{47} values that are all
7 342 indistinguishable when respective uncertainties are considered, their stable isotope
8 343 compositions are averaged in the following discussion. The Δ_{47} values are distributed in two
9 344 clusters with corresponding temperatures averaging at $183 \pm 17^\circ\text{C}$ for the C domain and
10 345 $51 \pm 8^\circ\text{C}$ for the A and B domains (Table 1).
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14 347 Table 1 also presents the oxygen isotopic compositions of the water ($\delta^{18}\text{O}_{\text{water}}$) in
15 348 equilibrium with the carbonate that can be calculated using both the $T\Delta_{47}$ and the $\delta^{18}\text{O}_{\text{carb}}$
16 349 values measured as well as the oxygen isotope fractionation between calcite and water from
17 350 [Watkins et al. \(2013\)](#). For samples of the A and B domains, the calculated $\delta^{18}\text{O}_{\text{water}}$ are
18 351 averaging at $1.7 \pm 1.2\text{‰}$ (1 S.D.; n=4), i.e., enriched in ^{18}O compared to expected Late
19 352 Cretaceous seawater ($\delta^{18}\text{O}_{\text{water}} \sim -1\text{‰}$; [Jenkyns et al. 1994](#)). Contrastingly, for the C domain,
20 353 the calculated oxygen isotope composition of the fluid in equilibrium with the micrite samples
21 354 are way more enriched in ^{18}O , with $\delta^{18}\text{O}_{\text{water}}$ averaging at $17 \pm 1\text{‰}$ (1 S.D.; n=4) – that is hard
22 355 to reconcile with known $\delta^{18}\text{O}_{\text{water}}$ of crustal fluids in carbonate settings (e.g., [Karhaka et al.](#)
23 356 [2003](#)). [It is noteworthy that [Dassié et al. \(2018\)](#) recently showed that $\delta^{18}\text{O}_{\text{water}}$ values directly
24 357 measured in fluid inclusions from diagenetic cements and the $\delta^{18}\text{O}_{\text{water}}$ independently
25 358 calculated from the Δ_{47} and $\delta^{18}\text{O}_{\text{carb}}$ data, within the same cements, agree within 1‰. These
26 359 findings demonstrate the viability of coupling Δ_{47} and $\delta^{18}\text{O}_{\text{carb}}$ for determining the $\delta^{18}\text{O}_{\text{water}}$ of
27 360 the mineralizing fluid, at least in absence of solid-state diffusion].
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34 362 **Organic matter maturity**

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37 365 The “sublithographic limestones” do not contain organic matter. However, thermal
38 366 maturity data of organic matter bearing rocks from several locations and different
39 367 stratigraphic intervals of the northern subalpine chains have been previously published. These
40 368 data come either from vitrinite reflectance (Ro%) measurements ([Kübler et al. 1974](#); [Kisch,](#)
41 369 [1980](#); [Gorin & Monteil, 1990](#); [Moss 1992](#); [Schegg, 1992a,b](#); [Deville & Sassi, 2006](#)) or from
42 370 Rock-Eval pyrolysis analyses ([Gorin et al. 1989](#); [Gorin & Monteil; 1990](#)). Here we have
43 371 chosen to integrate and discuss only the dataset of [Gorin & Monteil, \(1990\)](#), because organic
44 372 matter analyses were completed on the Maastrichtian Wang formation ([Stacher, 1980](#); [Villard](#)
45 373 [1988](#)) which directly overlies the “sublithographic limestones” (Fig. 2). [These authors](#) showed
46 374 that in the northern subalpine massif, the Maastrichtian Wang formation has reached a wide
47 375 range of maturities (Table 1). Vitrinite reflectance Ro ranges from $0.45 \pm 0.05\%$ to $0.55 \pm$
48 376 0.05% in the area covered by the A domain (corresponding to A1 and A6 samples of this
49 377 study), is equal to $0.7 \pm 0.1\%$ in the B domain (B9 sample of this study) and increases up to
50 378 $1.3 \pm 0.2\%$ in the C domain (C16 and C17 samples of this study). Rock-Eval 2 pyrolysis data
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3 379 eastern domain C ($T_{\max} > 460^{\circ}\text{C}$), whereas OM remains immature ($T_{\max} < 430^{\circ}\text{C}$) in the western
4 380 domain A and B of the subalpine massifs (Gorin & Monteil, 1990).
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6 382 **DISCUSSION**

7 383 8 384 **Thermal evaluation recorded by clay minerals and organic matter**

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10 386 In the western part of the studied Bauges and Bornes massifs (domain A of figure 1), the clay
11 387 assemblages of the Upper Cretaceous “sublithographic limestones” are largely dominated by
12 388 I-S of R0 type. The frequent occurrence of these minerals, also found in the underlying Lower
13 389 Cretaceous formations, indicates that the thermal influences are very weak (Deconinck et al.,
14 390 1985). Indeed, smectite illitization processes are known to take place when temperatures
15 391 reach about $60\text{--}70^{\circ}\text{C}$ (Środoń & Clauer, 2001; Środoń et al., 2009; Thyberg et al., 2010),
16 392 though these values also depend on lithology and were mainly apply to argillaceous rocks and
17 393 volcanic ashes layers (Šucha et al., 1993). Therefore, the clay mineralogy suggests that the
18 394 westernmost domain A did not undergo temperatures above 70°C . Since the influence of
19 395 thermal diagenesis is negligible in the western part of the subalpine massifs, clay mineral
20 396 sedimentation was possibly dominated by I-S R0 which can be assimilated to smectites. This
21 397 result is in line with findings from Upper Cretaceous deposits from numerous sedimentary
22 398 basins, where smectites dominate the sedimentation record (Jeans et al., 2001; Deconinck et
23 399 al., 2005; Chenot et al., 2018). The negligible influence of thermal diagenesis highlighted by
24 400 clay assemblages in the western part of the study area, is in agreement with the low T_{\max}
25 401 values ($T_{\max} \leq 430^{\circ}\text{C}$; Gorin & Monteil, 1990) and with the vitrinite reflectance values (0.45%
26 402 to 0.55%) pointing at an immature organic matter. Conclusively, all the available paleo-
27 403 thermicity proxies suggest that the western part (A domain) of the subalpine massifs (Bauges
28 404 and Bornes) did not experience burial temperature above $70\text{--}80^{\circ}\text{C}$ (Fig. 7).
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37 406 In the eastern part (C domain) of the studied subalpine massifs, the clay mineral
38 407 assemblages are dominated by chlorite, illite and I-S R3 containing a small proportion
39 408 (mostly below 10%) of smectite sheets. This type of assemblage results from the illitization of
40 409 I-S R0 through smectite dissolution/precipitation processes (Nadeau et al., 1985) and from the
41 410 transformation of these smectitic minerals into chlorite. The C-S present in the eastern
42 411 sections are likely the intermediates of smectite to chlorite transformations. The difference in
43 412 the composition of clay assemblages between the western and the eastern part of the subalpine
44 413 massifs was already noticed and interpreted as due to tectonic overload triggered by the
45 414 prealpine nappes (Deconinck & Debrabant, 1985). New data provided in this study suggest
46 415 that samples from the C domain likely experienced maximum temperatures up to 140°C ,
47 416 confirming that thermal diagenesis was responsible for the illitization and chloritization of I-S
48 417 R0 (Fig. 7), the increase of vitrinite reflectance (up to 1.3%) and of Rock-Eval T_{\max}
49 418 ($T_{\max} > 460^{\circ}\text{C}$) in these localities. The relationship observed in the studied area between the
50 419 Rock-Eval T_{\max} and the illite content in illite-smectite (I-S) mixed layers agrees with the one
51 420 observed by Dellisanti et al. (2010) in similar syn-orogenic successions from the Northern
52 421 Apennines (Italy). These results are also concordant with the maximum burial temperature of
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3 422 180°C estimated in the studied area by [Butler, \(1991\)](#).

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5 423 Samples from the B domain show an intermediate clay mineral assemblage with the
6 424 occurrence of I-S R1 and incipient chloritization of I-S R0, associated with values of vitrinite
7 425 reflectance (~0.7%) and T_{max} (~437°C) pointing at moderate maturity . Altogether, clay
8 426 minerals and organic maturity data indicate that the B domain experienced a moderate
9 427 thermal influence compared to the external and internal domains (A and C, respectively).
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11 429 **Effects of lithology on clay mineral diagenesis**

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13 431 Although the investigated lithology consists of a micritic limestone with a $CaCO_3$
14 432 content of up to 95%, and potassium deficiency, the illitization processes described in this
15 433 study are comparable to those described in argillaceous rocks or ashes layers, confirming that
16 434 temperature is the dominant controlling factor at regional scale ([Środoń & Clauer, 2001](#)).
17 435 However, in the B and C domains, chloritization processes are progressively increasing from
18 436 West to East where and the chlorite proportion reaches 50% of the clay fraction. Such chlorite
19 437 proportions cannot be explained by depositional heterogeneities linked to detrital input.
20 438 Indeed, the hot and hydrolyzing climates dominating the Late Cretaceous time did not allow
21 439 chlorite preservation. Furthermore, in the absence of diagenetic transformations, the chlorite
22 440 proportions are always very low in Upper Cretaceous sediments ([Jeans et al., 2001](#);
23 441 [Deconinck et al., 2005](#)). The chloritization processes in the studied carbonate succession were
24 442 probably favored by the magnesium release from the transformation of High-Magnesium
25 443 Calcite (HMC) into Low-Magnesium Calcite (LMC) during diagenesis. This process is
26 444 particularly evident in marl-limestone alternations of the subalpine ranges where I-S R0
27 445 evolved into illites within the marls and into chlorites within the limestones (*e.g.* [Deconinck
28 446 & Chamley, 1983](#), [Ferry et al., 1983](#); [Deconinck & Debrabant, 1985](#); [Levert & Ferry, 1988](#)).
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30 448 **Interpretation of stable isotope data of micrites**

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32 450 In the studied sublithographic limestones, the micrite samples record contrasting Δ_{47}
33 451 temperatures clustered in two distinct groups, depending on their geographic locations. The
34 452 micrites from the A and B domains have $T\Delta_{47}$ clustered at $51\pm 8^\circ C$ (n=4 samples) which
35 453 sharply contrast with the micrites from the more internal C domain, displaying $T\Delta_{47}$ clustered
36 454 at $183\pm 17^\circ C$ (n=4 samples). Given the fact that all the investigated micritic calcites from all
37 455 domains show very similar micro-texture, petrophysical properties, as well as $\delta^{13}C$ and
38 456 $\delta^{18}O_{carb}$ isotopic compositions (Fig.4, 5 and Table 1), it is unlikely that this sharp difference in
39 457 $T\Delta_{47}$ values could result from different recrystallization events. We suggest that the high
40 458 temperatures recorded in samples of the eastern C domain result from ^{13}C - ^{18}O bonds re-
41 459 equilibration via solid-state diffusion at temperatures higher than the blocking temperature.
42 460 Such hypothesis also finds support in the fact that: (1) the calculated $\delta^{18}O_{water}$ of about 19‰
43 461 for micrites of the C domain are too high to be reconciled with the most common $\delta^{18}O_{water}$ of
44 462 diagenetic fluids in sedimentary basins ([Karhaka et al. 2003](#)); (2) clay mineral and vitrinite
45 463 reflectance data indicate a maximal burial temperature up to 160-180°C for this area.
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3 464 Following the kinetic model of [Henkes et al. 2013](#), such temperature conditions can lead to a
4 465 fully-re-equilibration of Δ_{47} compositions.

6 466 It is noticeable that the observed $\delta^{18}\text{O}_{\text{carb}}$ composition of micrites are slightly depleted in ^{18}O
7 467 compared to carbonates precipitated in equilibrium with Late Cretaceous shallow seawater
8 468 (see light grey box in Figure 5; [Veizer et al. 1999](#)). However, the micrite oxygen and carbon
9 469 isotopic compositions are comparable to those observed in analogue deep-chalk sediments
11 470 with similar facies (e.g. $\delta^{18}\text{O}_{\text{carb}}$ between -1.5 and -3‰ for Upper Cretaceous chalk deposits
12 471 from different areas; [Jenkyns et al. 1994](#) and [Schiinfeld et al. 1991](#); black box in Figure 5).
13 472 This suggests that all the micrites from this study likely recrystallized at higher temperatures
14 473 than the original one at depositional site. Such hypothesis finds support in two observations.
15 474 First, the limestone units, initially composed of calcareous ooze with planktonic foraminifera
16 475 and coccoliths fragments, now exhibit numerous petrographic hints of recrystallization (i.e.
17 476 particle shapes, type of contact between grains and crystallometry parameters). Second, the
18 477 measured $T\Delta_{47}$ show higher temperatures than coeval shallow seawater (i.e., 20-26°C
19 478 following [Jenkyns et al. 1994](#)). Noticeably, the $T\Delta_{47}$ of micrite samples from the external
20 479 domains (A and B), not affected by Δ_{47} resetting, point toward a recrystallization event
21 480 occurring during shallow burial, at temperatures close to 50°C and by fluids with $\delta^{18}\text{O}_{\text{water}}$
22 481 values of $+1.7\pm 1.2\text{‰}$. Such recrystallization event may correspond to the transformation of
23 482 the metastable High-Magnesium Calcite (HMC) into Low-Magnesium Calcite (LMC) of the
24 483 micritic sediment ([Schlager & James, 1978](#)).

25 484 Overall, the micrite samples investigated here exhibit apparent $T\Delta_{47}$ values that are
26 485 expected to be an integration of: (1) temperature, timing, and extent of the shallow burial
27 486 recrystallization occurring for all geographic domains (A, B and C) and (2) an additional
28 487 overprint by solid-state C-O bond reordering only in samples from the C domain, which was
29 488 function of the thermal history and of specific C-O bond reordering kinetics of Δ_{47}
30 489 compositions.

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32 491 **Forward thermal modeling approach (Δ_{47} , Ro% and %I in I-S mixed layer)**

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34 493 Guided by the paleothermometric results acquired on three samples representative of
35 494 the three geographic domains investigated in this study, we employed a forward modeling
36 495 approach to find the best thermal scenario to reconcile all the obtained Δ_{47} , vitrinite
37 496 reflectance and clay mineral data. This approach is devoted to refine the burial and
38 497 exhumation history of the sampled areas. The model results are shown in Figure 7 where
39 498 seven different time-temperature scenarios, with varying maximal burial temperature (MBT)
40 499 are considered. These scenarios are: (1) pre-thrusting burial (88-65Ma); (2) Eocene inversion
41 500 (65Ma-45Ma); (3) main emplacement of thrust units and associated heat increase (40Ma to
42 501 8Ma); and (4) erosion (8Ma-present).

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44 503 First of all, the results of the forward models for each paleothermometric proxy,
45 504 demonstrate that model predictions and data may converge for a set of thermal histories (TH)

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3 505 with maximal burial temperature (MBT) ranging from 60°C to 180°C. More specifically,
4 506 given the measured $R_o\%$, Δ_{47} and % illite in I-S mixed layer for the three selected samples
5 507 (c.f. A1, B9 and C16 samples), the forward modeling results predict that:
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8 509 TH1-TH2 (MBT between 60°C and 80°C) are the most likely scenarios suggested for
9 510 A1 sample (A domain) because these time-temperature paths are the only ones prone to
10 511 generate a substantial agreement between all the available paleothermometric data. As
11 512 discussed previously, sample A1 exhibits a $T\Delta_{47}$ of $61\pm 15^\circ\text{C}$ suggesting a recrystallization
12 513 event under shallow burial temperatures, without any record of the successive solid-state
13 514 diffusion overprint. In this case, Δ_{47} thermometry only preserves a screenshot of punctual
14 515 recrystallization temperature and does not provide important information on the sample
15 516 thermal history. The weak maturity recorded for the A domain by vitrinite reflectance data
16 517 ($R_o\%$: 0.45 ± 0.05) correlated with a low %illite ($:25\pm 4\%$) in I-S mixed-layers, and is also in
17 518 good agreement with TH1-TH2 model prediction, suggesting that A1 sample likely
18 519 experienced maximum burial temperature in the range 60-80°C.
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23 521 Following the same model predictions, it comes out that mid-scenarios TH3- TH4,
24 522 with MBT between 100 and 120°C, are the most susceptible scenarios to conjointly increase
25 523 the illite content in I-S (between 51 to 93 %illite) and vitrinite reflectance (between 0.55 to
26 524 0.67%), without providing sufficient activation energy to initiate Δ_{47} kinetic C-O bond
27 525 reordering. The paleothermometric data available for sample B9 (c.f., $R_o\%$: 0.7 ± 0.1 ; I% in I-
28 526 S: $48\pm 9\%$ and $T\Delta_{47}$: $54\pm 9^\circ\text{C}$) from the B domain agree perfectly with model predictions for
29 527 TH3-TH4. Therefore, sample B9 likely experienced maximal burial temperatures ranging
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31 528 from 100 to 120°C.
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34 530 Finally, sample C16 from the C domain exhibits $T\Delta_{47}$ in excess of 120°C compared to
35 531 samples A1 and B9, a clear increase of vitrinite reflectance values ($R_o\% = 1.3\pm 0.2$) and a
36 532 near total illitization of I-S mixed layer (up to 90% illite). These data clearly indicate a
37 533 significantly higher level of thermal maturity in the C domain. First, Δ_{47} data in sample C16
38 534 have been previously interpreted as reflecting the attainment of Δ_{47} blocking temperatures
39 535 reached during the cooling stage (i.e. from 8Ma to present-day), that followed a complete re-
40 536 equilibration of Δ_{47} compositions at maximal burial temperatures (see Fig.7.B for more
41 537 detail). Δ_{47} kinetic modeling results showed that only TH7 (maximal burial temperature
42 538 $>180^\circ\text{C}$), or hotter scenarios, may provide sufficient activation energy to generate the
43 539 observed complete re-equilibration of Δ_{47} in C16 samples. This finding is a strong argument
44 540 in favor of maximum burial temperatures higher than 180°C in this area. Then, the available
45 541 $R_o\%$ values and the near complete illitization of I-S mixed layer observed in C16 sample,
46 542 also showing a substantial agreement with TH7 modeling predictions, conclusively point
47 543 toward a temperature regime with maximum temperature close to 180°C.
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53 545 Guided by the data-model comparisons presented on three representative samples of
54 546 the studied area, we provide quantitative information on paleotemperatures and, indirectly, on
55 547 sample burial and exhumation histories. In light of these results, it is clear that samples
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3 548 collected from the same stratigraphic interval (Upper Cretaceous “sublithographic
4 549 limestones”), and from closed geographic areas, may have experienced very contrasting
5 550 thermal histories, with maximum burial temperatures varying from 60-80°C in the western
6 551 external domains (A and B), up to 180°C in the internal domain (C) of the studied area. These
7 552 heterogeneities in the paleothermal record may reflect significant changes in overburden,
8 553 induced by the emplacement of thrust-sheet units with variable thickness. Indeed, by
9 554 considering a regional geothermal gradient of 25 ± 5 °C/km for the time encompassing tectonic
10 555 loading and exhumation (Schegg, 1992b), the paleothermometric data suggest that the
11 556 prealpine nappes, presently eroded, were 4-7 km and 1.3-2km thick in the eastern and western
12 557 domains, respectively. These results are consistent with previous estimation of Deville &
13 558 Sassi (2006) who calculated that more than 4-6 km of prealpine nappes was thrust in the
14 559 North-West of the studied area. However, we cannot rule out that the East to West increase in
15 560 paleotemperatures, recorded in this study, may also reflect an heat flow increase without
16 561 significant additional burial. The definition of the precise process causing this temperature
17 562 gradient is beyond the scope of this study and would require in-depth thermokinematic
18 563 modeling to be addressed.

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20 565 CONCLUSIONS

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22 567 The three proxies (i.e. clay diagenesis, organic matter maturity and carbonate clumped
23 568 isotope composition) used to reconstruct the thermal history of an Upper Cretaceous
24 569 limestone unit from the northern subalpine domain (Bauges and Bornes massifs, northern
25 570 French Alps) provided a coherent dataset showing the existence of a prograde diagenetic
26 571 gradient from West to East, notably due to the tectonic emplacement of the prealpine nappes.
27 572 Although the studied sediments correspond to micritic limestones, clay mineral diagenesis is
28 573 expressed, similarly to what is expected for argillaceous rocks, by the progressive illitization
29 574 of smectites. The degree of illitization makes it possible to identify three mineralogical zones
30 575 within the studied massifs: a western zone where sedimentary I-S R0 are preserved,
31 576 suggesting that the burial temperatures never exceeded 70°C; an intermediate zone marked by
32 577 the presence of I-S R1, indicating burial temperatures in the range 100-120 °C; and an eastern
33 578 zone marked by the presence of I-S R3, indicating temperatures in the order of 160 to 180°C.
34 579 Organic matter maturity data (from T_{max} and $Ro\%$) are consistent with the clay mineral
35 580 dataset, pointing at an immature organic matter in the western part of the subalpine massif and
36 581 a prograde increase of T_{max} and $Ro\%$ values toward the East. The low Δ_{47} temperatures
37 582 recorded in micrite samples from the western area of the subalpine massifs are in excess of
38 583 $\sim 20^\circ\text{C}$ of plausible depositional temperatures, suggesting that micrite recrystallized at such
39 584 temperatures. However, in the eastern part of the massifs, four samples collected 30km apart,
40 585 exhibit Δ_{47} temperatures of $\sim 180^\circ\text{C}$ that is a clear evidence of a regional-scale solid-state re-
41 586 ordering process, allowing to apply the newly developed Thermal History Reordering Model
42 587 (THRM; Henkes et al. 2014). Altogether, the paleothermometric data presented in this study,
43 588 combined with the results of forward thermal modeling, allow to propose thermal scenarios
44 589 suggesting that the thickness of the prealpine nappes was between 4 and 7 km and between
45 590 1.3 to 2 km in the inner and outer parts of the subalpine massifs, respectively.

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38 872 FIGURES CAPTIONS

39 873

40 874 **Figure 1.** Geological context of the studied area. A. Simplified structural sketch map of the
41 875 northern subalpine chains (Bornes and Bauges massifs, France, showing the main thrust units.
42 876 B. Detailed elevation map of the area. The different numbers (1 to 18) refer to the location of
43 877 the studied sections, whereas the colors refer to the geographic and tectonic domains they
44 878 belong to: outer A domain (yellow), intermediate B domain (orange) and inner C domain
45 879 (red). C. Simplified stratigraphic succession (Late Jurassic-Paleogene) of the northern
46 880 subalpine massifs, with location of the stratigraphic intervals targeted for paleothermal
47 881 reconstruction. Black star: “sublithographic limestones” investigated for clay mineral
48 882 diagenesis and Δ_{47} thermometry. Red star: Wang formation used to measure organic matter
49 883 maturity by [Gorin & Monteil, \(1990\)](#).

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52 884 **Figure 2.** Relative proportions of clay minerals in each investigated samples collected from
53 885 eighteen sites falling in three structural domains (A, B, C), with respect to their illite content
54 886 in I-S mixed layers. From top to base, are illustrated the results for samples (numbers 1 to 18)
55 887 located from the external A domain toward the internal C domain of the Bauges and Bornes
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massifs. The estimations of illite content in I-S mixed layers are highlighted with black dots when using the methods of [Środoń \(1980; 1984\)](#) and with red dots when using the method of [Inoue et al. \(1989\)](#). Note how samples from a single stratigraphic interval, within in a small geographic area, can be significantly differentiated based on their clay mineral assemblages and illite content in the I-S mixed layers.

Figure 3. Example of X-ray diffraction pattern of I-S (002/003) peak, for the $<2\mu\text{m}$ fraction after glycolation. The results for six representative samples, belonging to the A, B and C domains, are shown.

Table 1. Summary of mineralogical, petrophysical and geochemical data available for the studied area

Figure 4. Petrographic and petrophysical properties of the investigated samples. A. Macrophotography of the Upper Cretaceous sublithographic limestones outcropping in the studied area. B. Scanning electron microscopy (SEM) microphotographs used to characterize micrite microtextures and quantify crystallometry parameter of the investigated samples. Picture are taken at the magnification $\times 10000$. C. Histograms illustrating the variability of the crystallometry parameter measured for the micrite samples, defined by the maximum 2D length of particles measured on SEM photomicrographs at $\times 5000$ magnification. Note that all the investigated samples, belonging to the A, B and C domains, do not display any significant difference in term of microtextures (particles shapes, contact between grains, crystallometry) and petrophysical properties (porosity and permeability).

Figure 5. Micrite stable isotope data. **A.** Cross-plot $\delta^{18}\text{O}_{\text{carb}}$ versus $\delta^{13}\text{C}_{\text{carb}}$ composition of micrite samples from the A, B and C domains. Uncertainties are smaller than the dot size. \square $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ values from unaltered Upper Cretaceous marine shells ([Veizer et al. 1999](#)) are illustrated with grey boxes, whereas those of deep-chalk deposits suffering some amount of alteration are highlighted with a black box ([Jenkyns et al. 1994](#) and [Schiinfeld et al. 1991](#)). **B.** Cross-plot of $\delta^{18}\text{O}_{\text{carb}}$ versus the temperatures calculated from Δ_{47} in the micrite samples from the A, B and C domains. Circled 1 and 2 and associated black arrows refer to trends resulting from recrystallization of calcite at temperatures higher than depositional ones (1) and Δ_{47} thermal resetting (2). The grey box represents $\delta^{18}\text{O}_{\text{carb}}$ composition of unaltered Upper Cretaceous marine shells ([Veizer et al. 1999](#)), combined with coeval shallow seawater temperature from [Jenkyns et al. 1994](#) (ie. between 20 and 26°C). Reported uncertainties on data are 1 S.D. of the replicate analyses for $T\Delta_{47}$, and are smaller than the dot size for $\delta^{18}\text{O}$. **C.** 3D diagram showing the relationship between $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$ and $T\Delta_{47}$ measured in the investigated samples. The solid arrow illustrates the observed trend of Δ_{47} thermal resetting from the A and B domains toward the C domain. Uncertainties are not represented in the 3D diagram.

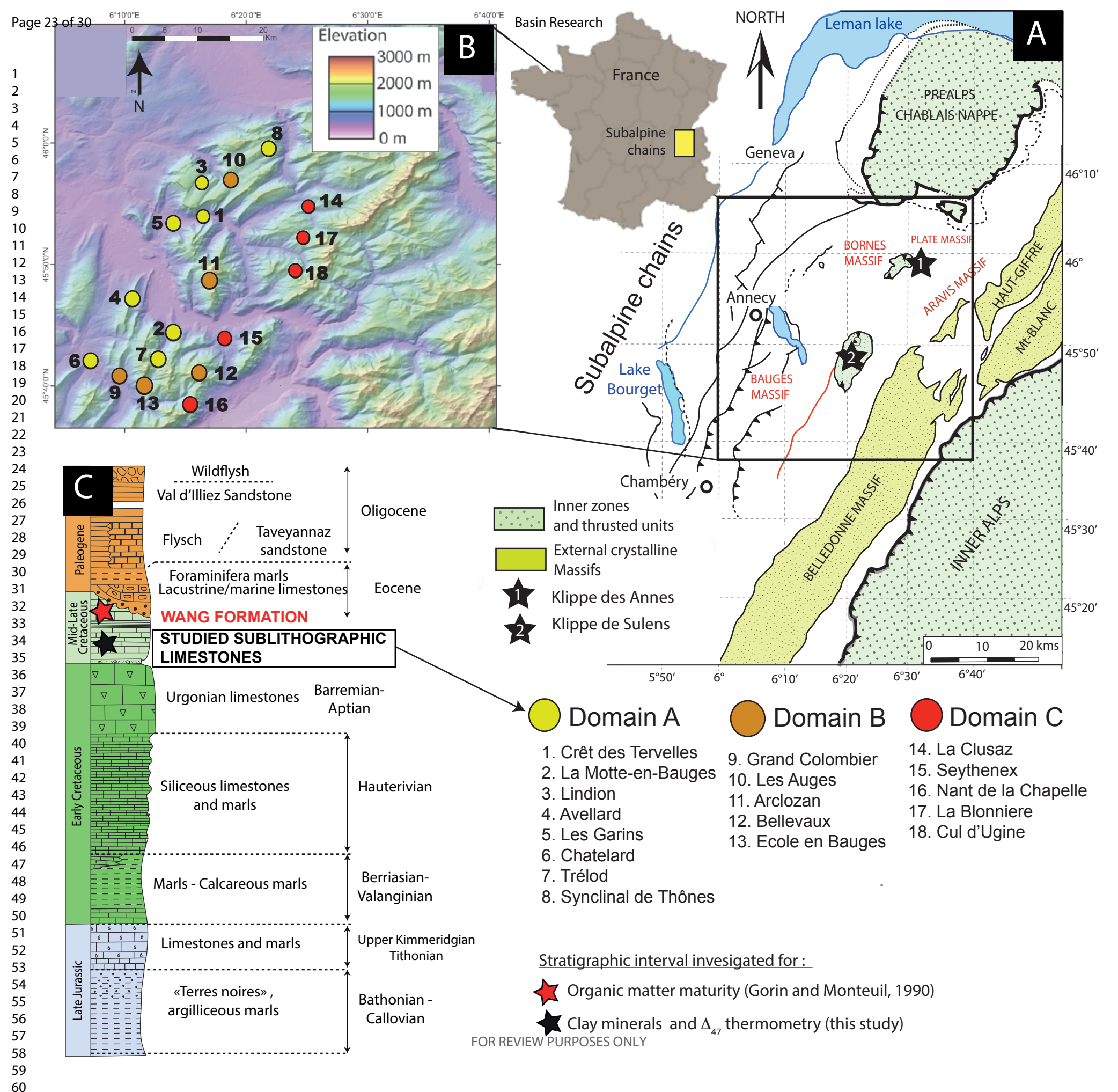
Figure 6. Summary of the paleothermometric data available for the Upper Cretaceous series of the studied area. A general correlation has been recognized between the amount of illite layers in I-S (panel B), vitrinite maturity (panel C), Rock-Eval T_{max} (panel D) and Δ_{47} temperatures (panel E). Samples from the most internal C domain display illite content in I-S mixed layer systematically higher than 90%, vitrinite reflectance $R_o\%$ values up to 1.3% and Δ_{47} temperatures higher than 150°C. In contrast, samples from the most external A domain record % illite in I-S between 20 and 50% (I-S R_0), lower vitrinite maturity ($R_o\% = 0.45-$

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3 931 0.55) and cooler Δ_{47} temperatures of $\sim 40\text{-}60^\circ\text{C}$. Such results point out a clear increase of
4 932 thermal maturity of samples from the A domain toward the C domain and demonstrate that
5 933 samples collected within a restricted geographic area may record very different thermal
6 934 maturities.

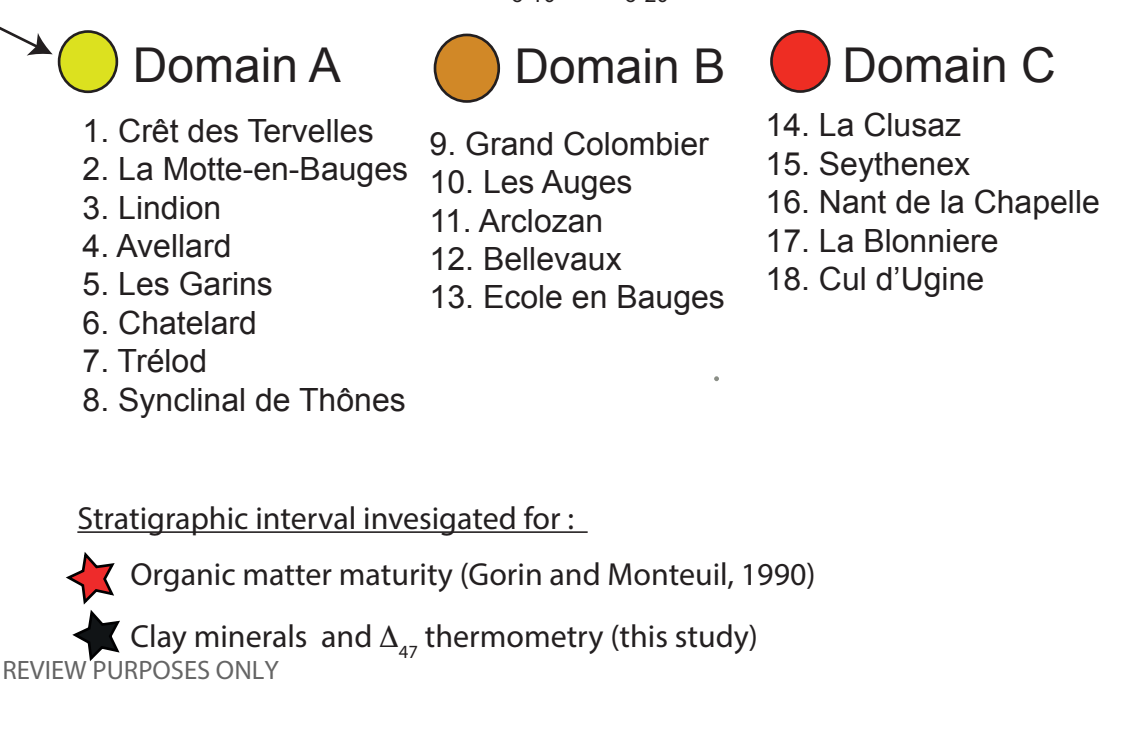
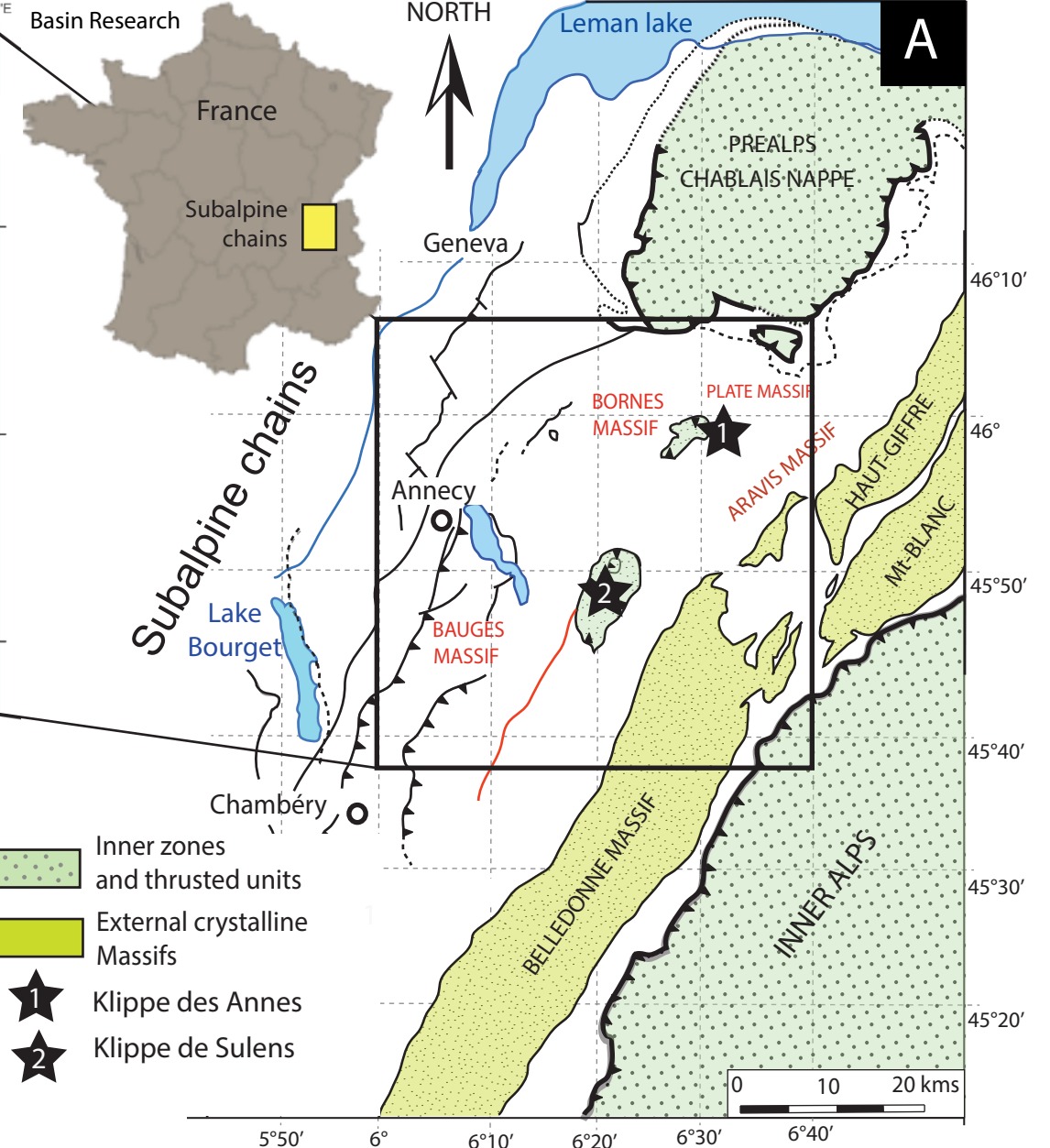
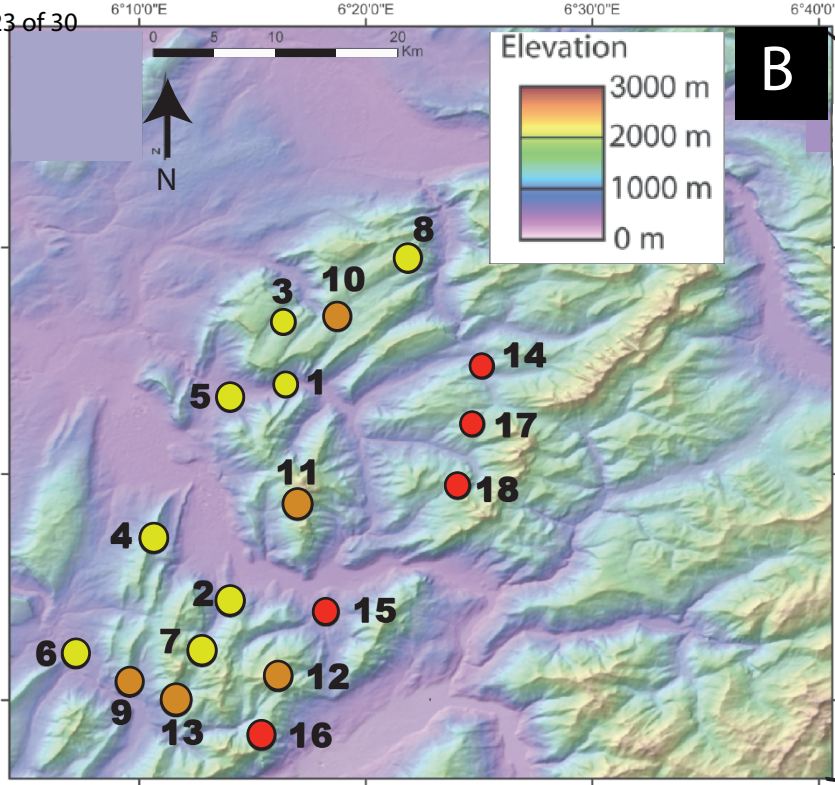
8 935 **Figure 7.** Thermal modeling of paleothermometric data using seven conceptual time-
9 936 temperature scenarios (Th1 to Th7) and the respective kinetic algorithms relevant to the
10 937 employed paleothermometers (c.f. [Sweeney and Burnham, 1990](#) for Ro% model; [Henkes et](#)
11 938 [al. \(2013\)](#) for Δ_{47} C-O bond reordering and [Huang et al., 1993](#) for smectite to illite conversion
12 939 in I-S). The model predictions are here compared to the measured values in samples A1, B9
13 940 and C16 from which paired $T\Delta_{47}$, Ro% and I% data were available. In B, C and D is shown
14 941 the evolution of Δ_{47} temperatures, Ro% values, and % illite in I-S mixed layer over time
15 942 computed using the different input thermal histories (i.e. maximal burial temperature from
16 943 80°C for TH1 in blue, up to 180°C for TH7 in red). The two prograde thermal histories
17 944 proposed by [Burrus, \(1991\)](#) (TH1 in blue and TH6 in orange) are noted here with an asterisk,
18 945 whereas all the others mid-scenarios were conceptually defined. The black rectangles on the
19 946 right side of the diagrams represent the measured values for each paleothermometric proxy.

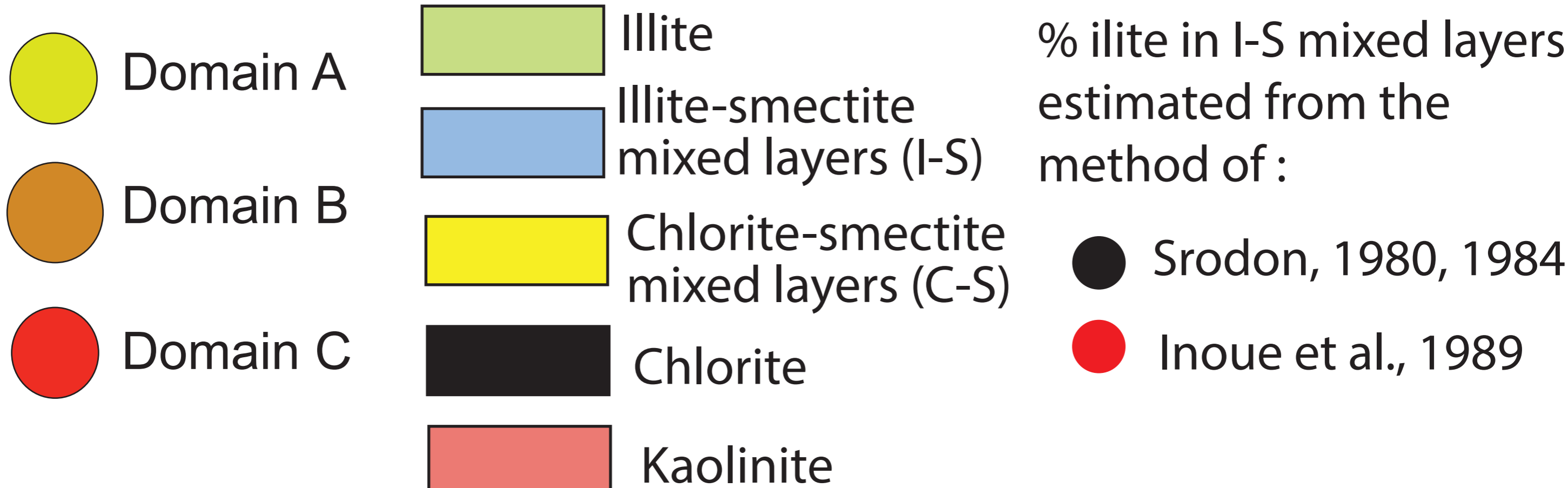
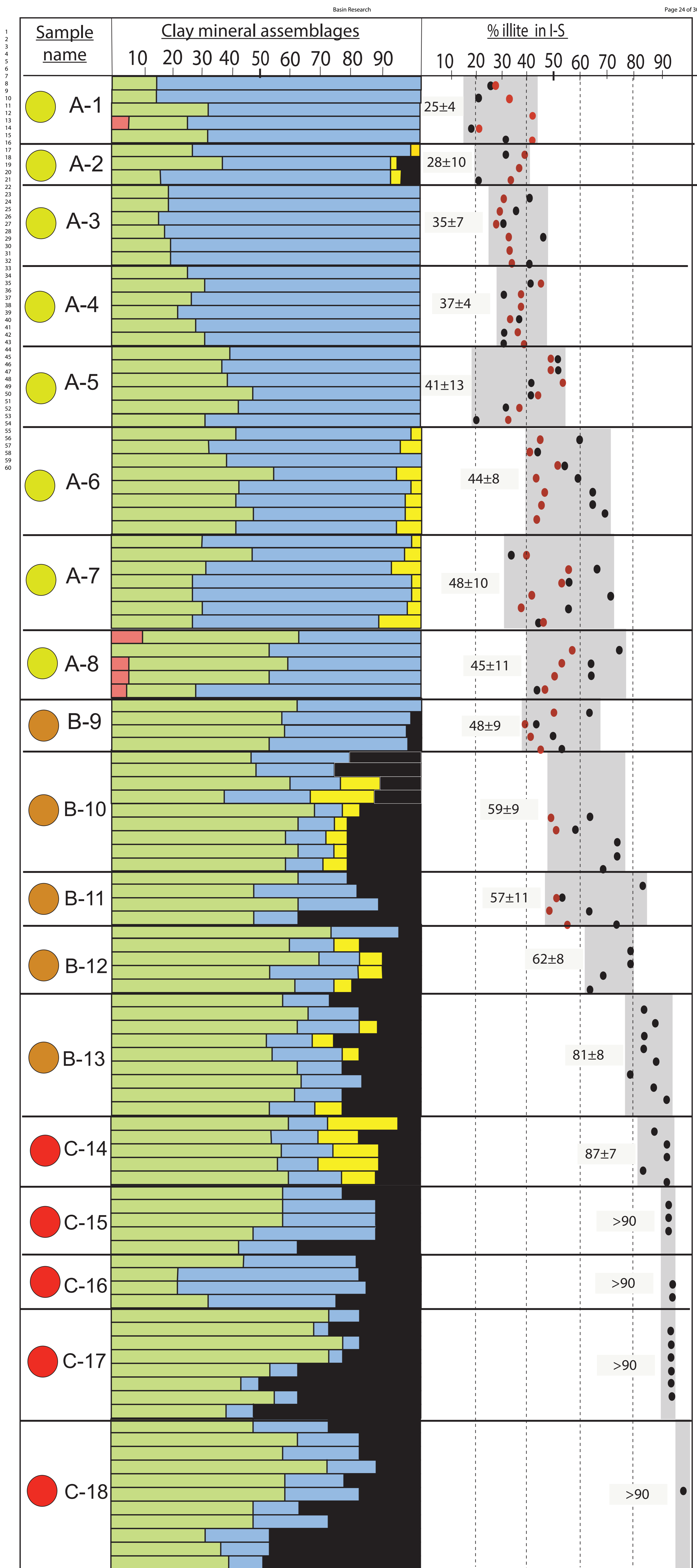
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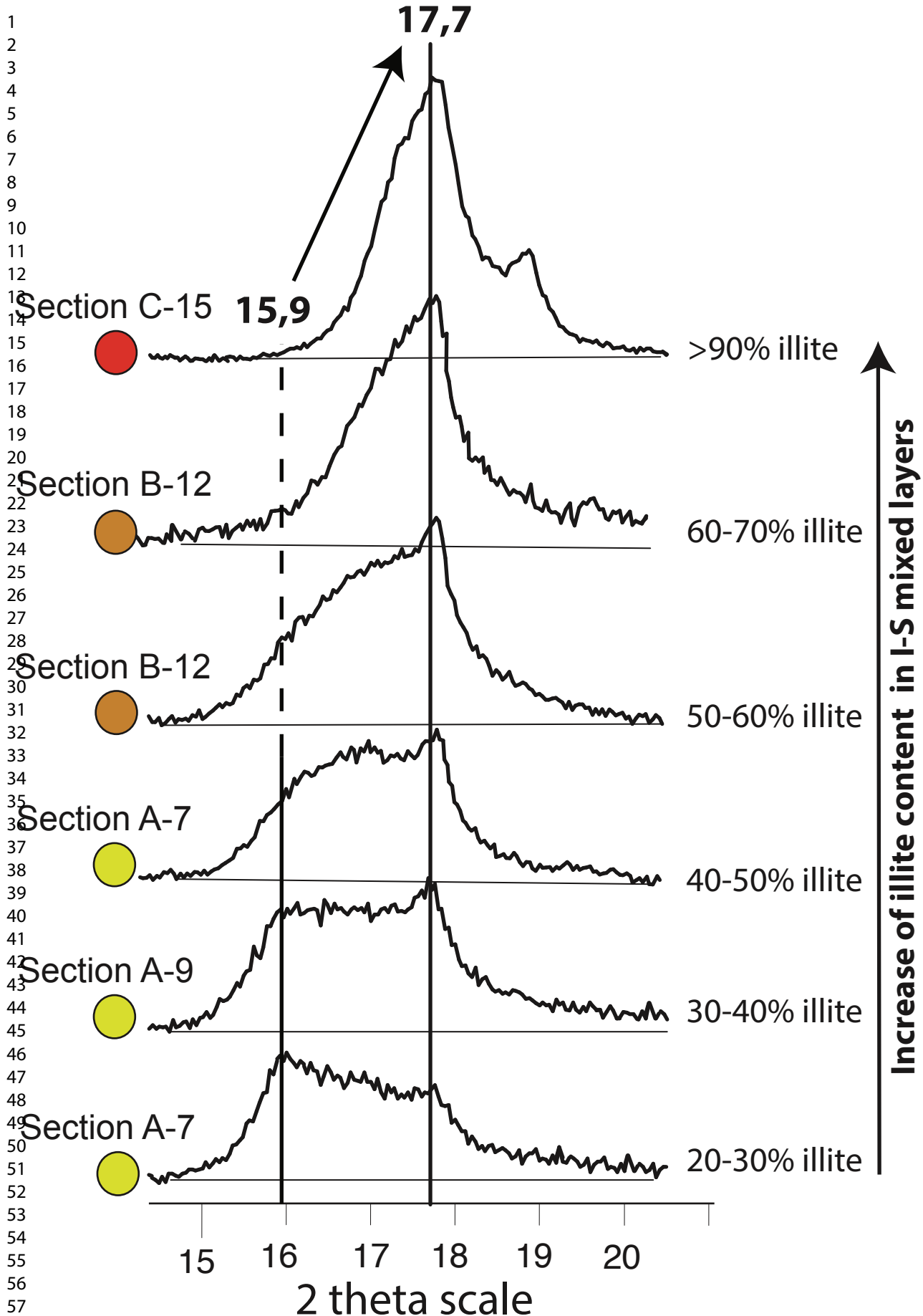


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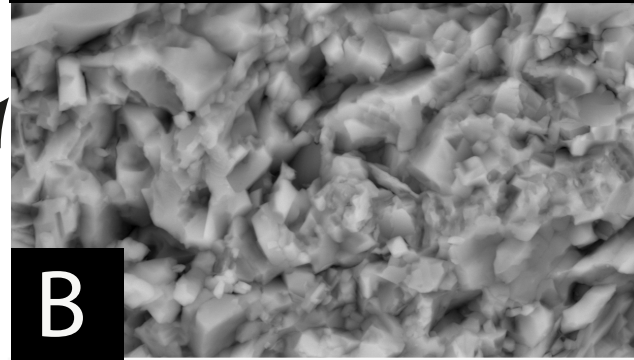


pure illite (002)

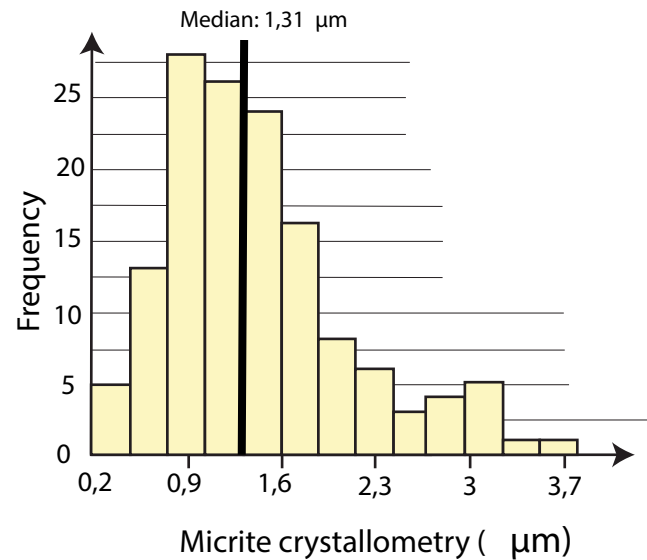


A4 μm

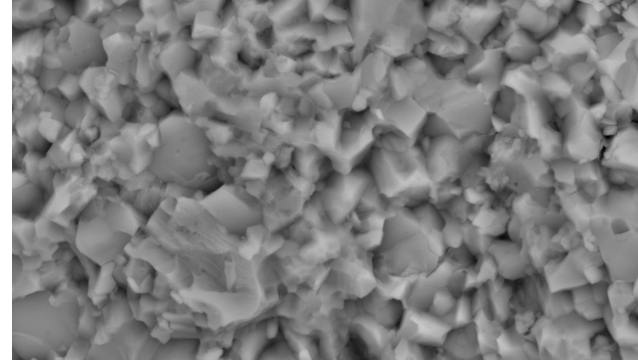
Sample A-6 ●

B

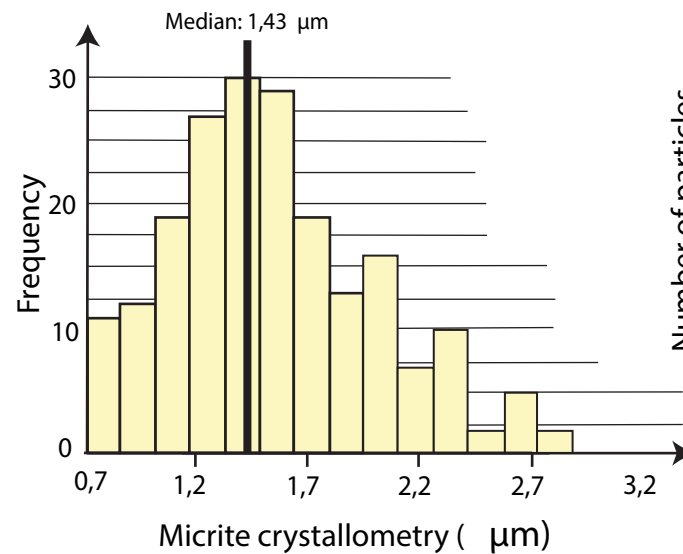
Particle shape : Anhedral-subhedral compact
 Contact : Coalescent
 Crystallometry : 1.31 μm
 \emptyset : 1,07%, K < 0.001MDa

4 μm

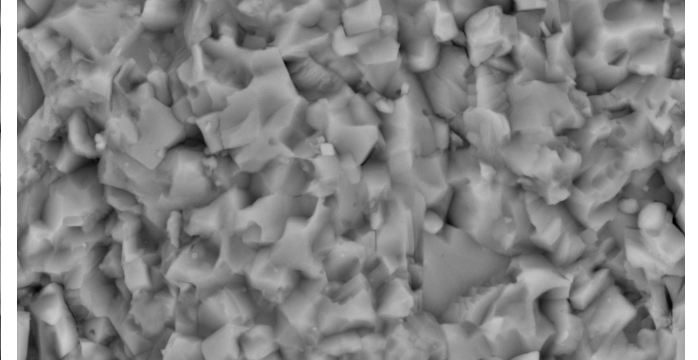
Sample B-11 ●



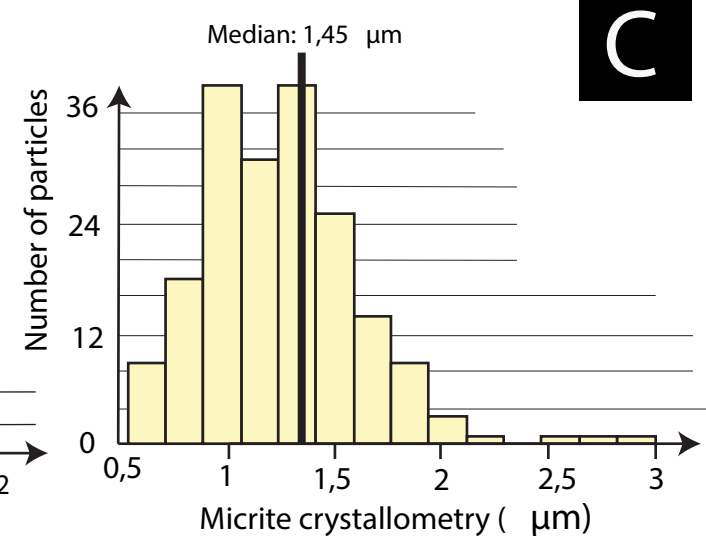
Particle shape : Anhedral-subhedral compact
 Contact : Coalescent
 Crystallometry : 1.43 μm
 \emptyset : 0,51% ; K < 0.001MDa

4 μm

Sample C-17 ●



Particle shape : Anhedral-subhedral compact
 Contact : Coalescent
 Crystallometry : 1,45 μm
 \emptyset : 0,56% ; K < 0.001MDa

**C**

Basin Research

Sample	Clay fraction (<5%)			Carbonated fraction (>95%)							Organic matter-bearing Wang Formation ⁽⁶⁾				
	Illite content in I _S ⁽¹⁾			Micrite particles ⁽²⁾		Petrophysical		Stable isotope data			Ro%	Tmax (°C)			
	Min	Max	Reichweite Nb.	Text.	Crystallo.	ϕ	K	δ ¹⁸ O	δ ¹³ C	Δ47 ⁽³⁾			T _{AN} ⁽⁵⁾	δ ¹⁸ O _{water} ⁽⁵⁾	
%	%	-	um	%	mD	%	mD	‰ (VPDB)	‰ (VPDB)	(CDES24)	°C	‰ (SMOW)	%	(°C)	
DOMAIN A															
A1	18	42	R0	Anhed.Comp. 1,43 (141)	0.522	<0.001	-3.48±0.05	0.04±0.01	0.597±0.032 (4)	61±14	3.6	0.45±0.05	428		
A2	21	40	R0	-	-	-	-	-	-	-	-	-	-	-	-
A3	28	42	R0	-	-	-	-	-	-	-	-	-	-	-	-
A4	30	45	R0	-	-	-	-	-	-	-	-	-	-	-	-
A5	20	50	R0	-	-	-	-	-	-	-	-	-	-	-	-
A6	40	65	R0/R1	Anhed.Comp. 1,31 (189)	1.073	0.001	-3.89±0.05	1.69±0.01	0.633±0.010 (2)	46±7	0.7	0.55±0.05	430		
A7	35	65	R0/R1	-	-	-	-	-	-	-	-	-	-	-	-
A8	40	70	R0/R1	-	-	-	-	-	-	-	-	-	-	-	-
DOMAIN B															
B9	40	65	R0/R1	-	-	1.36	0.008	-3.54±0.04	2.01±0.07	0.613±0.022 (3)	54±9	2.4	0.7±0.1	437	
B10	50	78	R1	-	-	-	-	-	-	-	-	-	-	-	-
B11	50	82	R1	Anhed.Comp. 1,43 (132)	0.508	<0.001	-3.53±0.21	2.39±0.07	0.634±0.076 (2)	45±30	0.8	-	-	-	-
B12	60	80	R1	-	-	0.555	<0.001	-3.53±0.21	2.39±0.07	0.634±0.076 (2)	45±30	0.8	-	-	-
B13	78	90	R1	-	-	-	-	-	-	-	-	-	-	-	-
Average for domain A and B															
								-3.61±0.19‰	1.53±1 ‰	0.619±0.017	51±7°C	1.7±1.3			
DOMAIN C															
C14	80	90	R1/R3	-	-	-	-	-	-	-	-	-	-	-	-
C15	90	100	R3	Anhed.Comp. 1,78 (146)	0.984	<0.001	-3.27±0.05	2.42±0.05	0.429±0.049 (2)	174±54	17.3	-	-	-	-
C16	90	100	R3	-	-	-	-3.15±0.06	2.02±0.06	0.434±0.018 (3)	169±19	17	1.3±0.2	461-474		
C17	90	100	R3	Anhed.Comp. 1,45 (205)	0.559	<0.001	-3.57±0.15	2.90±0.06	0.400±0.041 (2)	208±56	19.9	-	-	-	-
C18	90	100	R3	-	-	-	-3.66±0.09	2.55±0.03	0.423±0.039 (4)	181±44	17.5	-	-	-	-
Average for domain C															
								-3.41±0.24‰	2.47±0.4 ‰	0.421±0.015	183±17°C	17.9±1.3			

(1) Illite content in I-S mixed layers were estimated following the methods of Srodon, 1984 and Inoue et al. 1989. R0 = illite <50% ; R1 = illite between 50 and 90% ; R3 = illite >90%

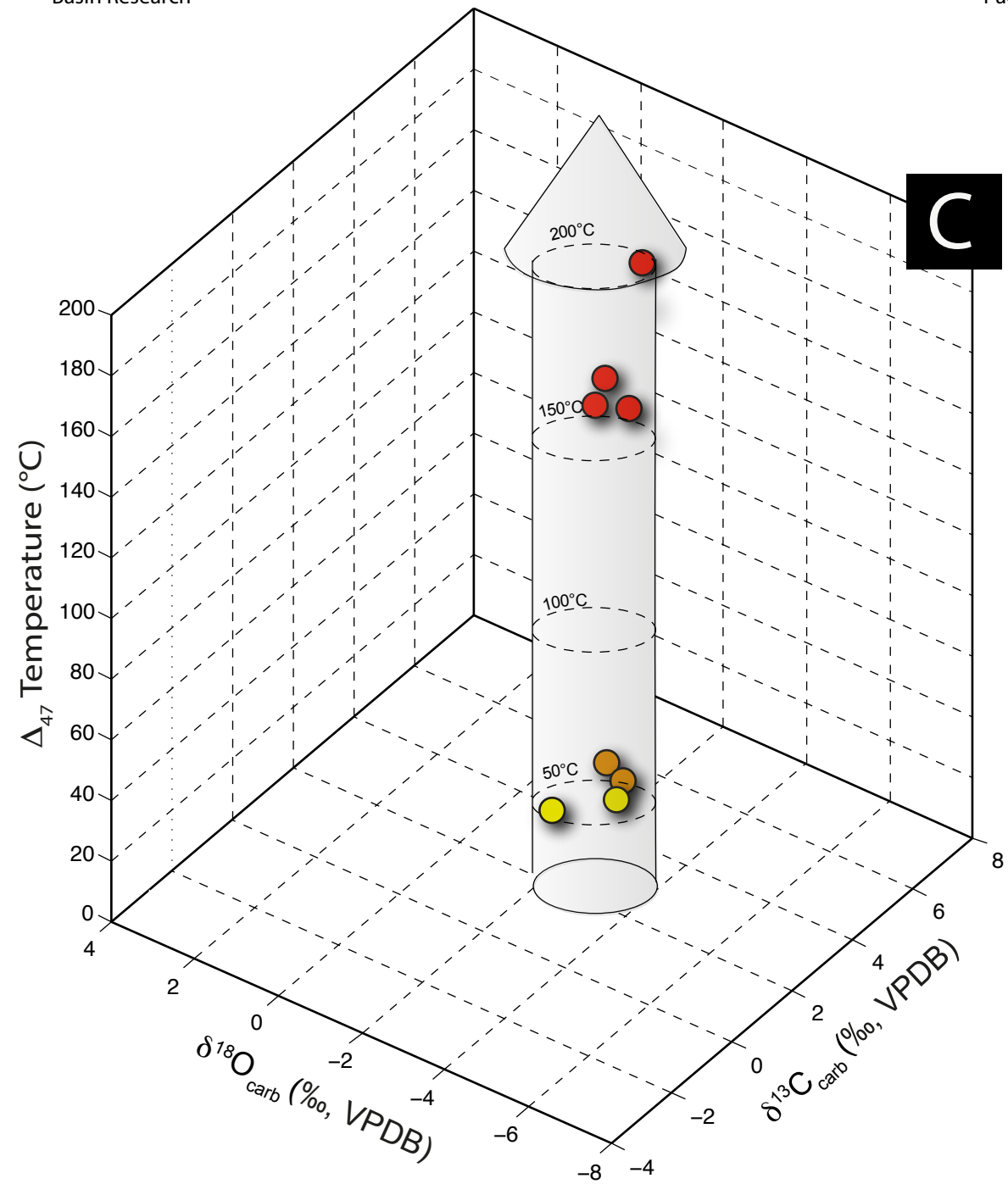
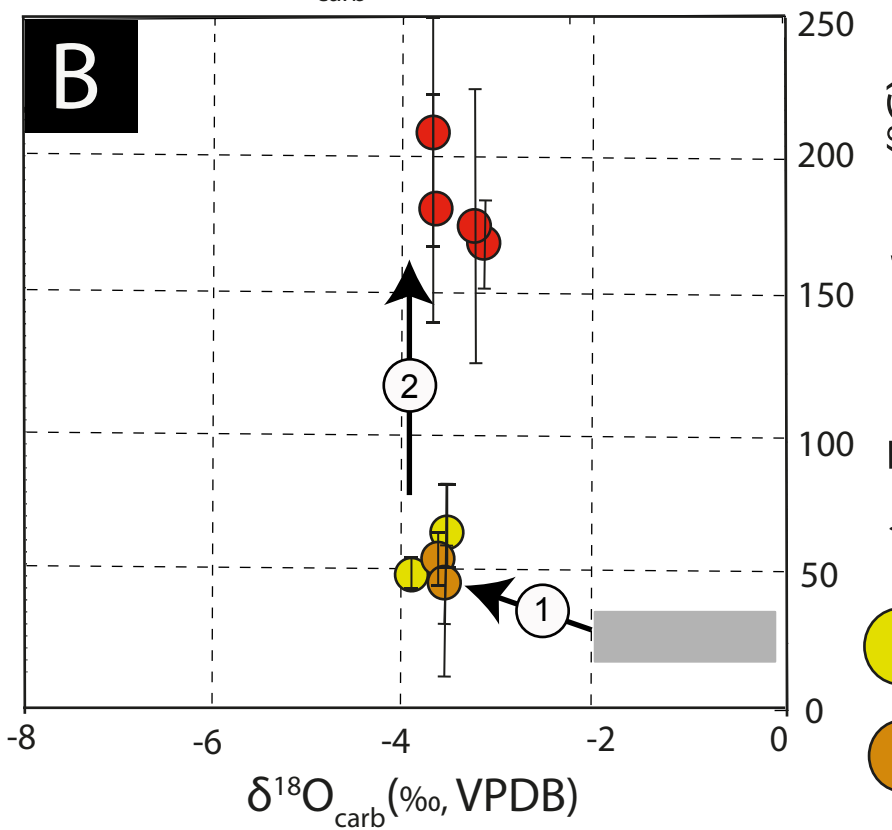
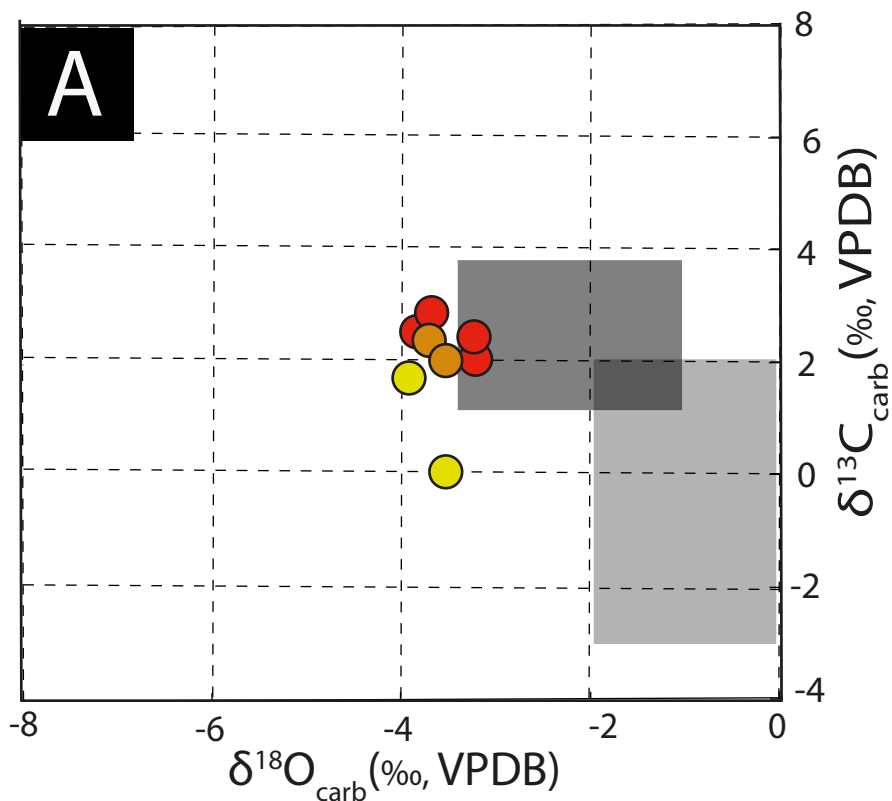
(2) Micrite particles texture (text.) and crystallography parameter (Crystallo.) were characterized by SEM images point counting. The number of crystallography values measured for each section is notify in brackets.

(3) A₄₇ values relative to the CDES (or 'carbon dioxide equilibrium scale') and the 25°C acid digestion frames (an acid correction factor of 0.092% was applied) following Henkes et al. 2013). Δ47 values are reported with their respective one standard deviation of the mean (±1 S.D.) for replicate measurements of the same powder. In brackets is the number of replicate measurements of the same carbonate powder. (4)

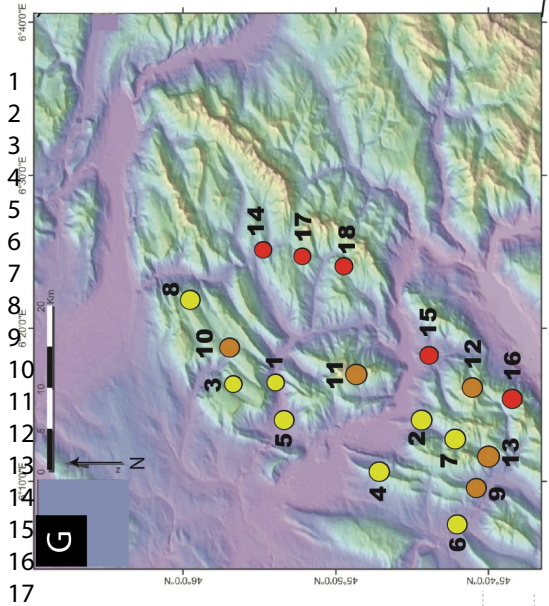
Paleotemperatures calculated using the universal Δ47-temperature calibration from Bonifacie et al. 2017. Reported uncertainties are calculated based on the S.D. reported for A₄₇ values.

(5) Oxygen isotope compositions of the fluid in equilibrium with the carbonate calculated using T_{AN} and the fractionation factor of oxygen isotopes between calcite and water of Watkins et al. (2013). (6)

Vitrinite reflectance and Tmax values were measured by Gorin and Monteil, 1990 in the overlying Cretaceous Wang Formation, and in the same or very close localities.



- **Domain A**
samples A1, A6
- **Domain B**
samples B9, B12
- **Domain C**
samples C15, C16, C17, C18
- Upper Cretaceous Low Magnesium Calcite shells
Veizer et al. (1999)
- Upper Cretaceous chalk with diagenetic alteration
Jenkyns et al. (1994)
- 1 Recrystallization at $\pm 50^\circ\text{C}$ and $\delta^{18}\text{O}_{\text{water}}$ of $1.7 \pm 1.2\text{‰}$
- 2 Δ_{47} thermal resetting



- Domain A**
 - 1. Crêt des Tervelles
 - 2. La Motte-en-Bauges
 - 3. Lindion
 - 4. Avellard
 - 5. Les Garins
 - 6. Chatelard
 - 7. Trélob
 - 8. Synclinal de Thônes
- Domain B**
 - 9. Grand Colombier
 - 10. Les Auges
 - 11. Arclozan
 - 12. Bellevaux
 - 13. Ecole en Bauges
- Domain C**
 - 14. La Clusaz
 - 15. Seythenex
 - 16. Nant de la Chapelle
 - 17. La Blonnrière
 - 18. Cui d'Ugine

Selected samples for the data-model comparison

