

Permian-Triassic red-stained albitized profiles in the granitic basement of NE Spain: Evidence for deep alteration related to the Triassic palaeosurface

Carles Fàbrega^a, David Parcerisa^{a,*}, Médard Thiry^b, Christine Franke^b, Andrey Gurenko^c, David

Gòmez-Gras^d, Jesús Solé^{e,f}, Anna Travé^g

^a *Departament d'Enginyeria Mìnera, Industrial i TIC, Escola Politècnica Superior d'Enginyeria de Manresa (UPC – Campus Manresa), Av. Bases de Manresa, 61-73, 08242, Manresa.*

^b *MINES ParisTech, PSL Research University, Center of Geosciences, 35 rue St. Honoré, 77305, Fontainebleau, Cedex, France.*

^c *Centre de Recherches Péetrographiques et Géochimiques, UMR 7358, Université de Lorraine, 15 rue Notre-Dame des Pauvres, BP 20, 54501 Vandoeuvre-lès-Nancy, France.*

^d *Departament de Geologia, Edifici C, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain.*

^e *Instituto de Geología, Universidad Nacional Autónoma de México, Ciudad Universitaria, Coyoacán, 04510 México DF, México*

^f *Laboratorio Nacional de Geoquímica y Mineralogía, Universidad Nacional Autónoma de México, Ciudad Universitaria, Coyoacán, 04510 Mexico DF, Mexico*

^g *Departament de Geoquímica, Petrologia i Prospecció Geològica, Facultat de Geologia. Universitat de Barcelona. Zona Universitària de Pedralbes, 08028 Barcelona*

* *Corresponding autor: David Parcerisa. E-mail: dparcerisa@epsem.upc.edu*

Tel.: +34 938 777 991

ABSTRACT

Extensive areas of the Variscan granitic basement in NE Spain display profiles of red-stained albitized facies characterized by albitization of Ca-plagioclase, chloritization of biotite and microclinization of orthoclase, along with the alteration of igneous quartz to secondary CL-dark quartz. These profiles have a geopetal structure beneath the Triassic unconformity, with a very intense and pervasive alteration in the upper part that progressively decreases with depth to 150-200 m where the alteration is restricted to the walls of fractures. The red albitized facies contains secondary maghemite and hematite that indicate oxidizing conditions. Dating of microclinized orthoclase and secondary monazite that have formed in the red-stained albitized facies yielded K-Ar and U-Th-Pb_{total} ages of 240 and 250 Ma, respectively, suggesting that the alteration developed during the Permian-Triassic period. The geopetal disposition of the red albitized profile with respect to the Triassic unconformity, its large regional extent, and the fracture-controlled alteration in the lower part of the profile indicate groundwater interaction. The $\delta^{18}\text{O}$

32 values of albitized plagioclase (+11‰), microclinized orthoclase (+13‰), and secondary CL-dark quartz
33 (+12‰), suggest that the alteration temperature was about 55°C. This “low” temperature suggests that the
34 alteration occurred during interaction of the granitic rocks with Na-rich fluids below a surficial
35 weathering mantle on the Permian-Triassic palaeosurface. The latter is possibly related to Triassic
36 evaporitic environments in long-lasting, stable landscapes in which Na-rich solutions infiltrated deep
37 regional groundwaters.

38

39

40

41 *Keywords:* red-stained; albitization; alteration; Permian-Triassic; palaeosurface; isotope; dating;

42

43

44 Introduction

45 Albitization of Ca-plagioclase is a widespread replacement process described in sedimentary deposits
46 (Coombs, 1954; Kastner and Siever, 1979; Ramseyer et al., 1992) and crystalline rocks (Baker, 1985; Lee
47 and Parsons, 1997; Parsons and Lee, 2009; Plümper and Putnis, 2009; Parsons et al., 2009; Morad et al.,
48 2010; Petersson et al., 2012, 2014; Fallourd et al., 2014). It is a marker for the interaction of the
49 respective facies with Na-rich brines and has been described as occurring over a wide temperature range
50 from 65 to 160°C in basinal settings (Boles, 1982; Saigal et al., 1988) and between 200 and 400°C in
51 hydrothermal conditions (Petersson and Eliason, 1997; Boulvais et al., 2007; Poujol et al., 2010). Usually,
52 depths from 2 to 4 km are reported for current and fossil albitization processes in sedimentary basins and
53 geothermal fields (Aagaard et al., 1990; Morad et al., 1990; Perez and Boles, 2005).

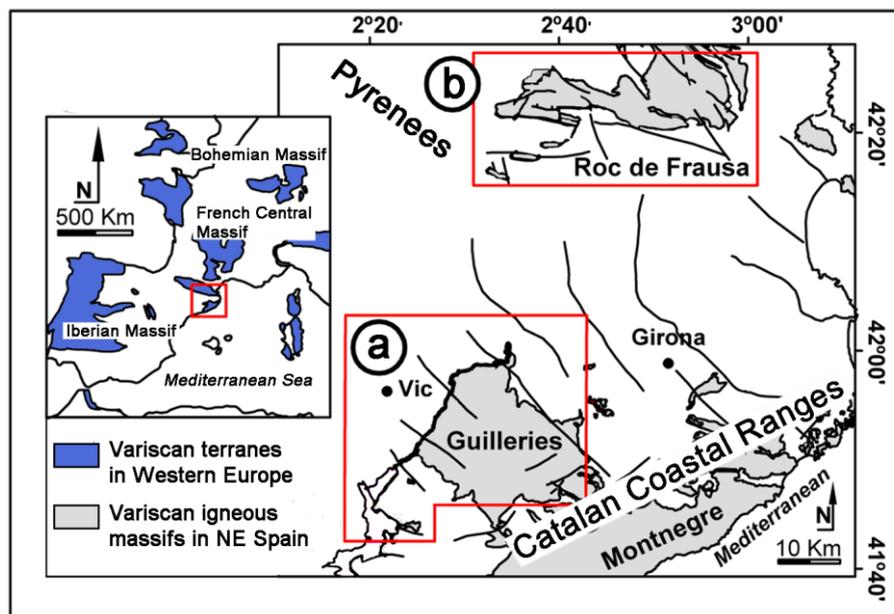
54 Extensive ~150 to 200 m thick vertical profiles characterized by red-staining and albitization of the
55 crystalline basement have been described beneath the Triassic unconformity in various parts of Western
56 Europe. In many cases a Permian-Triassic age has been established for them by direct (radiometric and
57 paleomagnetic dating) or indirect evidences (geological cartography). Significant occurrences of the red-
58 stained albitized profiles have been reported in the French Massif Central, including some affecting
59 Carboniferous and Permian deposits (Yerle and Thiry, 1979; Clément, 1986; Schmitt, 1986, 1992;
60 Schmitt et al., 1984; Simon-Coinçon, 1999; Thiry et al., 1999, 2014), the Morvan Massif (Ricodel et al.,
61 2007; Parcerisa et al., 2010b), the Alps (Battiau-Queney, 1997), the Polish Sudetes (Yao et al., 2011;
62 Yao, 2013) and the Spanish Guillerries and Roc de Frausa Massifs (Fàbrega et al., 2013; Franke et al.,
63 2010; Parcerisa et al., 2010a; 2013). Away from the above sites, the age of granite albitization and even
64 red-staining have rarely been documented. However, a profile-like alteration diminishing in intensity with
65 depth and characterized by reddening by hematite and accompanying recrystallization of feldspars has
66 been reported in the Long Mountain Granite of the Wichita Mountains igneous province, southwestern
67 Oklahoma (Hamilton et al., 2014, 2016). This alteration is considered to have been caused by low-
68 temperature weathering fluids while the granite was exposed near the surface in the late Palaeozoic.

69 The present study focusses on the spatial distribution, geometry, petrology, age and oxygen isotope
70 composition of the red-stained albitized profiles in the Variscan granitic basement beneath the Triassic
71 unconformity of the Guillerries and Roc de Frausa massifs (NE Spain), with aims to: 1) determine the
72 genetic relationship of the alteration with the Permian-Triassic palaeosurface, 2) constrain the age of the

73 alteration event, 3) evaluate the origin and temperature of the albitizing fluid, and 4) gain an
74 understanding of subsurface processes that operated beneath the Triassic palaeosurface.

75 Geological setting and study sites

76 The granitic massifs of the Guilleries (Catalan Coastal Ranges) and Roc de Frausa (Eastern Pyrenees)
77 form part of the Variscan crystalline basement of NE Spain (Fig. 1a, b) and are made up of late-orogenic
78 batholiths intruded into the upper part of the crust (Roberts et al. 2000; Vilà et al. 2005; Aguilar et al.
79 2014, 2015). The Guilleries Massif consists of granodiorite, leucogranite and diorite bodies (Fig. 2a) that
80 intruded a Cambro-Ordovician metamorphic series (Julivert and Duran, 1990; Enrique, 1990). The
81 igneous and metamorphic rocks are cross-cut by a swarm of ENE-WSW trending vertical dikes of
82 granitic to monzonitic composition. Martínez et al. (2008) reported bimodal cooling ages of 305.9 ± 1.5
83 and 323.6 ± 2.8 Ma from U-Pb dating of zircon in, respectively, biotite granites and diorite bodies. In the
84 south of the massif and in the Tagamanent area the crystalline basement is covered by Middle Triassic
85 (Anisian) red-beds (Fig. 2a, b) that were deposited in the Permian-Triassic rift basins of northeastern
86 Spain (Solé de Porta et al., 1987; Dinarès-Turell et al., 2005; Gómez-Gras, 1993). In the north (Fig. 2a),
87 the unconformity is covered by Palaeocene red-beds deposited in the eastern boundaries of the Ebro Basin
88 (Anadón et al., 1986).



89

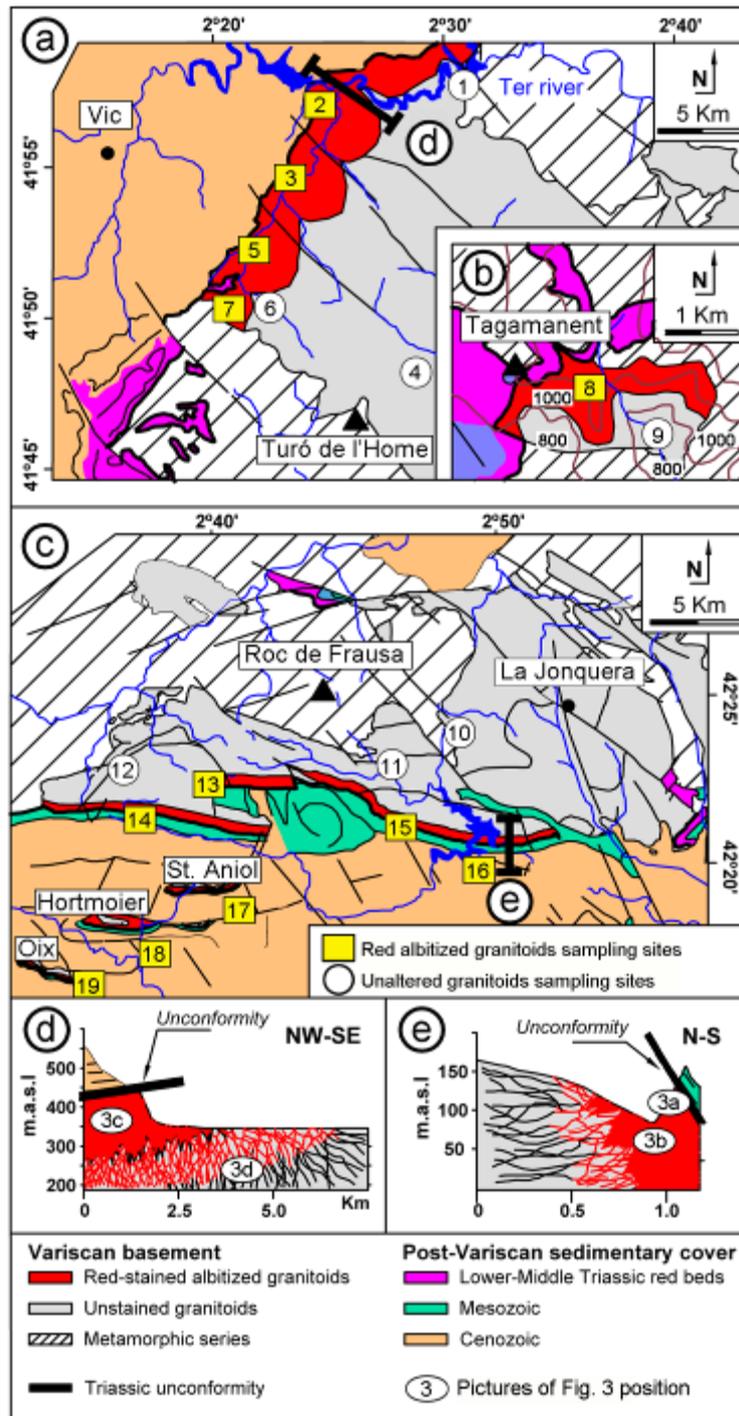
90 **Fig. 1.** Location of the Guilleries (a) and Roc de Frausa (b) massifs in the Variscan terranes of the Catalan Coastal
91 Ranges and Eastern Pyrenees.

92 The igneous basement of the Roc de Frausa Massif is formed of biotite-hornblende granite, granodiorite,
93 leucogranite, monzo-granite, and porphyritic granites (Fig. 2c) that intruded a Proterozoic to early
94 Cambrian sequence of metapelites, ortho-gneiss, and metagreywackes (Aguilar et al., 2015). To the
95 southwest, the areas of Hortmoier, Oix and St. Aniol are made up of porphyritic granite with K-feldspar
96 phenocrysts (Fig. 2c). U-Pb dating of zircons yielded two cooling episodes for the granites corresponding
97 to 314.2 ± 1.5 and 311.0 ± 0.9 Ma (Aguilar et al., 2014). The sedimentary cover is formed of south-tilted
98 (40-50°) Upper Cretaceous (Maastrichtian) red-beds (Oms et al., 2007; Gómez-Gras et al., 2016).

99 In the Guilleries Massif, the red-stained albitized granitoids crop out along the Triassic unconformity,
100 which is situated in the western boundary of the massif (Fig. 2a). The rocks affected by the red-stained
101 albitization are exposed in a total area about 20 km long by 2-3 km wide in a N-S direction (Fig. 2a). In
102 the Tagamanent area (Fig. 2b), the red-stained albitized granites crop out between 1100 to 900 meters
103 above sea level in a topography-related ~200 m thick profile beneath the Triassic unconformity.

104 In the Roc de Frausa Massif, the red-stained albitized rocks are exposed along the Triassic unconformity
105 in the southern limit of the massif (Fig. 2c). The total area affected by albitization is about 25 km long by
106 ~2 km wide in an E-W direction (Fig. 2c). In the areas of Oix, Hortmoier and St. Aniol (Fig. 2c), the red-
107 stained albitized rocks also occur along the Triassic unconformity situated in the southern limit of the
108 three areas.

109 The study sites in both massifs (Table 1) focussed on the red-stained albitized granitoids cropping out
110 under the Triassic unconformity and on their unaltered counterparts (Fig. 2a, b, c). Several cross sections
111 were constructed to determine the structure and depth of the red-stained albitization with respect to the
112 Triassic unconformity (Fig. 2d, e). Further detailed information on the study sites is included in the
113 **Supplementary Information S1**, available at the dataset of Fàbrega et al. (2018).



114

115 **Fig. 2.** Geological setting, sampling sites and cross-sections. (a) Guilleries Massif. (b) Tagamanent hill, located on
 116 the south of the Guilleries Massif. (c) Roc de Frausa Massif, St. Aniol, Hortmoier and Oix. (d) Sau dam cross
 117 section. (e) Boadella dam cross section. **Main sampling sites:** Guilleries Massif: (1) Susqueda dam; (2) Sau dam; (3)
 118 Bojons; (4) Arbúcies and St. Coloma de Farners; (5) Osormort; (6) Viladrau; (7) Mas Vidal-Timonar; (8)
 119 Tagamanent; (9) Vallfornès. Roc de Frausa Massif: (10) La Vajol; (11) Maçanet de Cabrenys; (12) St. Laurent
 120 Cerdans; (13) Coustoges; (14) Villerouge; (15) Puig Creu de Mondavà; (16) Boadella dam; (17) St. Aniol; (18)
 121 Hortmoier; (19) Oix.

122 Methods and materials

123 The analytical data for this study are included in **Supplementary Information S2** and **S3** and are
 124 available also in the institutional repository [dataset] [Fàbrega et al. \(2018\)](#).

125 Sampling and mapping

126 Sampling, mapping and construction of cross-sections of the red albitized granitoids were systematically
 127 carried out along the Triassic unconformity of both massifs ([Fig. 2](#)). Due to a dense forest cover in most
 128 of the study areas, the work was mostly carried out along linear features including roads, trails and creeks.
 129 A total of about 280 and 100 samples were collected in the Guilleries and Roc de Frausa Massifs,
 130 respectively, including pervasively albitized rocks, albitization restricted to fractures and unaltered rocks
 131 ([Table 1](#)).

132 **Table 1. Sampling sites, their numbering in Figure 1, nature of the host rocks and their alteration features.**

| massif | sampling sites | N. in (Fig. 1) | host rock | samples major features |
|---------------|-----------------------|----------------|---------------------------------|-------------------------------------|
| Guilleries | Susqueda dam | 1 | granodiorite | unaltered |
| | Sau dam | 2 | leucogranite | pervasive red albitized |
| | Bojons | 3 | granodiorite + dikes | pervasive red albitized |
| | Arbúcies / St. Coloma | 4 | granodiorite + leucogranite | red albitized fracture walls |
| | Osormort | 5 | granodiorite + dykes | pervasive red albitized |
| | Viladrau | 6 | granodiorite | unaltered |
| | Mas Vidal-Timonar | 7 | granodiorite + dykes | pervasive red albitized |
| | Tagamanent | 8 | porphyritic granite | pervasive red albitized |
| | Vallfornès | 9 | porphyritic granite | unaltered |
| Roc de Frausa | La Vajol | 10 | hornblende-biotite granodiorite | unaltered |
| | Maçanet de Cabrenys | 11 | hornblende-biotite granodiorite | unaltered |
| | St. Laurent Cerdans | 12 | hornblende-biotite granodiorite | unaltered |
| | Coustoges | 13 | porphyritic granite | pervasive red albitized |
| | Villeroige | 14 | porphyritic granite | pervasive red albitized |
| | Puig Creu Mondavà | 15 | porphyritic granite | pervasive red albitized |
| | Boadella dam | 16 | porphyritic granite | pervasive red albitized + unaltered |
| | St. Aniol | 17 | porphyritic granite | red albitized fracture walls |
| | Hortmoier | 18 | porphyritic granite | red albitized fracture walls |
| | Oix | 19 | porphyritic granite | red albitized fracture walls |

133

134 **Petrological and geochemical analyses**

135 About 80 samples were prepared as thin sections and epoxy-embedded mounts for petrographical
136 analyses. Samples were observed by optical microscopy and optical cathodoluminescence (CL) using a
137 Technosyn Cold Cathodoluminescence 8200-MKII-CL operating at 15-18 kV gun potential and 150 -
138 350 μ A beam current at the Facultat de Ciències de la Terra of the Universitat de Barcelona (Spain). The
139 quality of the CL-microphotographs was improved by following the recommendations of [Witkowski et](#)
140 [al. \(2000\)](#). SEM-cathodoluminescence (SEM-CL) of quartz was undertaken using a FESEM JEDL J-7100
141 equipped with a GATAN MONO-CL4 cathodoluminescence spectrometer at the Centres Científics i
142 Tecnològics (CCiTUB) of the Universitat de Barcelona (Spain). The textural features of quartz under
143 SEM-CL were analysed according to the techniques of [Bernet and Basset \(2005\)](#), [Rusk and Reed \(2002\)](#)
144 and [Rusk et al. \(2006\)](#).

145 The chemical composition of bulk rock was determined by laser X-ray fluorescence (LXRF) at the
146 Instituto de Geología of the Universidad Nacional Autónoma de México (México) using a Rigaku Primus
147 II spectrometer. Detailed chemical composition of minerals was determined by electron probe
148 microanalyses (EPMA) using a JEOL JXA-8230 instrument at the Centres Científics i Tecnològics
149 (CCiTUB) of the Universitat de Barcelona (Spain). The operating conditions were acceleration voltage of
150 20 kV and probe current of 1.5 nA. The surfaces of thin sections and epoxy mounts used in EPMA
151 analyses were polished metallographically. EPMA analyses were carried out on several kinds of
152 granitoids, including leucogranite and granodiorite in the Guilleries and porphyritic granite in the Roc de
153 Frausa and on similar red-stained albitized rocks. In total about 1400 spots were analysed.

154 The degree of microclinalization of 73 K-feldspar phenocrysts was quantified by X-ray diffraction (XRD)
155 at the Center of Geosciences, Mines ParisTech, Fontainebleau (France). Identification of the orthoclase,
156 microcline and albite was carried out by peak deconvolution using the *Fityk* software ([Wojdyr, 2010](#))
157 adjusting the shape of the deconvoluted peaks by the Pearson VII function ([Hall et al., 1977](#)). The
158 position of the peaks was calibrated with respect to the quartz peaks, which are present in the samples.

159 K-Ar dating of K-feldspar phenocrysts was carried out at the Instituto de Geología of the Universidad
160 Nacional Autónoma de México. The analyses were done on 1 unaltered and 7 pinkish phenocryst
161 subsamples from Hortmoier ([see Fig. 2](#)). Fragments of the K-feldspar phenocrysts about 2-5 mm in size
162 were hand-picked with the aid of a stereo microscope. The selected fragments were cleaned with distilled

163 water and acetone. The K content was measured by XRF on 50 mg aliquots using a specific regression for
164 measuring K in K-Ar samples (Solé and Enrique, 2001). Analytical precision was > 2%. Duplicate
165 samples weighing between 1 and 2 mg were mounted on holes of a copper plate. This plate was placed on
166 an ultra-high vacuum chamber that was degassed at ~150°C for twelve hours before analysis to reduce
167 atmospheric contamination. Argon was extracted by complete sample fusion using a 50 W CO₂ laser
168 defocused to 1 - 3 mm diameter. The evolved gasses were mixed with a known amount of ³⁸Ar spike and
169 purified with a cold finger immersed in liquid nitrogen and two SAES getters in a stainless-steel
170 extraction line. Measurements were done in static mode with an MM1200B noble gas mass spectrometer
171 using electromagnetic peak switching controlled by a Hall probe. Analytical precision on ⁴⁰Ar and ³⁸Ar
172 peak heights was better than 0.2%, and better than 0.5% for ³⁶Ar. The data were calibrated with internal
173 standards and the international reference materials LP-6 biotite, B4M muscovite and HD-B1 biotite. All
174 ages were calculated using the constants recommended by Steiger and Jäger (1977). A detailed
175 description of the procedure and calculations is given by Solé (2009).

176 **U-Th-Pb_{total} EPMA monazite dating**

177 Monazite geochronology was carried out by EPMA U-Th-Pb_{total} dating following the recommendations of
178 Cocherie et al. (1998), Cocherie and Albarede (2001) and Williams et al. (2006). The technique assumes
179 a negligible amount of common vs. radiogenic Pb (Parrish, 1990), very slow Pb diffusion (Cherniak et al.,
180 2004; Cherniak and Pyle, 2008) and the complete removal of prior Pb during the formation of secondary
181 monazite domains, thus resetting the U-Th-Pb_{total} chemical geochronometer (Williams et al., 2011).

182 Monazite grains were first identified in the thin sections by means of BSE imaging in a Hitachi TM-1000
183 electron microscope operating at 15 kV at the Escola Politècnica Superior d'Enginyeria de Manresa
184 (EPSEM) of the Universitat Politècnica de Catalunya (Spain). The U-Th-Pb_{total} EPMA analyses were
185 carried out using a JEOL JXA-8230 electron probe operating at 20 kV at the Centres Científics i
186 Tecnològics (CCiTUB) of the Universitat de Barcelona (Spain). The session-to-session consistency of the
187 EPMA analyses was controlled using an in-house monazite standard from Coats pegmatite (Petaca
188 district, New Mexico). The reference U-Th-Pb isotopes standard age was 1332.6 ± 4.6 Ma (2σ), obtained
189 by LA-ICP-MS at Geosciences Rennes, Université de Rennes 1 (France). The U-Th-Pb_{total} ages of the
190 standard obtained in each EPMA session were, respectively, 1313 ± 30 , 1307 ± 36 , 1308 ± 44 , and

191 1305 ± 32 Ma (2σ), being consistent, within 2σ, with the U-Pb and Th-Pb age obtained by laser ablation
192 coupled with MC-ICP-MS.

193 In the unaltered igneous rocks, primary monazite occurred as euhedral (20 - 50 μm) or rounded (usually
194 150 - 200 μm) grains that did not show internal BSE-zoning. In the red-stained albitized granitoids,
195 monazite is exclusively preserved in a mm-scale rock volume attached to the reaction front. In this
196 volume, monazite is pseudomorphosed by secondary monazite and apatite, and displays dissolution-
197 reprecipitation textures including corroded grain boundaries and widespread μm-size porosity (Putnis,
198 2002; Harlov et al., 2011).

199 The analyses were performed on three representative samples of unaltered rock and two representative
200 samples plus 2 subsamples of red albitized rock. A total of 530 spots were analysed. Afterwards, the
201 EPMA raw U-Th-Pb_{total} results presenting a sum of oxides less than 95% and/or a relative standard
202 deviation of U and/or Th and/or Pb larger than 20% were rejected. Finally, 117 and 80 analyses were used
203 to estimate the U-Th-Pb ages for the Guilleries and Roc de Frausa, respectively. The U-Th-Pb_{total} dates of
204 the individual EPMA points were calculated using the *MonaziteAge* software included in the JEOL JXA-
205 8230 electron probe, which uses the approach of Suzuki and Adachi (1991, 1994) and Suzuki et al.
206 (1994). Subsequently, the standard error of each single date was estimated using the Microsoft Excel
207 (Microsoft Inc.) add-in *EPMA dating 2007* developed by A. Pommier, A. Cocherie and O. Legrenge at the
208 BRGM. The final U-Th-Pb_{tot} ages of the primary and secondary monazite were calculated by
209 deconvolution of the histograms of the punctual U-Th-Pb_{total} dates using the Microsoft Excel add-in
210 *ISOPLOT 4.15* from the Berkeley Geochronology Center (Ludwig, 2003).

211 ***In-situ* δ¹⁸O SIMS analyses**

212 In-situ δ¹⁸O (to VSMOW) SIMS analyses of plagioclase, K-feldspar and quartz were carried out using a
213 CAMECA IMS 1280HR ion microprobe at the Centre de Recherches Pétrographiques et Géochimiques,
214 Centre National de la Recherche Scientifique (Nancy, France). Rock samples were cut into 4×4×4 mm
215 pieces, mounted in cylindrical 25 mm diameter/5 mm thick epoxy mounts accompanied by mm-sized
216 fragments of in-house feldspar and quartz standards and metallographically polished. Optical-CL
217 microphotographs of the surfaces of samples and standards were obtained and were subsequently used
218 during the SIMS session to locate the oxygen isotope analyses on the desired textural position. The SIMS
219 analyses were carried out using a ¹³³Cs⁺ primary ion beam of +10 kV and intensity of 5 – 6 nA. Vacuum

220 conditions in the sample chamber were about $\sim E^{-9}$ Torr. Positive charging of the sample surface was
221 prevented by means of a gold coating and a normal incident electron flood gun. Secondary negative ions
222 were accelerated by a 10 kV potential. After pre-sputtering, the secondary ion beam was automatically
223 centered onto the field aperture by the electrostatic deflectors LT1DefX and LT1DefY. The produced
224 $^{16}\text{O}^-$ and $^{18}\text{O}^-$ were simultaneously collected in multicollection mode using two Faraday cups (FC; L'2 for
225 counting $^{16}\text{O}^-$ ions, and H1 for $^{18}\text{O}^-$ ions). Each single analysis included 30×5 -s-long counting cycles,
226 with a total span time of ~ 4 min, including 60 s of pre-sputtering.

227 The in-house standards used for the correction of the SIMS instrumental mass fractionation (IMF)
228 included eight plagioclase, two K-feldspar and one quartz specimens. The textural characteristics,
229 chemical and bulk $\delta^{18}\text{O}$ compositions of the in-house standards are described in [Fàbrega et al. \(2017\)](#) and
230 hosted in the institutional repository *UPCommons* of the Universitat Politècnica de Catalunya, Spain
231 ([Parcerisa et al., 2016](#)). The averaged internal precision (within-spot uncertainty) of the standards
232 analyses was 0.06‰ (1σ) for the whole session. The external precision (spot-to-spot reproducibility) was
233 in the range 0.29 - 0.5‰ (1σ). Mount-to-mount reproducibility was 0.29‰ (1σ), estimated as the standard
234 deviation of four $\delta^{18}\text{O}$ values, and obtained by averaging sets of five analyses of a K-feldspar standard
235 ($\delta^{18}\text{O} = 9.3 \pm 0.1\text{‰}$, 1σ) in four different mounts during the session.

236 The IMF of the plagioclase, K-feldspar and quartz $\delta^{18}\text{O}$ SIMS analyses were predicted by response
237 surface methodology (RSM) using the three response surface models described in [Fàbrega et al. \(2017\)](#).
238 The predictor (input) variables were the instrumental parameters X and Y stage position, primary beam
239 intensity (PI), chamber pressure (CP) and, electrostatic deflectors LT1DefX and LT1DefY. In addition,
240 the models for feldspars included the compositional inputs An% (plagioclase model) and Or% and BaO%
241 (K-feldspar model). The IMF was considered as the predicted (output) variable or response. This RSM
242 approach permitted to predict a unique IMF value for each SIMS analysis.

243 The SIMS $\delta^{18}\text{O}$ analyses of unaltered rock were carried out on 2 samples in Guilleries and 2 samples in
244 the Roc de Frausa. On red-stained albitized rock, $\delta^{18}\text{O}$ analyses were also performed on 2 samples in
245 Guilleries and 2 samples in Roc de Frausa. A total of 54 and 90 $\delta^{18}\text{O}$ SIMS analyses were carried out on
246 the Guilleries and Roc de Frausa samples, respectively.

247 **Structure and petrology of the alteration**

248 **Unaltered facies**

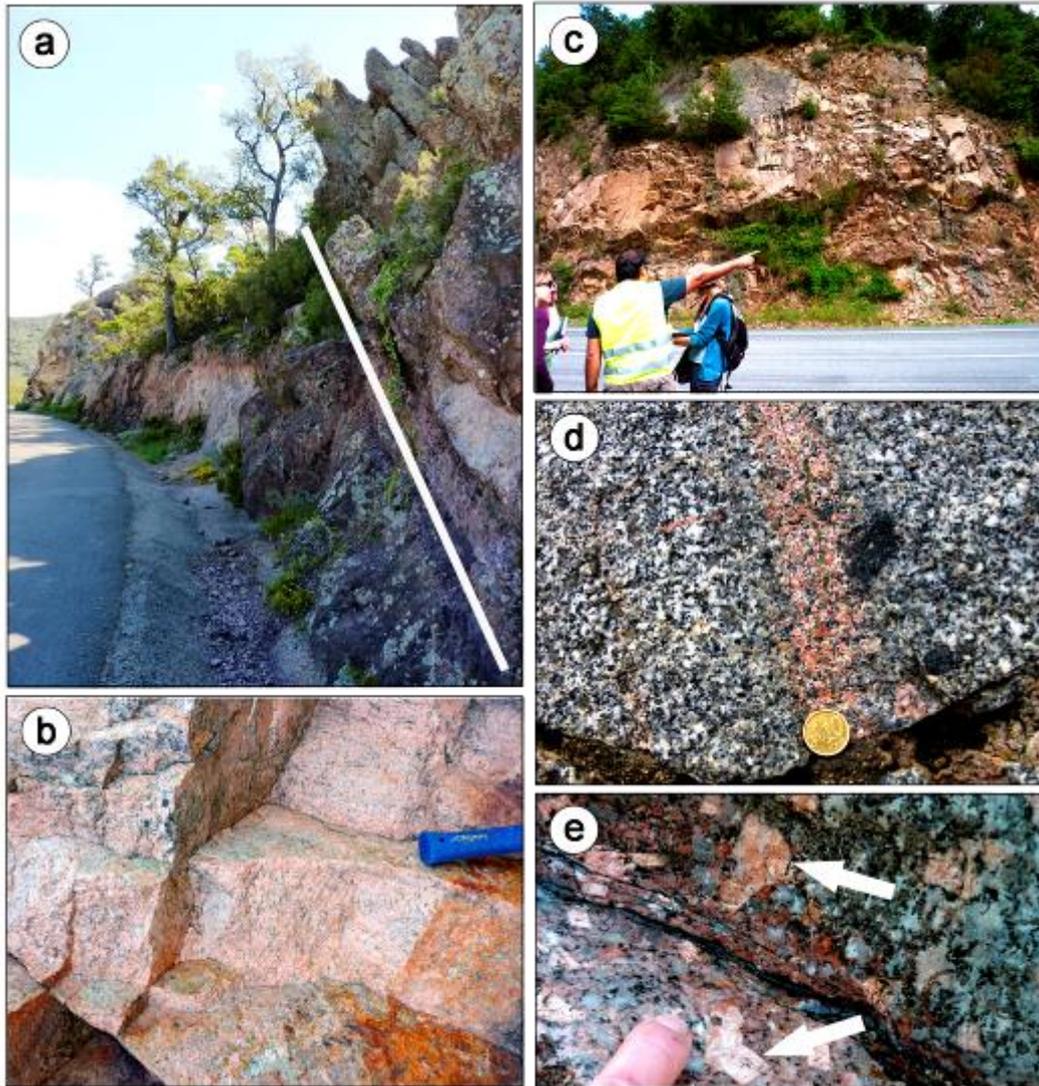
249 The unaltered facies of the Guilleries consists of granodiorite and leucogranite. Primary Ca-plagioclase
250 occurs as euhedral 1 – 3 mm zoned crystals with polysynthetic twinning and yellow-green luminescence.
251 Ca-plagioclase grains have compositions in the core and rim of, respectively, Ab₇₉₋₉₀ and Ab₈₉₋₉₉ in the
252 leucogranite and Ab₆₀₋₉₀ and Ab₉₂₋₉₉ in the granodiorite (Table 2). Primary K-feldspar is orthoclase
253 characterized by subhedral 0.5 - 3 mm crystals with micro and crypto perthite lamellae, blue
254 luminescence and a chemical composition in the range Or₈₄₋₉₆ for both the leucogranite and the
255 granodiorite (Table 2). The porphyritic granite of the Tagamanent area (see Fig. 2b) has white orthoclase
256 phenocrysts (2 - 3 cm) with blue luminescence containing micro and crypto perthite lamellae. Quartz
257 occurs as 0.1 – 2 mm anhedral grains with homogeneous grey SEM-CL and cooling microcracks. Biotite
258 occurs as brown to green 0.1 – 3 mm tabular grains with an Fe/Fe+Mg ratio ranging from 0.82 - 0.84 and
259 0.61 - 0.70 for the leucogranite and the granodiorite, respectively. The accessory minerals are zircon,
260 epidote, apatite-(F), monazite-(Ce) and xenotime. Zircon occurs as 10 – 50 µm zoned euhedral crystals,
261 epidote as euhedral 10 – 30 µm elongated crystals, and apatite as 5 – 20 µm rounded crystals within
262 biotite. Monazite is typically 20 – 50 µm euhedral or rounded grains that commonly reach 200 – 300 µm
263 in size. Xenotime mostly forms euhedral 30 – 50 µm crystals. Magnetite (Fe₃O₄) is the dominant
264 ferromagnetic mineral in the unaltered igneous rocks of the Guilleries Massif (Franke et al., 2010).

265 The unaltered facies in Roc de Frausa is mainly porphyritic granite with K-feldspar phenocrysts (2–3 cm),
266 and this also occurs in the St. Aniol, Hortmoier and Oix areas (Fig. 2c). Primary Ca-plagioclase occurs as
267 zoned euhedral 0.5 – 2 mm crystals with polysynthetic twinning, yellow-green luminescence and a
268 composition in the ranges Ab₆₆₋₇₄ and Ab₉₀₋₉₉ for the Ca-rich cores and the Na-rich zones, respectively
269 (Table 2). The matrix K-feldspar is subhedral to euhedral 0.5 – 2 mm crystals with micro- and crypto
270 perthite lamellae, blue luminescence and a composition of Or₇₄₋₉₈ (Table 2). The K-feldspar phenocrysts
271 (2 – 3 cm) are white orthoclase with blue luminescence, a composition in the range Or₇₀₋₉₀, and micro and
272 crypto perthite lamellae. Quartz is present as 0.5 – 3 mm anhedral crystals with homogeneous SEM-CL
273 and cooling microcracks. Biotite usually occurs as 1 - 3 mm tabular crystals with a Fe/Fe+Mg ratio in the
274 range 0.61 - 0.65. The accessory minerals are euhedral 10 – 50 µm zircon, 5 – 15 µm rounded apatite-(F),

275 euhedral 10 – 30 μm epidote, euhedral or rounded 20 – 40 μm monazite-(Ce), and occasional euhedral
276 20 – 50 μm xenotime.

277 **Red-stained albitized facies**

278 The red-stained albitized facies beneath the Triassic unconformity has the form of a ~150-200 m deep
279 geopetal structure characterized by a decreasing intensity of alteration from the top to the bottom (Fig. 2d,
280 e). The alteration in the upper part is very pervasive and the rock is a red facies (Fig. 3a). The degree of
281 alteration progressively decreases with depth and the rock is a pink facies in the intermediate zone of the
282 profile (Fig. 3b, c). In the lower part of the profile, the red-stained albitization is restricted to the walls of
283 fractures and the rock presents as a ‘spotted’ facies (Fig. 3d, 3e). The fractures controlling alteration in
284 the lower parts of the profile are likely to have developed by pre-existing cooling and decompression of
285 the granitic mass. In the upper part of the profile, closer to the unconformity, more pervasive alteration
286 was accomplished via a greater abundance of joints and fractures together with micro-fractures and grain
287 boundaries penetrating the matrix of the rock. Here, effective fluid pathways could also have
288 progressively self-generated through reaction-induced hierarchical fracturing (Røyne et al., 2008;
289 Jamtveit et al., 2009).

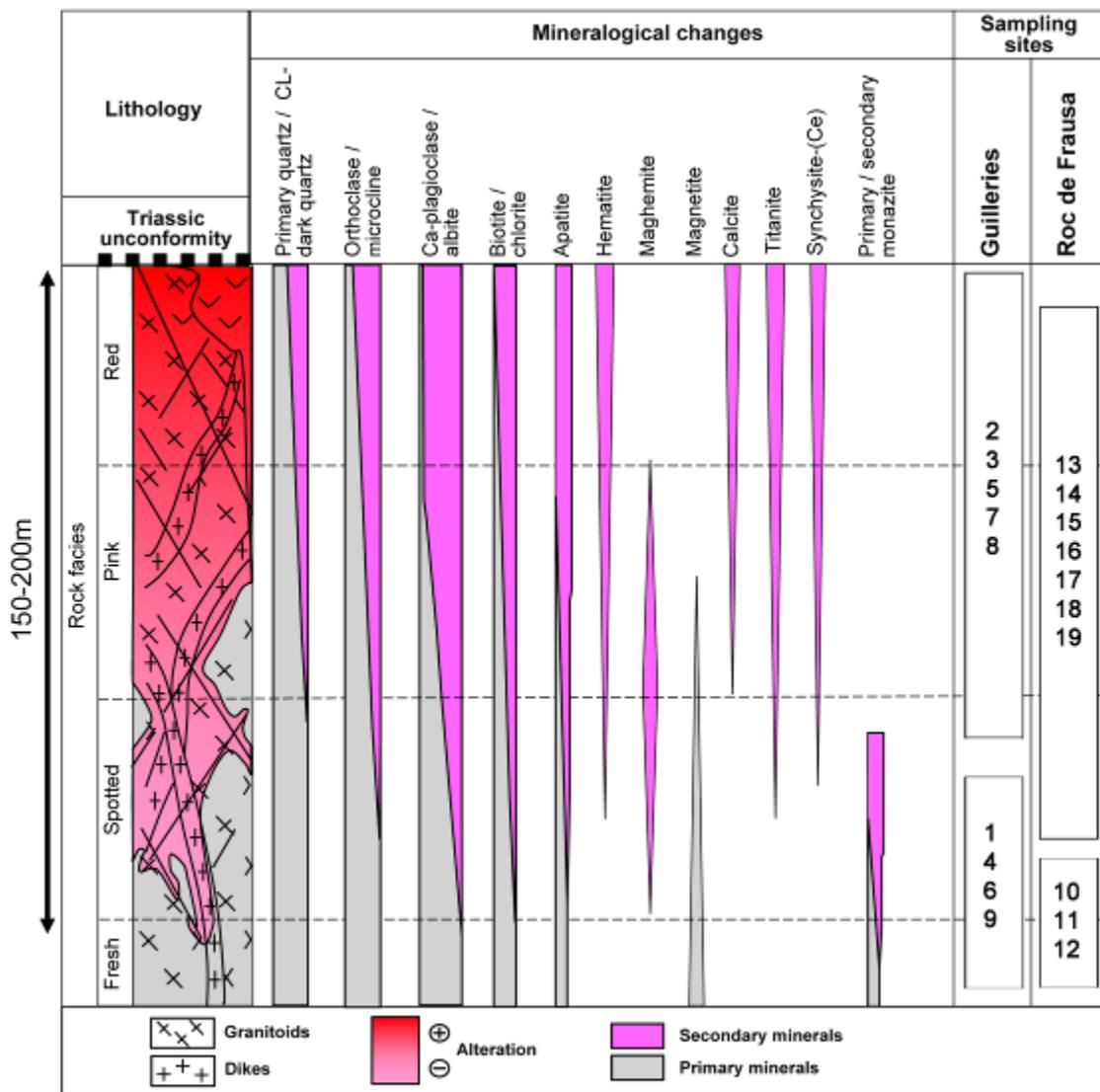


290

291 **Fig. 3.** Red stained albitized facies. (a) Red albitized porphyritic granite (lower left) unconformably overlain by
 292 south-dipping Upper Cretaceous (Maastrichtian) red-beds (upper right). Boadella dam, Roc de Frausa massif.
 293 (b) Pervasively albitized pink porphyritic granite near the top of the profile. Boadella dam, Roc de Frausa massif. (c)
 294 Completely albitized red - pink granodiorite in the upper part of the profile. Mas Vidal area, Guilleries massif.
 295 (d) Red albitization along fractures (coin) through unaltered granite in the bottom of the profile. Sau dam, Guilleries
 296 massif. (e) Red albitization along fractures including microclinized pink orthoclase phenocrysts (white arrows) in the
 297 lower part of the profile. Hortmoier area.

298 The nature of Fe-oxides evolves within the profile. Hematite (Fe_2O_3) dominates in the red facies of the
 299 upper part of the profile (Fig. 4), indicating stronger oxidizing conditions. Hematite crystals are micron-
 300 sized and occur inside the microporosity of secondary feldspars, suggesting that they formed by fluid-
 301 rock interaction rather than feldspar exsolution (Putnis et al., 2007). Hematite is considered to have
 302 formed by both the alteration of maghemite and authigenic precipitation. The composition of hematite in

303 the red facies is about Ilmenite₁₀ Geikielite₁ Pyrophanite₁ and Hematite₈₈, probably reflecting the
 304 introduction of Ti released during biotite chloritization into the hematite structure. The concentration of
 305 maghemite ($\gamma\text{-Fe}_2\text{O}_3$) increases with depth (Fig. 4), indicating progressively decreasing oxidizing
 306 conditions. Maghemite is considered to have formed by oxidation of primary magnetite and by authigenic
 307 precipitation at low temperature (Franke et al., 2010).



308

309 **Fig. 4.** Evolution of the albitized facies and the mineralogy of the profile. Numbers correspond to sampling sites
 310 presented in Fig. 2. Adapted from Yao (2013).

311

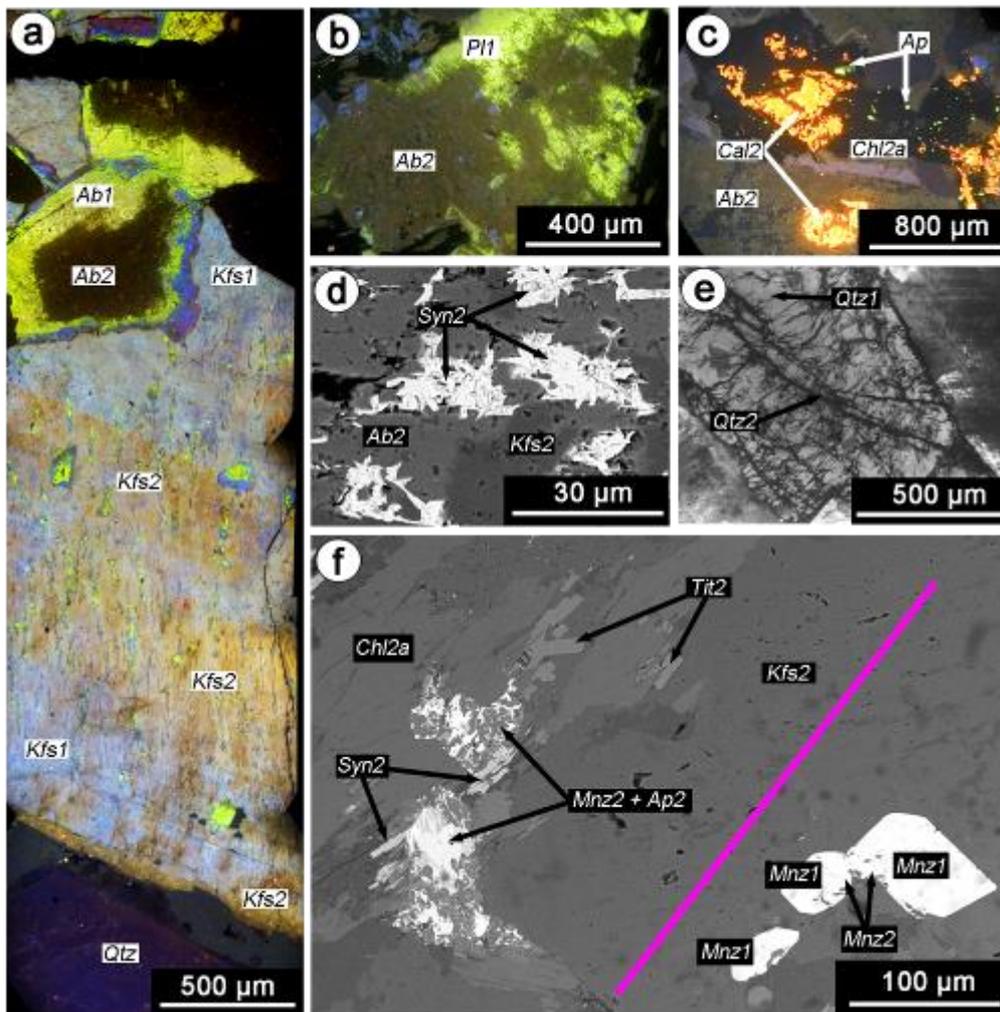
312 The reactions that affect the major minerals are albitization of Ca-plagioclase, chloritization of biotite,
 313 microclinization of orthoclase, and the alteration of igneous quartz to secondary CL-dark quartz (Fig. 4).

314 Primary Ca-plagioclase is pseudomorphosed by secondary albite. Albitized plagioclase grains (Fig. 5a, b,
315 c) have a turbid aspect, a lack of luminescence, widespread micron-sized non-connected euhedral porosity
316 (Fig. 5d) and a very pure chemical composition in the range of Ab₉₇₋₉₉ (Table 2). The replacement front
317 between the primary Ca-plagioclase and the secondary albite is very sharp (Fig. 5b), and the
318 crystallographic framework is preserved from the primary to the secondary phase. These textural features
319 are typical of a fluid-aided dissolution-reprecipitation process along micro-fractures without development
320 of dissolution pores prior to precipitation (Putnis, 2002; Engvik et al., 2008; Putnis, 2009). The albitized
321 plagioclase grains usually contain micron-sized non-luminescent secondary K-feldspar and orange-CL
322 calcite (Fig. 5c), the latter with a composition about Magnesite_{1.5} Siderite_{0.7} Calcite_{97.8}. The primary
323 green-yellow luminescent Na-rich rims of plagioclase, with the composition Ab₉₀₋₉₃, are preserved during
324 albitization (Fig. 5a).

325 Primary biotite is pseudomorphosed by secondary chlorite. Chloritized biotite is non-luminescent,
326 preserves the biotite sheet structure and usually contains lens-shaped inclusions of secondary K-feldspar,
327 quartz and orange-CL calcite (Fig. 5c). The composition of the calcite inclusions formed inside chlorite is
328 about Magnesite_{2.4} Siderite_{3.2} Calcite_{94.3}, reflecting a higher content of Mg and Fe released from primary
329 biotite during chloritization than available to the calcite inclusions formed within secondary feldspars.
330 The chloritized biotite grains systematically show a significant increase of yellow luminescent micron-
331 sized fluorapatite inclusions (Fig. 5c). In places, neofomed chlorite occurs in sheaf like arrangements of
332 micron-size sheets inside the micro porosity.

333 The microclinization of orthoclase is characterized by the recrystallization of primary orthoclase to
334 secondary microcline. The microclinized grains have a cloudy aspect, loss of luminescence (Fig. 5a), a
335 widespread micron-sized non-connected euhedral porosity, amoeboid-shaped patchy perthite texture and
336 a composition of about Or₉₆₋₉₉ and Or₈₇₋₉₃ in the Guilleries and Roc de Frausa, respectively (Table 2). The
337 patch perthite exclusively forms during the microclinization process and implies replacement of K-
338 feldspar by secondary albite. K-feldspar phenocrysts (2 – 3 cm) in the porphyritic granites progressively
339 change from the white color of the primary orthoclase to brown and finally red-pink as the degree of
340 microclinization increases. The most strongly microclinized phenocrysts have a composition (XRD) of
341 about 40 - 60% microcline, 20 - 30% albite and 10 - 40% orthoclase. The albite detected by XRD inside
342 the red-pink phenocrysts includes the patch perthite and plagioclase inclusions that were albitized during
343 microclinization.

344 The net of micro fractures in the red-stained albitized rocks is sealed by secondary CL-dark quartz that
 345 postdates the aforementioned reactions. Within quartz grains, this net of micron sized CL-dark quartz has
 346 a dendritic texture (Fig. 5e), suggesting that it propagated along sub-micron cracks and dislocations and
 347 may possibly record some degree of dissolution-precipitation process of the primary quartz.
 348



349
 350 **Fig. 5.** Cathodoluminescence and SEM petrography of the albitized facies. (a) Pink albitized granite near the top of
 351 the profile. Albitized plagioclase grains display non-luminescent albitized cores (Ab2) and preserve a primary Na-rich
 352 CL-yellow rim (Ab1) in contact with a K-feldspar grain with primary CL-blue zones (Kfs1) and CL-turbid
 353 microclinized areas (Kfs2). (b) CL-yellow primary plagioclase (Pl1) partially pseudomorphed by non-luminescent
 354 secondary albite (Ab2) penetrating along twin planes and micro fractures. (c) CL-image of very strongly albitized red
 355 granite at the top of the profile. Patches of secondary CL-orange calcite (Cal2) inside non-luminescent albitized
 356 plagioclase (Ab2) and chloritized biotite (Chl2a). Chloritized biotite also shows significant yellow apatite inclusions
 357 (Ap) compared with primary biotite. (d) BSE-image of clusters of synchysite-(Ce) ‘sticks’ inside the secondary

358 porosity of albitized plagioclase (*Ab*₂) and microclinized orthoclase (*Kfs*₂). (e) SEM-CL picture of igneous quartz
359 grain from the upper part of the profile showing a dendritic net of CL-dark secondary quartz (*Qtz*₂). Patches of
360 primary quartz (*Qtz*₁) are preserved. (f) BSE-image showing alteration of monazite in the reaction front
361 approximately indicated by the pink line. Left, monazite pseudomorphosed by secondary monazite (*Mnz*₂) and
362 apatite (*Ap*₂) and accompanied by euhedral synchysite (*Syn*₂) and titanite (*Tit*₂). Right, primary monazite grains
363 (*Mnz*₁) mostly preserved but showing some pseudomorphic secondary monazite (*Mnz*₂) in the boundaries. *Chl*_{2a}:
364 Chloritized biotite; *Kfs*₂: Microclinized orthoclase.

365 Authigenic synchysite-(Ce) [Ca(Ce, La)(CO₃)₂F] is the dominant REE-mineral in the red-stained albitized
366 rocks (Fig. 4) and its abundance decreased from the top to the bottom of the profile. It usually occurs in
367 clusters of 5-15 µm stick-shaped crystals inside the secondary micron-sized porosity of the albitized
368 plagioclase, microclinized orthoclase and chloritized biotite (Fig. 5d), strongly suggesting coeval
369 formation with these secondary minerals. Synchysite-(Ce) is mostly Th-poor (0 - 4.68 wt% Th [CO₃]₂)
370 with 33 to 54 wt% of *LREE*₂O₃ and 1.6 to 5.5 wt% of Y₂O₃ + *HREE*₂O₃. The Ca content (wt. % CaCO₃)
371 of Synchysite-(Ce) decreases from 29-32% at the top of the profile (n= 9) to 22-23% at the bottom (n=
372 10).

373 Monazite is strongly altered in the red and pink facies of the upper part of the profile, where the grains are
374 completely pseudomorphosed by apatite and quartz inside a millimetre-scale zone adjacent to the reaction
375 front (Fig. 5f). The secondary monazite shows evidence of dissolution-precipitation mechanisms
376 including corroded boundaries, fracturing, and secondary micron-sized porosity (see for example Putnis,
377 2002, 2009). The pseudomorphosed monazite grains are usually accompanied by micron sized authigenic
378 titanite, and synchysite (Fig. 5f).

379 The alteration of all silicates and non-silicates, namely albitization of Ca-plagioclase, microclinization of
380 orthoclase, chloritization of biotite, and precipitation of secondary CL-dark quartz, iron oxides and REE-
381 minerals, decreases from the top to the bottom of the profile (Fig. 4). In the same context, the succession
382 of mineral alteration adjacent to fractures decreases in intensity towards the cores of the granite blocks.
383 Decimetre-thick alteration zones occur adjacent to the major fractures, with restricted millimetre-thick
384 zones walls adjacent to secondary fractures, and less along micro-cracks. These relationships point clearly
385 to the influence of fluid circulation. As well, albitization was not associated with a volume change, i.e. the
386 texture and fabric of the altered rocks is not significantly different from that of the unaltered rocks, at
387 least at a macroscopic level.

388 **Table 2. Representative composition of feldspars in the Guilleries and Roc de Frausa Massifs**

| massif | unaltered rock | | | red albitized rock | |
|---------------|--------------------------|--------------------------|---------------------|-------------------------------|----------------------------------|
| | plagioclase core (n= 86) | plagioclase rim (n= 100) | k-feldspar (n= 57) | albitized plagioclase (n= 95) | microclinized k-feldspar (n=126) |
| Guilleries | Ab ₆₀₋₉₀ | Ab ₈₉₋₉₉ | Or ₈₄₋₉₆ | Ab ₉₇₋₉₉ | Or ₉₆₋₉₉ |
| Roc de Frausa | Ab ₆₆₋₇₄ | Ab ₉₀₋₉₉ | Or ₇₄₋₉₈ | Ab ₉₇₋₉₉ | Or ₈₇₋₉₃ |

389

390 **Geochemical characteristics of the alteration**

391 **Mass balance**

392 The evaluation of element mobility during fluid-rock interaction can be referred to an “immobile”
 393 geochemical framework (Ague and van Haren, 1996). This is usually undertaken using one or more
 394 ostensibly immobile elements that are ideally concentrated in minerals that do not change during fluid-
 395 rock interaction and that present a low analytical uncertainty (Beinlich et al., 2010).

396 To estimate the mass changes caused by albitization (Table 3), the concentrations of the elements in the
 397 albitized rock samples were recalculated with respect to Zr, considered as an immobile reference.
 398 Petrographic observations show that zircon grains in the albitized rocks remain mostly unchanged from
 399 those in the unaltered facies.

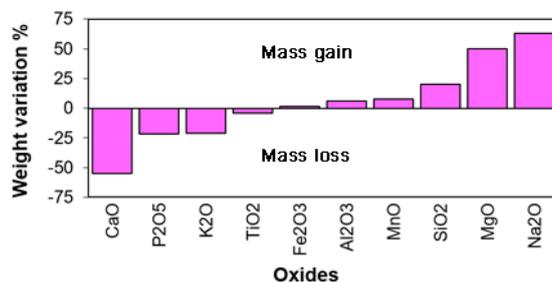
400 **Table 3. Mass balance between the unaltered and red-stained albitized rocks.**

| rock | n | averaged major elements concentrations (wt. %) | | | | | | | | | |
|---------------|---|--|------------------|-------------------------------|------------------|--------------------------------|------|--------------------------------|------------------|------|-------------------|
| | | CaO | K ₂ O | P ₂ O ₅ | TiO ₂ | Fe ₂ O ₃ | MnO | Al ₂ O ₃ | SiO ₂ | MgO | Na ₂ O |
| unaltered | 4 | 2.67 | 4.18 | 0.14 | 0.49 | 3.64 | 0.08 | 15.96 | 66.91 | 1.27 | 2.83 |
| red albitized | 3 | 1.06 | 2.38 | 0.12 | 0.46 | 3.63 | 0.08 | 17.01 | 78.41 | 1.64 | 5.40 |
| variation % | | -60 | -43 | -19 | -5 | -0.3 | -2 | +7 | +17 | +29 | +91 |

401

402 Petrographical observations of the red-stained albitized rocks show that albitization of plagioclase,
 403 microclinization of K-feldspar, and chloritization of biotite are intimately linked to the precipitation of
 404 secondary synchysite-(Ce), apatite, epidote, calcite and hematite that probably recycled some of the ions
 405 released by the major reactions. Consistent with the albitization of primary plagioclase, the amount of Na
 406 in the albitized rock presents a mass increase of about +91%, and a Ca loss of -60% (Fig. 6). By
 407 considering the atomic mass of Na and Ca, this means that only about half of the Ca released by
 408 replacement of plagioclase by albite has been removed from the system. The remnant Ca was likely

409 recycled into secondary synchysite-(Ce), apatite, epidote, and calcite. The K content presents a significant
 410 reduction of -43% (Fig. 6), which is consistent with the systematic biotite chloritization and some K-
 411 feldspar albitization. A fraction of the K is probably retained by the secondary K-feldspar lenses within
 412 chloritized biotite and micron-size patches of perthite in the albitized plagioclase. Mg presents a
 413 significant increase of +30% (Fig. 6). The Si content increases by about +17%, which agrees with the
 414 overall albitization of plagioclase (Fig. 6). Al released during albitization of plagioclase may have been
 415 consumed during chloritization of biotite and the formation of secondary K-feldspar. However, the
 416 albitization reflects an overall increase in Al of +7%. The Fe content remains stable (Fig. 6). The Fe
 417 released during chloritization of biotite was probably retained to form the secondary Fe-oxides. The
 418 amount of Ti decreased about -5% (Fig. 6), most of it probably released during chloritization of biotite
 419 and partly retained in secondary titanite. The variation in Mn shows a loss of -2% (Fig. 6). The loss of P
 420 was about -19% (Fig. 6), mostly due to the dissolution of monazite in the albitized profile. Some of the P
 421 participated in the formation of secondary fluorapatite in combination with F released during
 422 chloritization of biotite.



423

424 **Fig. 6.** Weight variation (%) diagram of the major elements in the red-stained albitized facies vs. unaltered rocks.
 425 Positive variation indicates an increase in the element concentration in the albitized facies with respect to the
 426 unaltered rocks.

427 $\delta^{18}\text{O}$ composition

428 *Primary minerals in the unaltered rocks*

429 The oxygen isotope compositions of primary feldspars and quartz were determined on unaltered
 430 leucogranite of the Guilleries Massif and porphyritic granite of the Roc de Frausa Massif and Hortmoier
 431 area (Fàbrega et al., 2016).

432 In the leucogranite of the Guilleries Massif, the zoned plagioclase has $\delta^{18}\text{O}$ values ranging from 8.52 to
 433 9.51‰ in the Ca-bearing cores and 11.14 to 11.93‰ in the Na-rich rims (Table 4), showing a positive

434 correlation of $\delta^{18}\text{O}$ values with increasing sodic composition (Fig. 7a). Primary K-feldspar grains have
 435 $\delta^{18}\text{O}$ values ranging from 10.42 to 11.65‰ (Table 4), without any correlation with the primary K-feldspar
 436 composition (Fig. 7b). Primary quartz has a $\delta^{18}\text{O}$ composition between 6.4 and 9.60‰ (Table 4). In the
 437 Tagamanent area (see Fig. 2b), the $\delta^{18}\text{O}$ of the K-feldspar phenocrysts is between 10.6 and 10.8‰, close
 438 to the mean value of the primary matrix K-feldspar grains in the Guilleries samples.

439 **Table 4. $\delta^{18}\text{O}$ (‰) of feldspars and quartz in the Guilleries and Roc de Frausa Massifs**

| massif | unaltered rock | | | | red albitized rock | | |
|---------------|--------------------|-------------------|-------------|-----------|-----------------------|--------------------------|----------------|
| | plagioclase (core) | plagioclase (rim) | k-feldspar | quartz | albitized plagioclase | microclinized k-feldspar | CL-dark quartz |
| Guilleries | 8.5 – 9.5 | 11.1–11.9 | 10.4 – 11.7 | 6.4 – 9.6 | 10.3 - 11.6 | 11.8 – 13.8 | * |
| Roc de Frausa | 7.2 – 9.5 | 9.9 – 12.0 | 11.5 – 12.4 | 7.4 | 11.1 – 12.8 | 12.3 – 14 | 12.0 |

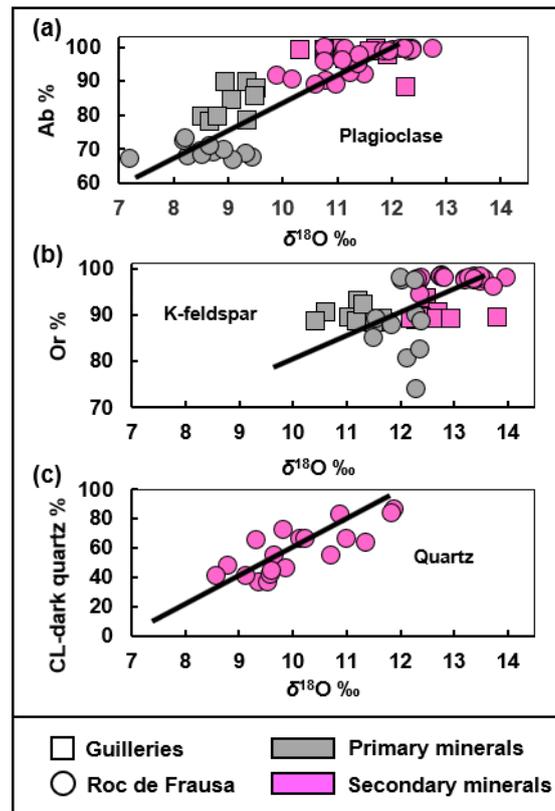
440

441 In the porphyritic granite of the Roc de Frausa Massif, $\delta^{18}\text{O}$ values for the primary plagioclase range
 442 between 7.18 and 9.45 in the Ca-rich cores and 9.88 to 11.94‰ in the Na-rich rims (Table 4), displaying a
 443 positive correlation of $\delta^{18}\text{O}$ values with the increase of sodium content (Fig. 7a). The primary K-feldspar
 444 grains in the granitic matrix have $\delta^{18}\text{O}$ values ranging from 11.50 to 12.39‰ (Table 4) and do not show
 445 any correlation with the K-feldspar composition (Fig. 7b). In the porphyritic granite of Hortmoier area,
 446 primary K-feldspar phenocrysts have steady $\delta^{18}\text{O}$ values ranging from 11.4 to 11.6‰, near the mean
 447 value of the primary matrix K-feldspar grains in the Roc de Frausa samples,

448 In the Guilleries, Roc de Frausa and Hormoier, the $\delta^{18}\text{O}$ compositions of the primary feldspars are
 449 consistent with high $\delta^{18}\text{O}$ crustal-derived magmas and follow the expected higher values in $\delta^{18}\text{O}$
 450 composition in the alkali feldspars characterized by *Anorthite* $\delta^{18}\text{O} < \text{K-feldspar} \approx \text{Albite}$ $\delta^{18}\text{O}$
 451 (Bindeman, 2008).

452 The oxygen isotope fractionation between primary plagioclase and K-feldspar ($\Delta^{18}\text{O}_{\text{Ab-Kfs}}$) were about
 453 +0.5‰ and -0.5‰ for the Guilleries and Roc de Frausa, respectively, suggesting that, within error,
 454 primary feldspars formed under equilibrium conditions (Fig. 8a). The oxygen isotope fractionation
 455 between primary quartz and primary plagioclase ($\Delta^{18}\text{O}_{\text{Qz-Pl}}$) are negative, with values about -3 and -4‰
 456 for the Guilleries and Roc de Frausa, respectively (Fig. 8b). In the case of the quartz and primary K-
 457 feldspar ($\Delta^{18}\text{O}_{\text{Qz-Kfs}}$) fractionation, values are also negative about -3 and -5‰ for the Guilleries and Roc
 458 de Frausa, respectively (Fig. 8c). These negative fractionation values of plagioclase and K-feldspar with

459 respect to quartz are reversed and indicate that the feldspars and quartz formed under disequilibrium
 460 conditions.



461

462 **Figure 7.** Plots of $\delta^{18}\text{O}$ values vs. mineral composition. (a) $\delta^{18}\text{O}$ values vs. plagioclase composition (Ab%). (b) $\delta^{18}\text{O}$
 463 vs. K-feldspar composition (Or%). (c) $\delta^{18}\text{O}$ values vs. the percentage of CL-dark quartz estimated in the craters of
 464 quartz SIMS analyses. The $\delta^{18}\text{O}$ values of the primary and secondary CL-dark quartz correspond to the regression at
 465 0 and 100%, respectively. These estimated values were rounded to the unit. Squares= Guilleries massif and circles =
 466 Roc de Frausa massif. Grey symbols = primary minerals and pink symbols = secondary minerals.

467 *Secondary minerals of the red-stained albitized rocks*

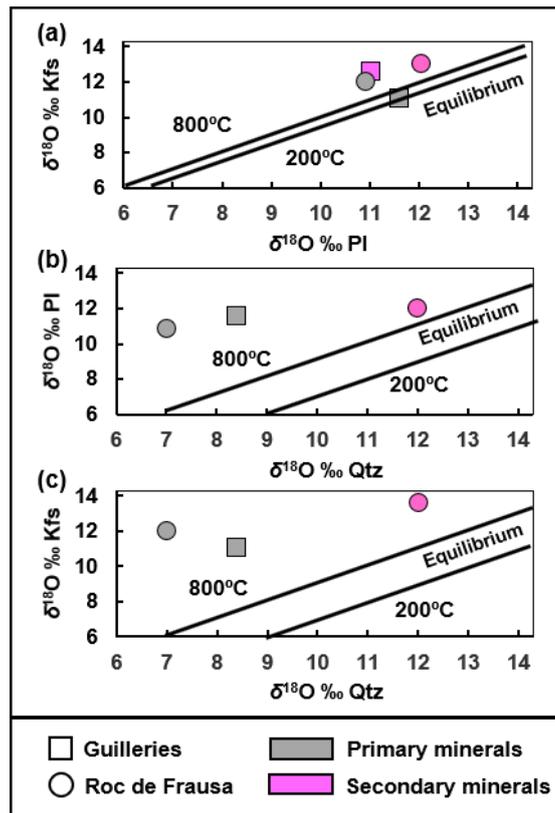
468 The $\delta^{18}\text{O}$ composition of the secondary feldspars and quartz of the red-stained rocks is higher than that for
 469 the respective primary phases, and significantly, each phase has similar values across the Guilleries and
 470 Roc de Frausa.

471 Albitized plagioclase from Guilleries has $\delta^{18}\text{O}$ ranging from 10.31 to 11.60‰ (Table 4), representing an
 472 average increase about +2‰ with respect to the $\delta^{18}\text{O}$ of the primary Ca-bearing plagioclase cores
 473 (Fig. 7a). At the Roc de Frausa, $\delta^{18}\text{O}$ values for albitized plagioclase range from 11.14 to 12.75 ‰ (Table
 474 4), an average increase about +2.5‰ compared to the primary Ca-rich plagioclase cores (Fig. 7a).

475 The microclinized orthoclase of Guilleries has $\delta^{18}\text{O}$ values ranging from 11.76 to 13.81‰ (Table 4), an
476 average increase about +1.5‰ compared with the primary orthoclase (Fig. 7b). At Roc de Frausa, the
477 $\delta^{18}\text{O}$ composition of microclinized orthoclase ranges from 12.31 to 13.96‰ (Table 4), an average
478 increase about +1‰ compared to the primary orthoclase (Fig. 7b).

479 SEM-CL images of secondary quartz in Roc de Frausa samples showed that the SIMS craters presented a
480 mix of primary and secondary CL-dark quartz. The percentage of secondary CL-dark quartz was
481 estimated using CAD software and the $\delta^{18}\text{O}$ values were plotted against it and regressed to estimate the
482 $\delta^{18}\text{O}$ in both primary and CL-dark secondary quartz (Fig. 7c). Using this method, the primary quartz and
483 secondary CL-dark quartz were estimated to have $\delta^{18}\text{O}$ values of about 7.5‰ and 12‰, respectively
484 (Table 4), representing an estimated increase of about +4.5‰ for the secondary with respect to the
485 primary quartz.

486 The $\delta^{18}\text{O}$ values of secondary feldspars and quartz in both massifs indicate disequilibrium fractionation
487 values ($\Delta^{18}\text{O}$) for the mineral pairs. The oxygen isotope fractionation between secondary albite and
488 microclinized orthoclase ($\Delta^{18}\text{O}_{\text{Ab2-Kfs2}}$) presents disequilibrium values about -1.8‰ and -1.6‰ for the
489 Guilleries and Roc de Frausa, respectively (Fig. 8a). In the Roc de Frausa samples, the oxygen isotope
490 fractionation between CL-dark secondary quartz and albitized plagioclase ($\Delta^{18}\text{O}_{\text{Qtz2-Ab2}}$) is about 0.4‰
491 (Fig. 8b), and between CL-dark secondary quartz and microclinized orthoclase ($\Delta^{18}\text{O}_{\text{Qtz2-Kfs2}}$) is about -
492 1.2‰ (Fig. 8c).



493

494 **Fig. 8.** δ - δ plots of primary and secondary mineral pairs of each massif. (a) Primary plagioclase vs. primary K-
 495 feldspar and secondary albite vs. secondary microclinized K-feldspar. (b) Primary plagioclase vs. primary quartz
 496 (grey) and albitized plagioclase vs. CL-dark quartz (pink). (c) Primary K-feldspar vs. primary quartz (grey) and
 497 microclinized orthoclase vs. CL-dark quartz (pink). The equilibrium fractionations at equilibrium of each mineral pair
 498 were calculated for 200 and 800 °C using the equations of Zheng (1993).

499 Geochronology

500 K-Ar dating of K-feldspar phenocrysts

501 K-Ar dating was carried out on K-feldspar phenocrysts collected in unaltered and red albitized rocks from
 502 Hortmoier (see Fig. 2c). In unaltered rocks, the white primary orthoclase yielded a K-Ar age of
 503 283 ± 10 Ma (2σ), which is consistent with the closure of the K-Ar system during magmatic cooling. Solé
 504 et al. (2002) obtained similar $^{40}\text{Ar}/^{39}\text{Ar}$ ages of 276 and 269 Ma for primary orthoclase from the
 505 Montnegre Massif (see Fig. 1) and considered them to register the time of magmatic cooling.

506 In the red albitized rocks, brown K-feldspar phenocrysts from albitized fracture walls (see Fig. 3e),
 507 represent a degree of microclinization of 30-40% and yielded K-Ar ages of 244.5 ± 6 , 237.6 ± 6 , and
 508 230.7 ± 6 Ma (2σ). The textural similarities and the overlapping of the three ages within the 2σ range

509 support a probable K-Ar resetting event during the Early Triassic. Given that these microclinized brown
510 K-feldspar phenocrysts occur near the reaction front (see Fig. 3e) and are accompanied by partially
511 albitized plagioclase and chloritized biotite, these Early Triassic dates are considered to constrain the age
512 of the alteration in these red fracture facies in the lower part of the albitized profile.

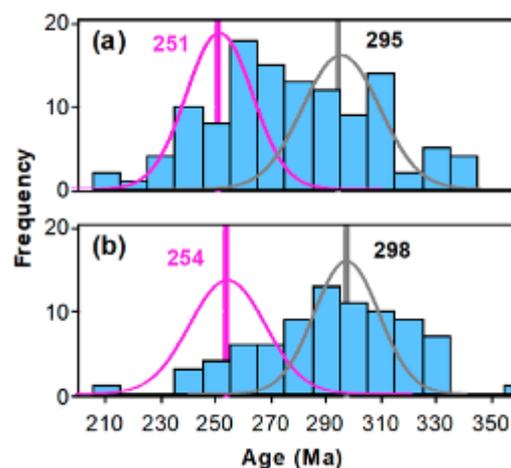
513 In the same locality, the red albitized granite commonly has braided networks of millimetric calcite-filled
514 fractures that cross-cut and thus post-date the albitized plagioclase, microclinized K-feldspar, chloritized
515 biotite and altered quartz grains. K-feldspar phenocrysts in these samples, characterized by intense pink
516 color, yielded K-Ar ages of 216.2 ± 6 , 175.9 ± 5 , 174.8 ± 5 , and 164.0 ± 5 Ma (2σ). These Late Triassic-
517 Early Jurassic ages may record an alteration that registers local resets of the K-Ar system relating to the
518 formation of the calcite-filled fractures.

519

520 **Monazite U-Th-Pb_{total} dating**

521 EPMA U-Th-Pb_{total} dating was carried out on primary monazite grains in the unaltered rocks and on
522 pseudomorphous secondary monazite associated with the reaction front in the red-stained albitized rocks.

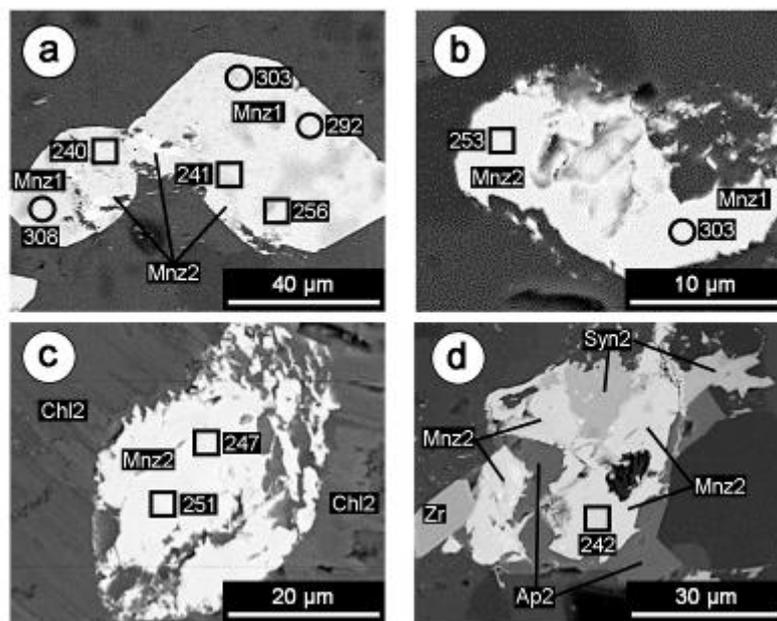
523 In the Guilleries Massif (Fig. 9a), the deconvolution of the histogram of the U-Th-Pb_{total} analyses
524 ($n = 117$) yielded two significant ages of 251.2 ± 12 and 295.2 ± 14 Ma (2σ), with a relative misfit of
525 0.925. The histogram deconvolution of the analyses ($n = 80$) of the Roc de Frausa Massif (Fig. 9b) also
526 indicates the existence of two significant ages of 254 ± 14 and 298 ± 12 Ma (2σ), presenting a relative
527 misfit of 0.966.



528

529 **Fig. 9.** Deconvoluted histograms of the U-Th-Pb_{total} monazite dates. **(a)** Guilleries Massif. **(b)** Roc de Frausa Massif.
 530 Grey vertical lines= Carboniferous – Permian ages. Pink vertical lines= Permian-Triassic ages. The two graphs **(a, b)**
 531 use the same X scale.

532 The distribution of the individual U-Th-Pb_{total} dates shows a clear relationship to the degree of albitization
 533 of the rock and the nature of the monazite grains. The analyses of primary monazite in the unaltered rocks
 534 systematically indicate Carboniferous-Permian dates, which are consistent, within error, with the ages of
 535 magmatic cooling of the granitoids reported by [Martínez et al. \(2008\)](#) and [Aguilar et al. \(2014\)](#) in the
 536 Guilleries and Roc de Frausa, respectively. These primary Carboniferous-Permian dates are also obtained
 537 in the relicts of primary monazite situated inside the monazite grains pseudomorphosed by secondary
 538 monazite ([Fig. 10a](#)). Differently, the analyses on the pseudomorph secondary monazite that formed in
 539 the albitized rocks near the reaction front ([Fig. 10a, b, c, d](#)) presented Permian-Triassic dates.



540
 541 **Fig. 10.** BSE-images of monazite grains situated near the reaction front from the Guilleries Massif. Circles: position
 542 of U-Th-Pb_{total} analyses that yielded primary Carboniferous-Permian ages. Squares: position of U-Th-Pb_{total} analyses
 543 that yielded Permian-Triassic ages. **(a)** Euhedral and rounded grains of primary monazite with incipient secondary
 544 monazite in some of the external boundaries. **(b)** Monazite grain with primary and secondary domains. **(c)** Primary
 545 monazite grain completely pseudomorphosed by secondary monazite. **(d)** Monazite grain pseudomorphosed by
 546 monazite, apatite and synchysite and surrounded by euhedral synchysite and apatite. *Ap2: Secondary apatite; Chl2:*
 547 *chloritized biotite; Kfs2: Microclinized orthoclase; Mnz1: Primary monazite; Mnz2: Secondary pseudomorph*
 548 *monazite; Qtz: Quartz; Syn2: secondary synchysite; Zr: zircon.*

550 Discussion

551 Age of the red-stained albitized profile

552 The microclinized orthoclase and secondary pseudomorphic monazite in the red-stained albitized rocks
553 have K-Ar and U-Th-Pb ages around 240 and 250 Ma, respectively, indicating that the alteration probably
554 developed between the Late Permian and the Early Triassic. The younger K-Ar ages for microclinized
555 orthoclase may indicate ^{40}Ar loss during alteration because of the development of dislocation-rich
556 microtextures like e.g., patchy perthites (Worden et al., 1990; Mark et al., 2008): the actual K-Ar age
557 could be slightly older. Consistent with this possibility is the BSE observation that the dated K-feldspar
558 phenocrysts have a significant component of patch perthite that could have acted as ^{40}Ar diffusion
559 pathways. An alternative possibility is that the 240 Ma K-Ar age is geologically meaningful and that the
560 alteration was ongoing in the red-stained upper part of the profile until 240 Ma, while the pseudomorphic
561 monazite occurring at the lower albitization reaction front ceased earlier at around 250 Ma at depth. This
562 does not accord with a common weathering profile evolution that becomes deeper with time, but in the
563 Triassic geodynamic context, it may respond to a water table that rose in concert with the overall
564 transgression.

565 The Permian-Triassic age of the alteration is also supported by preliminary studies of Early Triassic
566 remagnetization of the secondary hematite and maghemite in the red-stained albitized profile of the
567 Guilleries (Franke et al., 2010; Parcerisa et al., 2010a). The suggested age is also consistent with the
568 capping of the red-stained albitized profile by Lower Triassic red-beds, clearly post-dating the alteration,
569 in the southern area of the Guilleries Massif and the Tagamanent zone (see Fig. 2a, c).

570 All the age determinations using independent methods are coherent and point to the albitization and
571 related alteration having developed during the Late Permian to Early Triassic, while the Variscan granites
572 in NE Spain were exposed at the landsurface (López-Gómez et al., 2005; Linol et al., 2009; Galán-
573 Abellán et al., 2013). Thus, the red-stained albitization relates to the Triassic palaeosurface, and its
574 geopetal organization indicates that alteration of the granites most probably occurred under the influence
575 of palaeogeography, climate, weathering, and groundwater.

576 **$\delta^{18}\text{O}$ fluid-rock exchange during albitization**

577 The minerals in both the unaltered and red albitized rocks have $\delta^{18}\text{O}$ values that implicate fluid-rock
578 oxygen-isotope exchange processes during albitization. For example:

579 (1) All secondary phases in the red-stained albitized rocks (albitized plagioclase, microclinized
580 orthoclase and CL-dark quartz) have higher $\delta^{18}\text{O}$ values compared to their primary counterparts
581 in the unaltered rocks.

582 (2) The reactions follow this sequence: (a) albitization of plagioclase, (b) microclinization of
583 orthoclase and (c) formation of CL-dark quartz, and partially overlapped over time. The $\delta^{18}\text{O}$
584 values of the secondary phases are in disequilibrium, suggesting that the minerals re-equilibrated
585 with fluid with a changing $\delta^{18}\text{O}$ and/or temperature throughout the reaction sequence.

586 (3) The widespread and uniform character of the red-stained albitized rocks suggests that the
587 alteration developed under long-lasting stable physico-chemical conditions, and that mineral
588 reactions approached an equilibrium with oxygen isotopes in the fluid.

589 If the water-rock oxygen isotope exchange approaches equilibrium (i.e. forward and backward isotopic
590 exchange occurs between the rock and fluid), the oxygen isotope composition of the fluid after re-
591 equilibration with the rock (or a given mineral) can be estimated using a mass-balance equation (Taylor,
592 1977), by (Eq. 1):

$$\delta^{18}\text{O}_f^w = \delta^{18}\text{O}_i^w + \frac{R}{W} \times (\delta^{18}\text{O}_i^m - \delta^{18}\text{O}_f^m) \quad (1)$$

593 $\delta^{18}\text{O}_f^w$ and $\delta^{18}\text{O}_i^w$ being the initial and final oxygen isotope compositions of fluid, respectively, R and W
594 the percentage of oxygen atoms in the rock (or mineral) and water, respectively, and $\delta^{18}\text{O}_i^m$ and $\delta^{18}\text{O}_f^m$ the
595 oxygen isotope composition of the initial and final minerals, respectively.

596 Because the isotopic fractionation at equilibrium between minerals and fluid is also temperature
597 dependent (Zheng and Hoefs, 1993), then the equilibrium temperature can be estimated using the oxygen
598 isotope equilibrium equations of plagioclase (Eq. 2), K-feldspar (Eq. 3) and quartz (Eq. 4) with fluid,
599 being (Zheng, 1993):

$$1000 \ln \alpha_{Ab-H_2O} = \frac{4.33}{T^2} \times 10^6 - \frac{6.15}{T} \times 10^3 + 1.98 \quad (2)$$

$$1000 \ln \alpha_{Kfs-H_2O} = \frac{4.32}{T^2} \times 10^6 - \frac{6.27}{T} \times 10^3 + 2.00 \quad (3)$$

$$1000 \ln \alpha_{Qtz-H_2O} = \frac{4.48}{T^2} \times 10^6 - \frac{4.77}{T} \times 10^3 + 1.71 \quad (4)$$

600 Where T is the equilibrium temperature and $1000 \ln \alpha \sim (\delta^{18}O^m_f - \delta^{18}O^w_f)$ the oxygen isotope fractionation
 601 between mineral and fluid, being $\delta^{18}O^w_f$ determined by Eq. 1.

602 *Initial $\delta^{18}O$ composition of fluids and R/W ratio*

603 In fossil fluid-rock interactions, the initial oxygen isotope composition of the fluid, usually water, ($\delta^{18}O^w_i$)
 604 and the R/W ratio are usually unknown variables. This limitation makes it necessary to adopt reasonable
 605 $\delta^{18}O^w_i$ and R/W values to approach the final oxygen isotope composition of fluids and hence the
 606 equilibrium temperature of mineral and rock alteration. The geotectonic structure of the red-stained profile
 607 beneath the Triassic unconformity suggests that the alteration was probably triggered by infiltrating
 608 Permian-Triassic surficial waters and groundwaters hosted in the Variscan granites. Groundwaters deep in
 609 the stable crystalline basements, typically at depths between several hundreds or thousands of meters,
 610 have $\delta^{18}O$ values between -8 and -12‰ (Kloppmann et al., 2002). This negative shifting of groundwater
 611 $\delta^{18}O$ is promoted by water-rock interaction reactions including the formation of kaolinite from dissolution
 612 of smectite and feldspars, and the precipitation of Fe-hydroxides (Kloppmann et al., 2002). These
 613 negative $\delta^{18}O$ values have been described worldwide in groundwaters in crystalline basements, including
 614 e.g., the European French Massif Central (Kloppmann et al., 2002), the Black Forest (Stober and Bucher,
 615 1999a), the Alps (Barth, 2000) and the Fennoscandian and Ukrainian shields (Stober and Bucher, 1999b),
 616 the North American Canadian shield (Frape and Fritz, 1982, 1987; Frape et al., 1984a; Stober and Bucher,
 617 1999b), the African Ahaggar Massif and Dodoma area (Nkotagu, 1996; Saighi et al., 2001), and the
 618 Indian Ranchi area (Saha et al., 2001), suggesting that negative $\delta^{18}O$ values are intrinsic of deep
 619 groundwater (Kloppmann et al., 2002). Assuming an analogy between the current and the Permian-
 620 Triassic granitic basement, negative $\delta^{18}O$ values between -8 and -12‰ can be reasonably assumed for the
 621 Permian-Triassic palaeogroundwater in the granitoids of the Guilleries and Roc de Frausa Massifs.

622 The rock to water (R/W) oxygen mass ratio is also a key factor for an estimation of the isotopic evolution
 623 of the fluid. Reactions arising directly at fracture walls, where solution may be renewed by circulation,
 624 may correspond to relative low R/W ratios, whereas those occurring away from the fractures, at the
 625 reaction front within primary crystals in an almost closed system, most likely correspond to higher R/W

626 ratios. To determine a minimum and conservative estimate of the $\delta^{18}\text{O}$ evolution of water, calculations
627 were carried out applying R/W values of 0.5 and 1, considered to be high (≥ 1) water to rock ratios
628 (Taylor, 1977).

629 $\delta^{18}\text{O}$ evolution in fluids and precipitation temperature

630 The $\delta^{18}\text{O}$ disequilibrium values of the secondary phases are indicative of either the $\delta^{18}\text{O}$ evolution of fluid
631 or temperature variations during the alteration. Possible scenarios of $\delta^{18}\text{O}$ evolution in the fluids
632 facilitating the albitization and related temperatures were explored using the reactions of albitization of
633 plagioclase, microclinization of orthoclase and the formation of CL-dark quartz. The initial $\delta^{18}\text{O}_{\text{im}}$ and
634 final $\delta^{18}\text{O}_{\text{fm}}$ oxygen isotope compositions of minerals applied in Eq. 1 for each reaction were,
635 respectively, the averaged SIMS $\delta^{18}\text{O}$ values of primary plagioclase and albitized plagioclase, primary
636 orthoclase and secondary microclinized orthoclase, and primary quartz and secondary CL-dark quartz. To
637 overcome the uncertainty about the initial oxygen isotope composition of fluid and rock to fluid (R/W)
638 oxygen atomic abundance ratio, calculations were undertaken with minimum and maximum range values
639 to determine the influence of the different components and estimate the validity of the calculated
640 temperatures. Temperature calculations were tested for initial oxygen isotope compositions of fluid
641 ($\delta^{18}\text{O}_{\text{if}}$) of -8 and -12‰ and R/W in the range of 0.5 and 1.0 that might be consistent with fluid flow rate
642 in the main fractures and in restricted cracks, respectively.

643 Equilibrium calculations were conducted with two options about fluid behaviour within the system.

644 (1) A closed system, in which fluid is retained in the system and where the reactions follow each another
645 according to the sequence highlighted by petrographical relationships. The evolution of the oxygen
646 isotope composition of the water was calculated across the sequence: albitization of plagioclase,
647 microclinization of orthoclase and the formation of CL-dark quartz. The final oxygen isotope composition
648 of fluid (Eq. 1) obtained in the previous reaction was the initial value in the next reaction. This option is
649 relative to minimal chemical exchanges with the surrounding systems.

650 (2) An open system, in which fluid is renewed by circulation. The calculation (Eq. 1) considered
651 concomitant mineral alterations and with the same initial fluid composition for each reaction. It
652 corresponds to exchanges with surrounding systems, allowing imports and exports of chemical elements.
653 After calculation of the resulting oxygen isotope composition of fluid for each reaction, the corresponding

654 temperatures were calculated using Eq. (2), (3) and (4) for albitization of plagioclase, microclinitization of
655 K-feldspar and the CL-dark quartz formation, respectively.

656 The results of the calculations are summarized in Table 5 and call for a few remarks: (1) The
657 temperatures obtained for the Guilleries and Roc de Frausa massifs have very similar values, with an
658 averaged standard error in each reaction of about $\pm 7^\circ\text{C}$. (2) Calculated temperatures for the reactions
659 (Eq. 2, 3, 4) are higher if they were concomitant in an open system; (3) Calculated temperatures are
660 higher when considering a lower R/W oxygen mass ratio, i.e. more solution in the system; (4) There is a
661 systematic discrepancy in the calculated temperature with the various reactions: the lowest calculated
662 temperature is always for orthoclase microclinitisation and the highest for the precipitation of CL-dark
663 quartz. These discrepancies are attributed to interaction effects, like different rates between reactions or
664 fluid access to the minerals, and even shifts in the mineral isotope analyses. Whatever, the range of the
665 calculated temperatures remains relatively low about variation in the initial parameters. Increasing R/W
666 ratio from 0.5 to 1.0 lowers the calculated temperatures by about 10 to 20%. Lowering $\delta^{18}\text{O}$ in the initial
667 fluid from -8 to -12‰ lowers the calculated temperatures by about the same amount. Discrepancies
668 between the calculated temperature of microclinitisation of orthoclase and precipitation of CL-dark quartz
669 are of the same order of magnitude, about 25 - 30%. The maximum divergence between all the calculated
670 temperatures is 55°C , and the mean of all the calculated temperatures (if it makes sense) is $56.5 \pm 15^\circ\text{C}$
671 (1σ). The variation in the calculated temperatures seems to be relatively low, about the same as the
672 variation in the parameters introduced into the calculations, suggesting that evolution of the reaction fluid
673 can be considered, within its error estimation, as an isothermal process around 55°C .

674 Regardless of the lack of precision, these values show that the temperatures of the reactions associated
675 with development of red-stained albitized rocks are significantly below temperatures suggested for
676 hydrothermal albitisation (Cathelineau, 1986; Boulvais et al., 2007) and tardi-magmatic alteration (Lee
677 and Parsons, 1997; Fiebig and Hoefs, 2002), and are consistent with shallow near-landsurface conditions.

678 **Table 5. $\delta^{18}\text{O}$ fluid evolution and reaction temperatures.** Regarding the indefinite alteration conditions,
 679 temperature values are rounded to the unit.

| mineral reaction | R/W oxygen mass ratio | initial $\delta^{18}\text{O}$ fluid ‰ | final $\delta^{18}\text{O}$ fluid ‰ | reaction temperature °C |
|---|-----------------------|---------------------------------------|-------------------------------------|-------------------------|
| sequential reactions # closed system | | | | |
| albitization of plagioclase | 0.5 | -8.0 | -9.0 | 72 |
| | 1.0 | -8.0 | -10.0 | 65 |
| microclinization of orthoclase | 0.5 | -9.0 | -9.7 | 56 |
| | 1.0 | -10.0 | -11.5 | 47 |
| precipitation of CL-dark quartz | 0.5 | -9.7 | -12.1 | 79 |
| | 1.0 | 11.5 | -16.6 | 58 |
| albitization of plagioclase | 0.5 | -12.0 | -13 | 49 |
| | 1.0 | -12.0 | -14 | 44 |
| microclinization of orthoclase | 0.5 | -13.0 | -13.7 | 36 |
| | 1.0 | -14.0 | -15.5 | 36 |
| precipitation of CL-dark quartz | 0.5 | -13.7 | -16.1 | 58 |
| | 1.0 | 15.5 | -20.2 | 39 |
| concomitant reactions # open system | | | | |
| albitization of plagioclase | 0.5 | -8.0 | -9.0 | 72 |
| | 1.0 | -8.0 | -10.0 | 65 |
| microclinization of orthoclase | 0.5 | -8.0 | -8.7 | 62 |
| | 1.0 | -8.0 | -9.5 | 58 |
| precipitation of CL-dark quartz | 0.5 | -8.0 | -10.3 | 91 |
| | 1.0 | -8.0 | -12,6 | 77 |
| albitization of plagioclase | 0.5 | -12.0 | -13.0 | 49 |
| | 1.0 | -12.0 | -14.0 | 44 |
| microclinization of orthoclase | 0.5 | -12.0 | -12,7 | 41 |
| | 1.0 | -12.0 | -13.5 | 38 |
| precipitation of CL-dark quartz | 0.5 | -12.0 | -14.3 | 67 |
| | 1.0 | -12.0 | -16.6 | 55 |

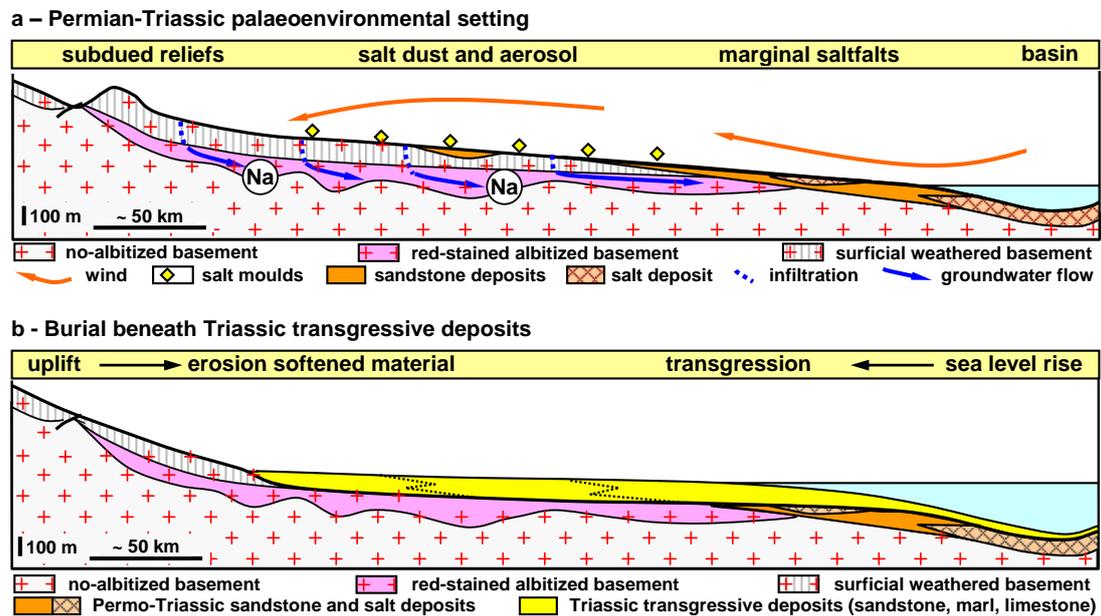
680

681 **Palaeoenvironmental setting of the albitization**

682 The dating of albitization to the late Permian-early Triassic unquestionably constrains the alteration to the
 683 Triassic palaeosurface that covers it. During the Late Permian-Early Triassic, northeastern Spain was
 684 situated in subtropical latitude (López-Gómez et al., 2005; Scotese and Schettino, 2017). The transition
 685 between Permian and Triassic times included a severe global warming described as an apocalyptic
 686 greenhouse palaeoclimate (Erwin, 1993; Retallack, 1999; Sun et al., 2012), making life difficult in
 687 equatorial latitudes (Brookfield, 2008; Joachimski et al., 2012). Land temperatures possibly approached
 688 40°C and may have fluctuated to even higher temperatures (Joachimski et al., 2012; Sun et al., 2012).

689 In addition, Triassic palaeoenvironments are known for their giant salt deposits connected with lagunal
 690 evaporitic environments (Hay et al., 2006; Brookfield, 2008; Bourquin et al., 2011) and the frequency of
 691 halite moulds in transgressive epicontinental and continental clastic deposits (Courel, 1982; Galán-
 692 Abellán and Martínez, 2018). It is possible that in continental settings halite may have been derived via

693 aeolian processes from marine-derived saline lakes and saltflats together with red desert dust typical of
 694 Triassic red sandstone deposits (Ruffell and Hounslow, 2006). Leaching of the salt accumulated in the
 695 landscape would have provided Na-rich solutions depleted in K relative to marine brines (Fig. 11a).



696

697 **Fig. 11.** Palaeoenvironmental settings during development of the red-stained albitized profiles. (a) Weathering
 698 mantles and saline environments of the postulated Triassic landscape with Na-enriched infiltrating waters and
 699 groundwater that probably triggered the formation of the albitized profiles. (b) Removal of the regolith mantle and
 700 burial of the albitized horizons by the Early Triassic transgression.

701 A geochemical mass balance for the studied Triassic red-stained albitized facies (Fig. 6) shows that
 702 albitization of plagioclase is triggered by an interaction between rock and Na-rich fluids with replacement
 703 of Ca by Na. Salt accumulated in the Triassic landscape is the most likely source of Na-rich solutions. For
 704 example, dense saline brines could have been a major contributor to the regional groundwater (Rogers
 705 and Dreiss, 1995; Wooding et al., 1997; Simmons et al., 2001) to depths of 1 km and more (Magri et al.,
 706 2009). The overall tectonic stability and subdued relief of the crystalline basement during the Permian-
 707 Triassic period (López-Gómez et al., 2005; Bourquin et al., 2011; Galán-Abellán et al., 2013) would have
 708 favoured slow groundwater flow rates, leading to long residence times and pervasive fluid/rock contact.

709 These unique settings of Triassic palaeogeography are considered to be responsible for the albitization of
 710 granitic rocks in Triassic landscapes that are recognized and dated in several basement massifs in Western
 711 Europe, i.e. French Massif Central affecting as well Carboniferous and Permian graben deposits (Yerle
 712 and Thiry, 1979; Schmitt et al., 1984; Clément, 1986; Schmitt, 1992), the Morvan Massif (Ricodel et al.,

713 [2007; Parcerisa et al., 2010b](#)), the Polish Sudetes ([Yao et al., 2011; Yao 2013](#)) and the Spanish Guillerias
714 and Roc de Frausa Massifs ([Fàbrega et al., 2013; Franke et al., 2010](#)).

715 A question remains about the depth at which the alteration leading to albitization occurred. Reaction
716 temperatures calculated from the oxygen isotope composition of minerals and hypotheses about the
717 oxygen isotope composition of reactant fluids and their circulation led to an estimate of the mean
718 temperature of albitization and associated reactions of about 55°C. Based on this temperature, an estimate
719 of the mean depth at which alteration occurred can be made by applying a geothermal gradient and a
720 surface temperature. A surficial temperature could be set to 30°C in consideration of the high
721 palaeotemperature proposed for the Permian-Triassic boundary ([Retallack, 1999; Joachimski et al., 2012](#))
722 and a geothermal gradient for crystalline basement in a stable tectonic context could be set at about 25–
723 30°C/km. Under such conditions, albitization may have taken place at about 1 km depth.

724 This finding must include the possibility that a thick regolith existed between the surface and the
725 albitization zone. The geopedal architecture of the profile is a key characteristic, and the greater intensity
726 of alteration in the upper zones compared with the lesser intensity and more clearly fracture-controlled
727 alteration at depth, suggests a transition between a near-surface unconfined aquifer and a deeper fractured
728 rock aquifer system with restricted flow rate. If the albitized zone was surmounted by a regolith, high
729 hydraulic conductivity and seepage from the surface to depth would probably have prevailed. The upper
730 part of the profile may have been formed of loose weathered rocks, most likely sands with kaolinite
731 resulting from the weathering of feldspar, as suggested by Triassic sand deposits ([Algeo and Twitchett,
732 2010; Benton and Newell, 2013](#)). The nature of deeper horizons immediately overlying the albitized
733 zones is more difficult to comprehend. Long-lasting infiltration and seepage through these horizons may
734 have led to alteration of its most sensitive minerals, like Ca-plagioclase and biotite, deconstructed the
735 granite fabric and generated a relatively erodible arkosic grit. Given the extreme stability and long
736 persistence of Triassic palaeosurface the regolith cover may have reached 100, or even 300m in thickness.

737 This loose regolith material was later eroded, most probably during the period of relief rejuvenation and
738 intra-belt basin erosion during the Early Triassic ([Bourquin et al., 2011](#)) corresponding to the widespread
739 unconformity observed in the German Triassic ([Trusheim, 1961; Wolburg, 1968; Röhling, 1991](#)). Erosion
740 and burial beneath Triassic deposits was driven by tectonic activity and sea level rise ([Fig. 11b](#)).

741 **Conclusions**

742 A widespread and distinctive red stained and albitized granitic facies beneath the Triassic unconformity in
743 NE Spain was formed in the Late Permian to Early Triassic based on three independent dating methods.
744 This major result indicates that the albitization and associated alteration are related to the Triassic
745 palaeosurface that unconformably overlies the albitized profile and developed in response to pervasive
746 infiltrating fluid flow while the Variscan granites of NE Spain were exposed at the land surface.

747 $\delta^{18}\text{O}$ isotope data show that the secondary phases of the red-stained albitized facies (i.e. albitized
748 plagioclase, microclinized orthoclase and CL-dark quartz) are $\delta^{18}\text{O}$ enriched with respect to their primary
749 counterparts in unaltered rocks. Calculation of the oxygen isotope equilibrium temperature between
750 minerals and albitizing fluids was undertaken by testing minima and maxima range values of initial
751 oxygen isotope composition of fluid and rock to fluid mass ratios consistent with fluid flow rates in main
752 and restricted fractures. This led to an estimate that albitized plagioclase, microclinized orthoclase and
753 CL-dark quartz formed between 45 and 65°C. These temperatures are far less than 200 to 400°C typically
754 assigned to late-magmatic and hydrothermal albitization processes. Instead, the low temperature range
755 accords with the geological settings and age dating that correlates the red-stained albitized profile with the
756 Triassic palaeosurface. It is possible that the albitized profile may have developed a few hundred meters
757 beneath the Triassic palaeosurface and was subsequently exposed at the surface after erosion of the
758 uppermost weathering mantles.

759 Albitization resulted from Na accumulation triggered by Na-rich reactant solutions. The source of Na is
760 considered to have been connected to the ubiquity of salt in the Triassic landscapes in the region, in
761 lagunal and marginal salt flats as well as aeolian accumulations on extensive continental surfaces. A
762 combination of surficial brines infiltrating groundwaters and a long period of tectonic stability could have
763 facilitated pervasive alteration in 100 to 200 m deep profiles.

764 The significant amounts of secondary apatite formed during this alteration must be taken into account if
765 fission track analysis or (U-Th)/He dating is carried out on these red-stained albitized rocks.

766 **Acknowledgements**

767 We would like to thank an anonymous reviewer and Douglas Elmore from University of Oklahoma,
768 whose comments helped considerably to improve the focus of the paper. Authors are also indebted to

769 Tony Milnes from University of Adelaide for his revision and helpful comments, and for language
770 edition, that strengthened the manuscript. Also, thanks to the technical staff of the Laboratorio General de
771 Isotopos Estables of the Universidad de Salamanca (Spain) for the oxygen isotope CO₂-fluorination
772 analyses and their useful technical comments. We wish to thank Dr. Xavier Llobet of the CCiTUB of the
773 Universitat de Barcelona (Spain) for his technical support in the EPMA analyses of silicates and the U-
774 Th-Pb_{total} monazite dating. Dr. Pura Alfonso, Escola Politècnica Superior d'Enginyeria de Manresa
775 (Spain), for her support in analyzing EPMA data. Abigail Jiménez, from the Escola Politècnica Superior
776 d'Enginyeria de Manresa (Spain), for the preparation of the epoxy mounts for EPMA monazite analyses.
777 Dr. Marc Poujol, from Geosciences Rennes, Université de Rennes 1, for the ICP-MS U/Pb and Th/Pb
778 dating of our monazite internal standard and for sharing with us his knowledge about monazite dating.
779 This research was performed within the framework of DIHIME (CGL2015-66355-C2-1-R) and FEIBOB
780 projects (PGC2018-093903-B-C22) of DGICYT, Ministerio de Economía y Competitividad, Gobierno de
781 España and Grup Consolidat de Recerca “Geologia Sedimentària” (2017-SGR-824) and Grup de Recerca
782 en Minería Sostenible (2017-SGR-198) supported by the Comissionat per a Universitats i Recerca del
783 Departament d'Empresa i Coneixement de la Generalitat de Catalunya.

784 **Data Availability**

785 The Electronic Supplementary Information related to this article can be obtained in the datasets:

786 [dataset] Parcerisa Duocastella, D. [et al.]. (2016). Geostandards of the Valentí Masachs Geology
787 Museum [Dataset]. 1 v. Universitat Politècnica de Catalunya. [DOI: 10.5821/data-2117-103444-](https://doi.org/10.5821/data-2117-103444-1)
788 [1\[https://upcommons.upc.edu/handle/2117/103444\]](https://upcommons.upc.edu/handle/2117/103444).

789 [dataset] Fàbrega, C. [et al.]. (2018). Geochemical data of albitized profiles in Europe [Dataset]. 1 v.
790 Universitat Politècnica de Catalunya. [DOI: 10.5821/data-2117-114114-](https://doi.org/10.5821/data-2117-114114-1)
791 [1\[https://upcommons.upc.edu/handle/2117/114114\]](https://upcommons.upc.edu/handle/2117/114114).

792 **References**

- 793 Aagaard P, Egeberg PK, Saigal GC (1990) Diagenetic albitization of detrital K-feldspars in Jurassic,
794 Lower Cretaceous and Tertiary clastic reservoir rocks from offshore Norway; II, Formation water
795 chemistry and kinetic considerations. *J Sediment Res* 60:575
- 796 Ague JJ, van Haren JLM (1996) Assessing metasomatic mass and volume changes using the bootstrap,
797 with application to deep crustal hydrothermal alteration of marble. *Econ Geol* 91:1169–1182. doi:
798 10.2113/gsecongeo.91.7.1169

- 799 Aguilar C, Liesa M, Castineiras P, Navidad M (2014) Late Variscan metamorphic and magmatic
800 evolution in the eastern Pyrenees revealed by U-Pb age zircon dating. *J Geol Soc London* 171:181–
801 192. doi: 10.1144/jgs2012-086
- 802 Aguilar C, Liesa M, Štípská P, Schulmann K, Muñoz JA, Casas JM (2015) P-T-t-d evolution of orogenic
803 middle crust of the Roc de Frausa Massif (Eastern Pyrenees): a result of horizontal crustal flow and
804 Carboniferous doming? *J Metamorph Geol* 33:273–294. doi: 10.1111/jmg.12120
- 805 Algeo TJ, Twitchett RJ (2010) Anomalous Early Triassic sediment fluxes due to elevated weathering
806 rates and their biological consequences. *Geol* 38:1023–1026. doi: 10.1130/G31203.1
- 807 Anadón P, Cabrera L, Colombo F, Marzo M, Riba O (1986) Syntectonic Intraformational Unconformities
808 in Alluvial Fan Deposits, Eastern Ebro Basin Margins (NE Spain). In: *Foreland Basins*. Blackwell
809 Publishing Ltd., Oxford, UK, pp 259–271
- 810 Baker JH (1985) Rare earth and other trace element mobility accompanying albitization in a Proterozoic
811 granite, W. Bergslagen, Sweden. *Mineral Mag* 49:107–115. doi: 10.1180/minmag.1985.049.350.17
- 812 Barth SR (2000) Geochemical and boron, oxygen and hydrogen isotopic constraints on the origin of
813 salinity in groundwaters from the crystalline basement of the Alpine Foreland. *Appl Geochemistry*
814 15:937–952. doi: 10.1016/S0883-2927(99)00101-8
- 815 Battiau-Queney Y (1997) Preservation of old palaeosurfaces in glaciated areas: examples from the French
816 western Alps. *Geol Soc London, Spec Publ* 120:125–132. doi: 10.1144/GSL.SP.1997.120.01.08
- 817 Beinlich A, Klemd R, John T, Gao J (2010) Trace-element mobilization during Ca-metasomatism along a
818 major fluid conduit: Eclogitization of blueschist as a consequence of fluid–rock interaction.
819 *Geochim Cosmochim Acta* 74:1892–1922. doi: 10.1016/j.gca.2009.12.011
- 820 Benton MJ, Twitchett RJ (2003) How to kill (almost) all life: The end-Permian extinction event. *Trends*
821 *Ecol Evol* 18:358–365. doi: 10.1016/S0169-5347(03)00093-4
- 822 Bernet M, Bassett K (2005) Provenance Analysis by Single-Quartz-Grain SEM-CL/Optical Microscopy. *J*
823 *Sediment Res.* doi: 10.2110/jsr.2005.038
- 824 Bindeman I (2008) Oxygen Isotopes in Mantle and Crustal Magmas as Revealed by Single Crystal
825 Analysis. *Rev Mineral Geochemistry* 69:445–478. doi: 10.2138/rmg.2008.69.12
- 826 Boles JR (1982) Active albitization of plagioclase, Gulf Coast Tertiary. *Am J Sci* 282:165–180
- 827 Boulvais P, Ruffet G, Cornichet J, Mermet M (2007) Cretaceous albitization and dequartzification of
828 Hercynian peraluminous granite in the Salvezines Massif (French Pyrénées). *Lithos* 93:89–106
- 829 Bourquin S, Bercovici A, López-Gómez J, Diez JB, Broutin J, Ronchi A, Durand M, Arche A, Linol B,
830 Amour F (2011) The Permian-Triassic transition and the onset of Mesozoic sedimentation at the
831 northwestern peri-Tethyan domain scale: Palaeogeographic maps and geodynamic implications.
832 *Palaeogeogr Palaeoclimatol Palaeoecol* 299:265–280
- 833 Brookfield ME (2008) Palaeoenvironments and palaeotectonics of the arid to hyperarid intracontinental
834 latest Permian- late Triassic Solway basin (U.K.). *Sediment Geol* 210:27–47
- 835 Cathelineau M (1986) The hydrothermal alkali metasomatism effects on granitic rocks: Quartz
836 dissolution and related subsolidus changes. *J Petrol* 27:945–965
- 837 Cherniak DJ, Pyle JM (2008) Th diffusion in monazite. *Chem Geol* 256:52–61. doi:
838 10.1016/j.chemgeo.2008.07.024

- 839 Cherniak D., Watson EB, Grove M, Harrison TM (2004) Pb diffusion in monazite: a combined
840 RBS/SIMS study. *Geochim Cosmochim Acta* 68:829–840. doi: 10.1016/j.gca.2003.07.012
- 841 Clément J.-Y. (1986) *Minéralogie, pétrologie et géochimie du Permien de Lodève (Hérault, France).
842 Diagenèse précoce, altération feldspathisante et mise en place des minéralisations uranifères.
843 ENSMP, Mém Sci de la Terre 2: 136 p.*
- 844 Cocherie A, Albarede F (2001) An improved U-Th-Pb age calculation for electron microprobe dating of
845 monazite. *Geochim Cosmochim Acta* 65:4509–4522. doi: 10.1016/S0016-7037(01)00753-0
- 846 Cocherie A, Legendre O, Peucat JJ, Kouamelan AN (1998) Geochronology of polygenetic monazites
847 constrained by in situ electron microprobe Th-U-total lead determination: Implications for lead
848 behaviour in monazite. *Geochim Cosmochim Acta*. doi: 10.1016/S0016-7037(98)00171-9
- 849 Coombs DS (1954) The nature and alteration of some Triassic sediments from Southland, New Zealand.
850 *Trans R Soc New Zeal* 82:65–109
- 851 Courel L (1982) Les facies de transgression du trias sur la bordure nord-est du Massif Central français.
852 *Geol Rundschau* 71:773–781
- 853 Dinarès-Turell J, Diez JB, Rey D, Arnal I (2005) “Buntsandstein” magnetostratigraphy and
854 biostratigraphic reappraisal from eastern Iberia: Early and Middle Triassic stage boundary
855 definitions through correlation to Tethyan sections. *Palaeogeogr Palaeoclimatol Palaeoecol*
856 229:158–177. doi: 10.1016/j.palaeo.2005.06.036
- 857 Engvik AK, Putnis A, Fitz Gerald JD, Austrheim H (2008) Albitization of granitic rocks: the mechanism
858 of replacement of oligoclase by albite. *Can Mineral* 46:1401–1415. doi: 10.3749/canmin.46.6.1401
- 859 Enrique P (1990) The Hercynian intrusive rocks of the Catalan Coastal Ranges (NE Spain). *Acta Geol
860 Hisp* 25:39–64
- 861 Erwin DH (1993) *The great Paleozoic crisis: life and death in the Permian*. Columbia University Press,
862 New York, US
- 863 Fàbrega C, Parcerisa D, Gómez-Gras D (2013) Multiple Feldspar replacement in Hercynian granites of
864 the Montseny-Guilleries Massif (Catalan Coastal Ranges, NE Spain). *Geophys Res Abstr* 15:
865 EGU2013-7193–2
- 866 Fàbrega C, Parcerisa D, Gómez-Gras D, Travé A, Franke C, Gurenko A (2016) Composició isotòpica de
867 l’oxigen ($^{18}O/^{16}O$) en els feldspats i el quars dels granitoides hercínians: Guilleries-Montseny i
868 Pirineus Orientals. In: Vilà M, Herms I, Cirés J (eds) *Geoquímica ambiental a Catalunya. Recull
869 d’articles*. Monografies tècniques de l’Institut Cartogràfic i Geològic de Catalunya, núm. 5. Institut
870 Cartogràfic i Geològic de Catalunya, Barcelona, Spain, pp 83–95 (**in Catalan**)
- 871 Fàbrega C, Parcerisa D, Rossell JM, Gurenko A, Franke C (2017) Predicting instrumental mass
872 fractionation (IMF) of stable isotope SIMS analyses by response surface methodology (RSM). *J
873 Anal At Spectrom* 32:731–748. doi: 10.1039/C6JA00397D
- 874 Fàbrega C, Parcerisa D, Gómez-Gras D, Travé A, Thiry M, Franke C, Gurenko A, Solé J (2018)
875 Geochemical data of albitized profiles in Europe [Dataset] URL:
876 <https://upcommons.upc.edu/handle/2117/102354>
- 877 Fallourd S, Poujol M, Boulvais P, Paquette JL, de Saint Blanquat M, Rémy P (2014) In situ LA-ICP-MS
878 U-Pb titanite dating of Na-Ca metasomatism in orogenic belts: The North Pyrenean example. *Int J
879 Earth Sci* 103:667–682

- 880 Fiebig J, Hoefs J (2002) Hydrothermal alteration of biotite and plagioclase as inferred from intragranular
881 oxygen isotope- and cation-distribution patterns. *Eur J Mineral* 14:49–60. doi: 10.1127/0935-
882 1221/2002/0014-0049
- 883 Franke C, Thiry M, Gómez-Gras D, Jelenska M, Kodzialko-Hofmohl M, Lagroix F, Parcerisa D, Spassov
884 S, Szuszkiewicz A, Turniak K (2010) Paleomagnetic age constrains and magneto-mineralogic
885 implications for the Triassic paleosurface in Europe. *Geophys Res Abstr* 12: EGU2010-7858
- 886 Frape SK, Fritz P (1982) The chemistry and isotopic composition of saline groundwaters from the
887 Sudbury Basin, Ontario. *Can J Earth Sci* 19:645–661. doi: 10.1139/e82-053
- 888 Frape SK, Fritz P (1987) Geochemical trends for groundwaters from the Canadian Shield. In: *Saline
889 water and gases in crystalline rocks*. Ottawa: Geological Association of Canada, pp 19–38
- 890 Frape SK, Fritz P, Blackmer AJ (1984) Saline groundwater discharges from crystalline rocks near
891 Thunder Bay. In: *Ontario, Canada: International Symposium on Hydrochemical Balances of
892 Freshwater Systems*, Upsala, Sweden. pp 369–379
- 893 Galán-Abellán AB, Martínez-Frías J (2018) Environmental conditions of E Iberia's Early Triassic: an
894 Earth example for understanding the habitability of ancient Mars. *Episodes* 41:33–50. doi:
895 10.18814/epiiugs/2018/v41i1/018004
- 896 Galán-Abellán B, López-Gómez J, Barrenechea JF, Marzo M, de la Horra R, Arche A (2013) The
897 beginning of the Buntsandstein cycle (Early–Middle Triassic) in the Catalan Ranges, NE Spain:
898 Sedimentary and palaeogeographic implications. *Sediment Geol* 296:86–102. doi:
899 10.1016/j.sedgeo.2013.08.006
- 900 Gómez-Gras D (1993) El Permotría de la Cordillera Costero Catalana: Facies y Petrología Sedimentaria
901 (Parte I). *Boletín Geológico y Min España* 104:115–161
- 902 Gómez-Gras D, Roigé M, Fondevilla V, Oms O, Boya S, Remacha E (2016) Provenance constraints on
903 the Tremp Formation paleogeography (southern Pyrenees): Ebro Massif VS Pyrenees sources.
904 *Cretac Res* 57:414–427. doi: 10.1016/j.cretres.2015.09.010
- 905 Hall MM, Veeraraghavan VG, Rubin H, Winchell PG (1977) The approximation of symmetric X-ray
906 peaks by Pearson type VII distributions. *J Appl Crystallogr* 10:66–68. doi:
907 10.1107/S0021889877012849
- 908 Hamilton M, Elmore D, Weaver B, Dulin S, Suneson NH (2014) Petrology and paleomagnetism of the
909 Long Mountain Granite, Wichita Mountains, Oklahoma. *Igneous Rocks of the Southern Oklahoma
910 Aulacogen: Oklahoma*. Geological Survey Guidebook 38: 319-326
- 911 Hamilton EM, Elmore RD, Weaver BL, Dulin S, Jackson J (2016) Paleomagnetic and petrologic study of
912 the age, origin, and significance of early and late Paleozoic events in the Long Mountain Granite,
913 Wichita Mountains, Oklahoma. *GSA Bull* 128: 187-202
- 914 Harlov DE, Wirth R, Hetherington CJ (2011) Fluid-mediated partial alteration in monazite: The role of
915 coupled dissolution-precipitation in element redistribution and mass transfer. *Contrib to Mineral
916 Petrol*. doi: 10.1007/s00410-010-0599-7
- 917 Hay WW, Migdisov A, Balukhovskiy AN, Wold CN, Flögel S, Söding E (2006) Evaporites and the
918 salinity of the ocean during the Phanerozoic: Implications for climate, ocean circulation and life.
919 *Palaeogeogr Palaeoclimatol Palaeoecol* 240:3–46
- 920 Jamtveit B, Putnis C V, Malthe-Sørenssen A (2009) Reaction induced fracturing during replacement
921 processes. *Contrib Mineral Petrol* 157:127–133. doi: 10.1007/s00410-008-0324-y

- 922 Joachimski MM, Lai X, Shen S, Jiang H, Luo G, Chen B, Chen J, Sun Y (2012) Climate warming in the
923 latest Permian and the Permian-Triassic mass extinction. *Geology* 40:195–198. doi:
924 10.1130/G32707.1
- 925 Julivert M, Durán H (1990) Paleozoic stratigraphy of the Central and Northern part of the Catalanian
926 Coastal Ranges (NE Spain). *Acta Geol Hisp* 25:3–12
- 927 Kastner M, Siever R (1979) Low temperature feldspars in sedimentary rocks. *Am J Sci* 279:435–479
- 928 Kloppmann W, Girard J-P, Négrel P (2002) Exotic stable isotope compositions of saline waters and
929 brines from the crystalline basement. *Chem Geol* 184:49–70. doi: 10.1016/S0009-2541(01)00352-7
- 930 Lee MR, Parsons I (1997) Dislocation formation and albitization in alkali feldspars from the Shap granite.
931 *Am Mineral*. doi: 10.2138/am-1997-5-616
- 932 Linol B, Bercovici A, Bourquin S, Diez JB, López-Gómez J, Broutin J, Durand M, Villanueva-Amadoz U
933 (2009) Late Permian to Middle Triassic correlations and palaeogeographical reconstructions in
934 south-western European basins: New sedimentological data from Minorca (Balearic Islands, Spain).
935 *Sediment Geol* 220:77–94. doi: 10.1016/j.sedgeo.2009.06.003
- 936 López-Gómez J, Arche A, Marzo M, Durand M (2005) Stratigraphical and palaeogeographical
937 significance of the continental sedimentary transition across the Permian-Triassic boundary in
938 Spain. *Palaeogeogr Palaeoclimatol Palaeoecol* 229:3–23
- 939 Ludwig KR (2003) User's Manual for Isoplot 3.00 - A Geochronological Toolkit for Microsoft Excel.
940 Berkeley Geochronol Cent Spec Publ Special Pu:25–32
- 941 Magri F, Bayer U, Pekdeger A, Otto R, Thomsen C, Maiwald U (2009) Salty groundwater flow in the
942 shallow and deep aquifer systems of the Schleswig–Holstein area (North German Basin).
943 *Tectonophysics* 470:183–194. doi: 10.1016/j.tecto.2008.04.019
- 944 Mark DF, Kelley SP, Lee MR, Parnell J, Sherlock SC, Brown DJ (2008) Ar–Ar dating of authigenic K-
945 feldspar: Quantitative modelling of radiogenic argon-loss through subgrain boundary networks.
946 *Geochim Cosmochim Acta* 72:2695–2710. doi: 10.1016/j.gca.2008.03.018
- 947 Martínez FJ, Reche J, Iriondo A (2008) U–Pb Shrimp-RG zircon ages of Variscan igneous rocks from the
948 Guillerics massif (NE Iberia pre-Mesozoic basement). Geological implications. *Comptes Rendus*
949 *Geosci* 340:223–232. doi: 10.1016/j.crte.2007.12.006
- 950 Morad S, Bergan M, Knarud R, Nystuen JP (1990) Albitization of detrital plagioclase in Triassic
951 reservoir sandstones from the Snorre Field, Norwegian North Sea. *J Sediment Petrol* 60:411–425
- 952 Morad S, El-Ghali MAK, Caja MA, Sirat M, Al-Ramadan K, Mansurbeg H (2010) Hydrothermal
953 alteration of plagioclase in granitic rocks from Proterozoic basement of SE Sweden. *Geol J* 45:105–
954 116
- 955 Nkotagu H (1996) Application of environmental isotopes to groundwater recharge studies in a semi-arid
956 fractured crystalline basement area of Dodoma, Tanzania. *J African Earth Sci* 22:443–457. doi:
957 10.1016/0899-5362(96)00022-X
- 958 Oms O, Dinarès-Turell J, Vicens E, Estrada R, Vila B, Galobart A, Bravo AM (2007) Integrated
959 stratigraphy from the Vallcebre Basin (southeastern Pyrenees, Spain): New insights on the
960 continental Cretaceous–Tertiary transition in southwest Europe. *Palaeogeogr Palaeoclimatol*
961 *Palaeoecol* 255:35–47. doi: 10.1016/j.palaeo.2007.02.039

- 962 Parcerisa D, Casas L, Franke C, Gómez-Gras D, Lacasa G, Núñez JA, Thiry M (2010a)
963 Geomorphological stability of Permo-Triassic albitized profiles - case study of the Montseny-
964 Guilleries High (NE Iberia). *Geophys Res Abstr* 12: EGU2010-15607
- 965 Parcerisa D, Thiry M, Schmitt JM (2010b) Albitisation related to the Triassic unconformity in igneous
966 rocks of the Morvan Massif (France). *Int J Earth Sci* 99:527–544. doi: 10.1007/s00531-008-0405-1
- 967 Parcerisa D, Franke C, Fàbrega C, Yao K, Thiry M (2013), Implications from paleomagnetic age
968 constrains and petrology analyses on the reconstruction of the Triassic paleosurface in Europe –
969 examples from Catalonia and the Polish Sudetes, Abstract GP12A-02 presented at 2013 Fall
970 Meeting, AGU, San Francisco, Calif., US, 9-13 Dec.
- 971 Parcerisa D, Fàbrega C, Gurenko A, Franke C (2016) Geostandards of the Valentí Masachs Geology
972 Museum [Dataset] URL: <https://upcommons.upc.edu/handle/2117/103444>
- 973 Parrish RR (1990) U–Pb dating of monazite and its application to geological problems. *Can J Earth Sci.*
974 doi: 10.1139/e90-152
- 975 Parsons I, Lee MR (2009) Mutual replacement reactions in alkali feldspars I: microtextures and
976 mechanisms. *Contrib to Mineral Petrol* 157:641–661. doi: 10.1007/s00410-008-0355-4
- 977 Parsons I, Magee CW, Allen CM, Shelley JMG, Lee MR (2009) Mutual replacement reactions in alkali
978 feldspars II: trace element partitioning and geothermometry. *Contrib to Mineral Petrol* 157:663–687
- 979 Perez R, Boles JR (2005) An empirically derived kinetic model for albitization of detrital plagioclase. *Am*
980 *J Sci* 305:312–343
- 981 Petersson J, Eliasson T (1997) Mineral evolution and element mobility during episyenitization
982 (dequartzification) and albitization in the postkinematic Bohus granite, southwest Sweden. *Lithos*
983 42:123–146
- 984 Petersson J, Stephens MB, Mattsson H, Möller C (2012) Albitization and quartz dissolution in
985 Paleoproterozoic metagranite, central Sweden - Implications for the disposal of spent nuclear fuel in
986 a deep geological repository. *Lithos* 148:10–26. doi: 10.1016/j.lithos.2012.06.001
- 987 Petersson J, Fallick AE, Broman C, Eliasson T (2014) Imprints of multiple fluid regimes on episyenites in
988 the Bohus granite, Sweden. *Lithos* 196–197:99–114
- 989 Plümper O, Putnis A (2009) The Complex Hydrothermal History of Granitic Rocks: Multiple Feldspar
990 Replacement Reactions under Subsolvus Conditions. *J Petrol* 50:967–987. doi:
991 10.1093/petrology/egp028
- 992 Poujol M, Boulvais P, Kosler J (2010) Regional-scale Cretaceous albitization in the Pyrenees: evidence
993 from in situ U-Th-Pb dating of monazite, titanite and zircon. *J Geol Soc London* 167:751–767. doi:
994 10.1144/0016-76492009-144
- 995 Putnis A (2002) Mineral replacement reactions: from macroscopic observations to microscopic
996 mechanisms. *Mineral Mag* 66:689–708
- 997 Putnis A (2009) Mineral Replacement Reactions. *Rev Mineral Geochemistry* 70:87–124. doi:
998 10.2138/rmg.2009.70.3
- 999 Putnis A, Hinrichs R, Putnis CV, Golla-Schindler U, Collins LG (2007) Hematite in porous red-clouded
1000 feldspars: Evidence of large-scale crustal fluid-rock interaction. *Lithos* 95:10–18
- 1001 Ramseyer K, Boles JR, Lichtner PC (1992) Mechanism of plagioclase albitization. *J Sediment Petrol*
1002 62:349–456

- 1003 Retallack GJ (1999) Postapocalyptic greenhouse paleoclimate revealed by earliest Triassic paleosols in
1004 the Sydney Basin, Australia. *Geol Soc Am Bull* 111:52–70
- 1005 Ricordel C, Parcerisa D, Thiry M, Moreau MG, Gómez-Gras D (2007) Triassic magnetic overprints
1006 related to albitization in granites from the Morvan massif (France). *Palaeogeogr Palaeoclimatol*
1007 *Palaeoecol* 251:268–282. doi: 10.1016/j.palaeo.2007.04.001
- 1008 Roberts MP, Pin C, Clemens JD, Paquette JL (2000) Petrogenesis of Mafic to Felsic Plutonic Rock
1009 Associations: the Calc-alkaline Querigut Complex, French Pyrenees. *J Petrol* 41:809–844. doi:
1010 10.1093/petrology/41.6.809
- 1011 Rogers DB, Dreiss SJ (1995) Saline groundwater in Mono Basin, California: 1. Distribution. *Water*
1012 *Resour Res* 31:3131–3150. doi: 10.1029/95WR02108
- 1013 Röhling, H.G. (1991) A lithostratigraphic subdivision of the Lower Triassic in the Northwest German
1014 Lowlands and the German sector of the North Sea, based on gamma-ray and sonic logs. *Geol Jb*
1015 A119: 3–24.
- 1016 Røyne A, Jamtveit B, Mathiesen J, Malthe-Sørenssen A (2008) Controls on rock weathering rates by
1017 reaction-induced hierarchical fracturing. *Earth Planet Sci Lett* 275:364–369. doi:
1018 10.1016/j.epsl.2008.08.035
- 1019 Ruffell A, Hounslow M (2006) Triassic: seasonal rivers, dusty deserts and saline lakes. In: Rawson PF,
1020 Brenchley P (eds) *The Geology of England & Wales*. Geological Society of London, pp 295–325
- 1021 Rusk BG (2006) Intensity of quartz cathodoluminescence and trace-element content in quartz from the
1022 porphyry copper deposit at Butte, Montana. *Am Mineral* 91:1300–1312. doi:
1023 10.2138/am.2006.1984
- 1024 Rusk B, Reed M (2002) Scanning electron microscope–cathodoluminescence analysis of quartz reveals
1025 complex growth histories in veins from the Butte porphyry copper deposit, Montana. *Geology*
1026 30:727. doi: 10.1130/0091-7613(2002)030<0727:SEMCAO>2.0.CO;2
- 1027 Saha D, Dwivedi SN, Roy GK, Reddy D V. (2013) Isotope-based investigation on the groundwater flow
1028 and recharge mechanism in a hard-rock aquifer system: the case of Ranchi urban area, India.
1029 *Hydrogeol J* 21:1101–1115. doi: 10.1007/s10040-013-0974-3
- 1030 Saigal GC, Morad S, Bjørlykke K, Egeberg PK, Aagaard P (1988) Diagenetic albitization of detrital K-
1031 feldspar in Jurassic, Lower Cretaceous, and Tertiary clastic reservoir rocks from offshore Norway,
1032 I. Textures and origin. *J Sediment Petrol* 58:1003–1013
- 1033 Saighi O, Michelot JL, Filly A (2001) Isotopic characteristic of meteoric water and groundwater in
1034 Ahaggar massif (central Sahara)
- 1035 Schmitt JM (1986) Albitisation triasique, hydrothermalisme jurassique et altération supergène récente:
1036 métallogénie des gisements uranifères du Rouergue. Louis Pasteur University
- 1037 Schmitt JM (1992) Triassic albitization in southern France: an unusual mineralogical record from a major
1038 continental paleosurface. In: Schmitt JM, Gall Q (eds) *Mineralogical and geochemical records of*
1039 *paleoweathering*. Paris, ENSMP, Mem Sci Terre. ENSMP, Mémoires des Sciences de la Terre,
1040 Paris, pp 115–131
- 1041 Schmitt JM, Baubron JC, Bonhomme MG (1984) Pétrographie et datations K-Ar des transformations
1042 minérales affectant le gîte uranifère de Bertholène (Aveyron-France). *Miner Depos* 19:123–131

- 1043 Scotese CR, Schettino A (2017) Late Permian-Early Jurassic Paleogeography of Western Tethys and the
1044 World. In: Soto J, Flinch J, Tari G (eds) Permo-Triassic Salt Provinces of Europe, North Africa and
1045 the Atlantic Margins. Elsevier, pp 57–95
- 1046 Simmons CT, Fenstermaker TR, Sharp JM (2001) Variable-density groundwater flow and solute transport
1047 in heterogeneous porous media: approaches, resolutions and future challenges. *J Contam Hydrol*
1048 52:245–275. doi: 10.1016/S0169-7722(01)00160-7
- 1049 Simon-Coinçon R (1999) Palaeolandscape reconstruction of the south-western Massif Central (France).
1050 Palaeoweathering, Palaeosurfaces *Relat. Cont. Depos.* 27:225–243
- 1051 Solé de Porta, N., Calvet, F., Torrentó L (1987) Análisis Palinológico del Triásico de los Catalanides
1052 (NE España). *Cuad Geol Ibérica* 11:237–254
- 1053 Solé J (2009) Determination of K-Ar ages in milligram samples using an infrared laser for argon
1054 extraction. *Rapid Commun Mass Spectrom* 23:3579–3590. doi: 10.1002/rcm.4280
- 1055 Solé J, Enrique P (2001) X-ray fluorescence analysis for the determination of potassium in small
1056 quantities of silicate minerals for K-Ar dating. *Anal Chim Acta.* doi: 10.1016/S0003-
1057 2670(01)01060-1
- 1058 Solé J, Cosca M, Sharp Z, Enrique P (2002) $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology and stable isotope geochemistry
1059 of Late-Hercynian intrusions from north-eastern Iberia with implications for argon loss in K-
1060 feldspar. *Int J Earth Sci* 91:865–881
- 1061 Steiger RH, Jäger E (1977) Subcommittee on geochronology: Convention on the use of decay constants
1062 in geo- and cosmochronology. *Earth Planet Sci Lett* 36:359–362. doi: 10.1016/0012-
1063 821X(77)90060-7
- 1064 Stober I, Bucher K (1999a) Origin of salinity of deep groundwater in crystalline rocks. *Terra Nov*
1065 11:181–185. doi: 10.1046/j.1365-3121.1999.00241.x
- 1066 Stober I, Bucher K (1999b) Deep groundwater in the crystalline basement of the Black Forest region.
1067 *Appl Geochemistry* 14:237–254. doi: 10.1016/S0883-2927(98)00045-6
- 1068 Sun Y, Joachimski MM, Wignall PB, Yan C, Chen Y, Jiang H, Wang L, Lai X (2012) Lethally Hot
1069 Temperatures During the Early Triassic Greenhouse. *Science* (80-) 338:366–370. doi:
1070 10.1126/science.1224126
- 1071 Suzuki K, Adachi M (1994) Middle Precambrian detrital monazite and zircon from the hida gneiss on
1072 Oki-Dogo Island, Japan: their origin and implications for the correlation of basement gneiss of
1073 Southwest Japan and Korea. *Tectonophysics* 235:277–292. doi: 10.1016/0040-1951(94)90198-8
- 1074 Suzuki K, Adachi M, Tanaka T (1991) Middle precambrian provenance of Jurassic sandstone in the Mino
1075 Terrane, central Japan: Th-U-total Pb evidence from an electron microprobe monazite study.
1076 *Sediment Geol* 75:141–147. doi: 10.1016/0037-0738(91)90055-1
- 1077 Suzuki K, Adachi M, Kajizuka I (1994) Electron microprobe observations of Pb diffusion in
1078 metamorphosed detrital monazites. *Earth Planet Sci Lett* 128:391–405. doi: 10.1016/0012-
1079 821X(94)90158-9
- 1080 Taylor HP (1977) Water/rock interactions and the origin of H₂O in granitic batholiths: Thirtieth William
1081 Smith lecture. *J Geol Soc London* 133:509–558. doi: 10.1144/gsjgs.133.6.0509
- 1082 Thiry M, Schmitt JM, Simon-Coinçon R (1999) Problems, progress and future research concerning
1083 palaeoweathering and palaeosurfaces. In: Thiry M, Simon-Coinçon R (eds) Palaeoweathering,

- 1084 Palaeosurfaces and Related Continental Deposits. Blackwell Science. Special Publications of the
1085 International Association of Sedimentologists, Oxford, pp 3–17
- 1086 Thiry M, Théveniaut H, Simon-Coinçon R, Prognon C, Lenoir F, Lacroix F (2014) Persistent
1087 paléosurfaces in the basement of French Massif Central: geodynamic implications. In: Diagenèse:
1088 avancées récentes et perspectives. Association des Sédimentologues Français (ASF), Orsay
1089 (France), pp 113–117
- 1090 Trusheim, F. (1961) Über Diskordanzen im mittleren Buntsandstein Norddeutschlands zwischen Weser
1091 und Ems. *Erdöl-Zeitschrift* 77: 361–367.
- 1092 Vilà M, Pin C, Enrique P, Liesa M (2005) Telescoping of three distinct magmatic suites in an orogenic
1093 setting: Generation of Hercynian igneous rocks of the Albera Massif (Eastern Pyrenees). *Lithos*
1094 83:97–127. doi: 10.1016/j.lithos.2005.01.002
- 1095 Williams ML, Jercinovic MJ, Goncalves P, Mahan K (2006) Format and philosophy for collecting,
1096 compiling, and reporting microprobe monazite ages. *Chem Geol* 225:1–15. doi:
1097 10.1016/j.mce.2005.09.009
- 1098 Williams ML, Jercinovic MJ, Harlov DE, Budzyń B, Hetherington CJ (2011) Resetting monazite ages
1099 during fluid-related alteration. *Chem Geol*. doi: 10.1016/j.chemgeo.2011.01.019
- 1100 Witkowski FW, Blundell DJ, Gutteridge P, Horbury AD, Oxtoby NH, Qing H (2000) Video
1101 cathodoluminescence microscopy of diagenetic cements and its applications. *Mar Pet Geol*
1102 17:1085–1093. doi: 10.1016/S0264-8172(00)00055-6
- 1103 Wojdyr M (2010) Fityk: a general-purpose peak fitting program. *J Appl Crystallogr* 43:1126–1128. doi:
1104 10.1107/S0021889810030499
- 1105 Wolburg, J. (1968) Vom zyklischen Aufbau des Buntsandsteins. *Neues Jb Geol. Paläontol. Mh.* 9: 535–
1106 559.
- 1107 Wooding RA, Tyler SW, White I (1997) Convection in groundwater below an evaporating Salt Lake: 1.
1108 Onset of instability. *Water Resour Res* 33:1199–1217. doi: 10.1029/96WR03533
- 1109 Worden RH, Walker FDL, Parsons I, Brown WL (1990) Development of microporosity, diffusion
1110 channels and deuteric coarsening in perthitic alkali feldspars. *Contrib to Mineral Petrol* 104:507–
1111 515. doi: 10.1007/BF00306660
- 1112 Yao KFE (2013) Albitization and oxidation of the granitoid rocks related to the Triassic paleosurface in
1113 the Sudetes (SW Poland). *École Nationale Supérieure des mines de Paris*
- 1114 Yao KFE, Franke C, Thiry M, Paweł A, Szuszkiewicz A, Turniak K (2011) Albitization as record of the
1115 Triassic Paleosurface in the Sudetic Crystalline basement (Poland). *Geophys Res Abstr* 13:
1116 EGU2011-5930
- 1117 Yerle JJ, Thiry M (1979) Albitisations et minéralisations uranifères dans le socle et les sédiments permo-
1118 houillers du bassin de Brousse-Broquiés (Aveyron, France). *Bull du BRGM Ser 2* 4:275–290
- 1119 Zheng Y-F, Hoefs J (1993) Carbon and oxygen isotopic covariations in hydrothermal calcites. *Miner*
1120 *Depos* 28. doi: 10.1007/BF00196332
- 1121 Zheng Y-F (1993) Calculation of oxygen isotope fractionation in anhydrous silicate minerals. *Geochim*
1122 *Cosmochim Acta* 57:1079–1091. doi: 10.1016/0016-7037(93)90042-U