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

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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\textsubscript{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 $\delta^{18}$O
values of albitized plagioclase (+11‰), microclinized orthoclase (+13‰), and secondary CL-dark quartz (+12‰), suggest that the alteration temperature was about 55°C. This “low” temperature suggests that the alteration occurred during interaction of the granitic rocks with Na-rich fluids below a surficial weathering mantle on the Permian-Triassic palaeosurface. The latter is possibly related to Triassic evaporitic environments in long-lasting, stable landscapes in which Na-rich solutions infiltrated deep regional groundwaters.

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

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

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

The present study focusses on the spatial distribution, geometry, petrology, age and oxygen isotope composition of the red-stained albitized profiles in the Variscan granitic basement beneath the Triassic unconformity of the Guillerries and Roc de Frausa massifs (NE Spain), with aims to: 1) determine the genetic relationship of the alteration with the Permian-Triassic palaeosurface, 2) constrain the age of the
alteration event, 3) evaluate the origin and temperature of the albitizing fluid, and 4) gain an understanding of subsurface processes that operated beneath the Triassic palaeosurface.

**Geological setting and study sites**

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

![Fig. 1. Location of the Guilleries (a) and Roc de Frausa (b) massifs in the Variscan terranes of the Catalan Coastal Ranges and Eastern Pyrenees.](image-url)
The igneous basement of the Roc de Frausa Massif is formed of biotite-hornblende granite, granodiorite, leucogranite, monzo-granite, and porphyritic granites (Fig. 2c) that intruded a Proterozoic to early Cambrian sequence of metapelites, ortho-gneiss, and metagreywackes (Aguilar et al., 2015). To the southwest, the areas of Hortmoier, Oix and St. Aniol are made up of porphyritic granite with K-feldspar phenocrysts (Fig. 2c). U-Pb dating of zircons yielded two cooling episodes for the granites corresponding to 314.2 ± 1.5 and 311.0 ± 0.9 Ma (Aguilar et al., 2014). The sedimentary cover is formed of south-tilted (40-50°) Upper Cretaceous (Maastrichtian) red-beds (Oms et al., 2007; Gómez-Gras et al., 2016).

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

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

The study sites in both massifs (Table 1) focussed on the red-stained albitized granitoids cropping out under the Triassic unconformity and on their unaltered counterparts (Fig. 2a, b, c). Several cross sections were constructed to determine the structure and depth of the red-stained albitization with respect to the Triassic unconformity (Fig. 2d, e). Further detailed information on the study sites is included in the Supplementary Information S1, available at the dataset of Fàbrega et al. (2018).
Fig. 2. Geological setting, sampling sites and cross-sections. (a) Guilleries Massif. (b) Tagamanent hill, located on the south of the Guilleries Massif. (c) Roc de Frausa Massif, St. Aniol, Hortmoier and Oix. (d) Sau dam cross section. (e) Boadella dam cross section. **Main sampling sites**: Guilleries Massif: (1) Susqueda dam; (2) Sau dam; (3) Bojons; (4) Arbúcies and St. Coloma de Farners; (5) Osormort; (6) Viladrau; (7) Mas Vidal-Timonar; (8) Tagamanent; (9) Vallformès. Roc de Frausa Massif: (10) La Vajol; (11) Maçanet de Cabrenys; (12) St. Laurent Cerdans; (13) Coustoges; (14) Villerouge; (15) Puig Creu de Mondavà; (16) Boadella dam; (17) St. Aniol; (18) Hortmoier; (19) Oix.
**Methods and materials**

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

**Sampling and mapping**

Sampling, mapping and construction of cross-sections of the red albitized granitoids were systematically carried out along the Triassic unconformity of both massifs (Fig. 2). Due to a dense forest cover in most of the study areas, the work was mostly carried out along linear features including roads, trails and creeks.

A total of about 280 and 100 samples were collected in the Guilleries and Roc de Frausa Massifs, respectively, including pervasively albitized rocks, albitization restricted to fractures and unaltered rocks (Table 1).

**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          |                                 |
| Villerouge            | 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     |                                 |
Petrological and geochemical analyses

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

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

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

K-Ar dating of K-feldspar phenocrysts was carried out at the Instituto de Geología of the Universidad Nacional Autónoma de México. The analyses were done on 1 unaltered and 7 pinkish phenocryst subsamples from Hortmoier (see Fig. 2). Fragments of the K-feldspar phenocrysts about 2-5 mm in size were hand-picked with the aid of a stereo microscope. The selected fragments were cleaned with distilled water.
water and acetone. The K content was measured by XRF on 50 mg aliquots using a specific regression for measuring K in K-Ar samples (Solé and Enrique, 2001). Analytical precision was > 2%. Duplicate samples weighing between 1 and 2 mg were mounted on holes of a copper plate. This plate was placed on an ultra-high vacuum chamber that was degassed at ~150°C for twelve hours before analysis to reduce atmospheric contamination. Argon was extracted by complete sample fusion using a 50 W CO₂ laser defocused to 1 - 3 mm diameter. The evolved gasses were mixed with a known amount of ⁸⁷Ar spike and purified with a cold finger immersed in liquid nitrogen and two SAES getters in a stainless-steel extraction line. Measurements were done in static mode with an MM1200B noble gas mass spectrometer using electromagnetic peak switching controlled by a Hall probe. Analytical precision on ⁴⁰Ar and ³⁸Ar peak heights was better than 0.2%, and better than 0.5% for ³⁶Ar. The data were calibrated with internal standards and the international reference materials LP-6 biotite, B4M muscovite and HD-B1 biotite. All ages were calculated using the constants recommended by Steiger and Jäger (1977). A detailed description of the procedure and calculations is given by Solé (2009).

**U-Th-Pb\textsubscript{total} EPMA monazite dating**

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

Monazite grains were first identified in the thin sections by means of BSE imaging in a Hitachi TM-1000 electron microscope operating at 15 kV at the Escola Politècnica Superior d’Enginyeria de Manresa (EPSEM) of the Universitat Politècnica de Catalunya (Spain). The U-Th-Pb\textsubscript{total} EPMA analyses were carried out using a JEOL JXA-8230 electron probe operating at 20 kV at the Centres Científics i Tecnològics (CCiTUB) of the Universitat de Barcelona (Spain). The session-to-session consistency of the EPMA analyses was controlled using an in-house monazite standard from Coats pegmatite (Petaca district, New Mexico). The reference U-Th-Pb isotopes standard age was 1332.6 ± 4.6 Ma (2σ), obtained by LA-ICP-MS at Geosciences Rennes, Université de Rennes 1 (France). The U-Th-Pb\textsubscript{total} ages of the standard obtained in each EPMA session were, respectively, 1313 ± 30, 1307 ± 36, 1308 ± 44, and
1305 ± 32 Ma (2σ), being consistent, within 2σ, with the U-Pb and Th-Pb age obtained by laser ablation coupled with MC-ICP-MS.

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

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

**In-situ δ¹⁸O SIMS analyses**

In-situ δ¹⁸O (to VSMOW) SIMS analyses of plagioclase, K-feldspar and quartz were carried out using a CAMECA IMS 1280HR ion microprobe at the Centre de Recherches Pétrographiques et Géochimiques, Centre National de la Recherche Scientifique (Nancy, France). Rock samples were cut into 4×4×4 mm pieces, mounted in cylindrical 25 mm diameter/5 mm thick epoxy mounts accompanied by mm-sized fragments of in-house feldspar and quartz standards and metallographically polished. Optical-CL microphotographs of the surfaces of samples and standards were obtained and were subsequently used during the SIMS session to locate the oxygen isotope analyses on the desired textural position. The SIMS analyses were carried out using a ¹³³Cs⁺ primary ion beam of +10 kV and intensity of 5 – 6 nA. Vacuum
conditions in the sample chamber were about ~E⁻⁹ Torr. Positive charging of the sample surface was prevented by means of a gold coating and a normal incident electron flood gun. Secondary negative ions were accelerated by a 10 kV potential. After pre-sputtering, the secondary ion beam was automatically centered onto the field aperture by the electrostatic deflectors LT1DefX and LT1DefY. The produced $^{16}\text{O}^-$ and $^{18}\text{O}^-$ were simultaneously collected in multicollection mode using two Faraday cups (FC; L’2 for counting $^{16}\text{O}^-$ ions, and H1 for $^{18}\text{O}^-$ ions). Each single analysis included 30×5-s-long counting cycles, with a total span time of ~4 min, including 60 s of pre-sputtering.

The in-house standards used for the correction of the SIMS instrumental mass fractionation (IMF) included eight plagioclase, two K-feldspar and one quartz specimens. The textural characteristics, chemical and bulk δ¹⁸O compositions of the in-house standards are described in Fàbrega et al. (2017) and hosted in the institutional repository UPCommons of the Universitat Politècnica de Catalunya, Spain (Parcerisa et al., 2016). The averaged internal precision (within-spot uncertainty) of the standards analyses was 0.06‰ (1σ) for the whole session. The external precision (spot-to-spot reproducibility) was in the range 0.29 - 0.5‰ (1σ). Mount-to-mount reproducibility was 0.29‰ (1σ), estimated as the standard deviation of four δ¹⁸O values, and obtained by averaging sets of five analyses of a K-feldspar standard ($δ^{18}\text{O} = 9.3 \pm 0.1‰, 1σ$) in four different mounts during the session.

The IMF of the plagioclase, K-feldspar and quartz δ¹⁸O SIMS analyses were predicted by response surface methodology (RSM) using the three response surface models described in Fàbrega et al. (2017). The predictor (input) variables were the instrumental parameters X and Y stage position, primary beam intensity (PI), chamber pressure (CP) and, electrostatic deflectors LT1DefX and LT1DefY. In addition, the models for feldspars included the compositional inputs An% (plagioclase model) and Or% and BaO% (K-feldspar model). The IMF was considered as the predicted (output) variable or response. This RSM approach permitted to predict a unique IMF value for each SIMS analysis.

The SIMS δ¹⁸O analyses of unaltered rock were carried out on 2 samples in Guilleries and 2 samples in the Roc de Frausa. On red-stained albitized rock, δ¹⁸O analyses were also performed on 2 samples in Guilleries and 2 samples in Roc de Frausa. A total of 54 and 90 δ¹⁸O SIMS analyses were carried out on the Guilleries and Roc de Frausa samples, respectively.
Structure and petrology of the alteration

Unaltered facies

The unaltered facies of the Guilleries consists of granodiorite and leucogranite. Primary Ca-plagioclase occurs as euhedral 1 – 3 mm zoned crystals with polysynthetic twinning and yellow-green luminescence. Ca-plagioclase grains have compositions in the core and rim of, respectively, Ab$_{79-90}$ and Ab$_{89-99}$ in the leucogranite and Ab$_{60-70}$ and Ab$_{92-99}$ in the granodiorite (Table 2). Primary K-feldspar is orthoclase characterized by subhedral 0.5 - 3 mm crystals with micro and crypto perthite lamellae, blue luminescence and a chemical composition in the range Or$_{84-96}$ for both the leucogranite and the granodiorite (Table 2). The porphyritic granite of the Tagamanent area (see Fig. 2b) has white orthoclase phenocrysts (2 - 3 cm) with blue luminescence containing micro and crypto perthite lamellae. Quartz occurs as 0.1 – 2 mm anhedral grains with homogeneous grey SEM-CL and cooling microcracks. Biotite occurs as brown to green 0.1 – 3 mm tabular grains with an Fe/Fe+Mg ratio ranging from 0.82 - 0.84 and 0.61 - 0.70 for the leucogranite and the granodiorite, respectively. The accessory minerals are zircon, epidote, apatite-(F), monazite-(Ce) and xenotime. Zircon occurs as 10 – 50 µm zoned euhedral crystals, epidote as euhedral 10 – 30 µm elongated crystals, and apatite as 5 – 20 µm rounded crystals within biotite. Monazite is typically 20 – 50 µm euhedral or rounded grains that commonly reach 200 – 300 µm in size. Xenotime mostly forms euhedral 30 – 50 µm crystals. Magnetite (Fe$_3$O$_4$) is the dominant ferromagnetic mineral in the unaltered igneous rocks of the Guilleries Massif (Franke et al., 2010).

The unaltered facies in Roc de Frausa is mainly porphyritic granite with K-feldspar phenocrysts (2–3 cm), and this also occurs in the St. Aniol, Hortmoier and Oix areas (Fig. 2c). Primary Ca-plagioclase occurs as zoned euhedral 0.5 – 2 mm crystals with polysynthetic twinning, yellow-green luminescence and a composition in the ranges Ab$_{66-74}$ and Ab$_{90-99}$ for the Ca-rich cores and the Na-rich zones, respectively (Table 2). The matrix K-feldspar is subhedral to euhedral 0.5 – 2 mm crystals with micro- and crypto perthite lamellae, blue luminescence and a composition of Or$_{74-98}$ (Table 2). The K-felspar phenocrysts (2 – 3 cm) are white orthoclase with blue luminescence, a composition in the range Or$_{70-90}$, and micro and crypto perthite lamellae. Quartz is present as 0.5 – 3 mm anhedral crystals with homogeneous SEM-CL and cooling microcracks. Biotite usually occurs as 1 - 3 mm tabular crystals with a Fe/Fe+Mg ratio in the range 0.61 - 0.65. The accessory minerals are euhedral 10 – 50 µm zircon, 5 – 15 µm rounded apatite-(F),...
euhedral 10 – 30 µm epidote, euhedral or rounded 20 – 40 µm monazite-(Ce), and occasional euhedral
20 – 50 µm xenotime.

**Red-stained albitized facies**

The red-stained albitized facies beneath the Triassic unconformity has the form of a ~150-200 m deep
geopetal structure characterized by a decreasing intensity of alteration from the top to the bottom (Fig. 2d,
e). The alteration in the upper part is very pervasive and the rock is a red facies (Fig. 3a). The degree of
alteration progressively decreases with depth and the rock is a pink facies in the intermediate zone of the
profile (Fig. 3b, e). In the lower part of the profile, the red-stained albitization is restricted to the walls of
fractures and the rock presents as a ‘spotted’ facies (Fig. 3d, 3e). The fractures controlling alteration in
the lower parts of the profile are likely to have developed by pre-existing cooling and decompression of
the granitic mass. In the upper part of the profile, closer to the unconformity, more pervasive alteration
was accomplished via a greater abundance of joints and fractures together with micro-fractures and grain
boundaries penetrating the matrix of the rock. Here, effective fluid pathways could also have
progressively self-generated through reaction-induced hierarchical fracturing (Røyne et al., 2008;
Jamtveit et al., 2009).
Fig. 3. Red stained albitized facies. (a) Red albitized porphyritic granite (lower left) unconformably overlain by south-dipping Upper Cretaceous (Maastrichtian) red-beds (upper right). Boadella dam, Roc de Frausa massif. (b) Pervasively albitized pink porphyritic granite near the top of the profile. Boadella dam, Roc de Frausa massif. (c) Completely albitized red - pink granodiorite in the upper part of the profile. Mas Vidal area, Guillerries massif. (d) Red albitization along fractures (coin) through unaltered granite in the bottom of the profile. Sau dam, Guilleries massif. (e) Red albitization along fractures including microclinized pink orthoclase phenocrysts (white arrows) in the lower part of the profile. Hortmoier area.

The nature of Fe-oxides evolves within the profile. Hematite (Fe₂O₃) dominates in the red facies of the upper part of the profile (Fig. 4), indicating stronger oxidizing conditions. Hematite crystals are micron-sized and occur inside the microporosity of secondary feldspars, suggesting that they formed by fluid-rock interaction rather than feldspar exsolution (Putnis et al., 2007). Hematite is considered to have formed by both the alteration of maghemite and authigenic precipitation. The composition of hematite in
the red facies is about Ilmenite, Geikielite, Pyrophanite, and Hematite, probably reflecting the introduction of Ti released during biotite chloritization into the hematite structure. The concentration of maghemite ($\gamma$-Fe$_2$O$_3$) increases with depth (Fig. 4), indicating progressively decreasing oxidizing conditions. Maghemite is considered to have formed by oxidation of primary magnetite and by authigenic precipitation at low temperature (Franke et al., 2010).

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

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**Fig. 4.** Evolution of the albitized facies and the mineralogy of the profile. Numbers correspond to sampling sites presented in Fig. 2. Adapted from Yao (2013).
Primary Ca-plagioclase is pseudomorphed by secondary albite. Albitized plagioclase grains (Fig. 5a, b, c) have a turbid aspect, a lack of luminescence, widespread micron-sized non-connected euhedral porosity (Fig. 5d) and a very pure chemical composition in the range of Ab$_{97.99}$ (Table 2). The replacement front between the primary Ca-plagioclase and the secondary albite is very sharp (Fig. 5b), and the crystallographic framework is preserved from the primary to the secondary phase. These textural features are typical of a fluid-aided dissolution-reprecipitation process along micro-fractures without development of dissolution pores prior to precipitation (Putnis, 2002; Engvik et al., 2008; Putnis, 2009). The albitized plagioclase grains usually contain micron-sized non-luminescent secondary K-feldspar and orange-CL calcite (Fig. 5c), the latter with a composition about Magnesite$_{1.5}$ Siderite$_{0.7}$ Calcite$_{97.8}$. The primary green-yellow luminescent Na-rich rims of plagioclase, with the composition Ab$_{90.93}$, are preserved during albitization (Fig. 5a).

Primary biotite is pseudomorphed by secondary chlorite. Chloritized biotite is non-luminescent, preserves the biotite sheet structure and usually contains lens-shaped inclusions of secondary K-feldspar, quartz and orange-CL calcite (Fig. 5c). The composition of the calcite inclusions formed inside chlorite is about Magnesite$_{2.4}$ Siderite$_{1.2}$ Calcite$_{94.3}$, reflecting a higher content of Mg and Fe released from primary biotite during chloritization than available to the calcite inclusions formed within secondary feldspars. The chloritized biotite grains systematically show a significant increase of yellow luminescent micron-sized fluorapatite inclusions (Fig. 5c). In places, neoformed chlorite occurs in sheaf like arrangements of micron-size sheets inside the micro porosity.

The microclinization of orthoclase is characterized by the recrystallization of primary orthoclase to secondary microcline. The microclinized grains have a cloudy aspect, loss of luminescence (Fig. 5a), a widespread micron-sized non-connected euhedral porosity, amoeboid-shaped patchy perthite texture and a composition of about Or$_{96.99}$ and Or$_{97.93}$ in the Guilleries and Roc de Frausa, respectively (Table 2). The patch perthite exclusively forms during the microclinization process and implies replacement of K-feldspar by secondary albite. K-feldspar phenocrysts (2 – 3 cm) in the porphyritic granites progressively change from the white color of the primary orthoclase to brown and finally red-pink as the degree of microclinization increases. The most strongly microclinized phenocrysts have a composition (XRD) of about 40 - 60% microcline, 20 - 30% albite and 10 - 40% orthoclase. The albite detected by XRD inside the red-pink phenocrysts includes the patch perthite and plagioclase inclusions that were albitized during microclinization.
The net of micro fractures in the red-stained albitized rocks is sealed by secondary CL-dark quartz that postdates the aforementioned reactions. Within quartz grains, this net of micron sized CL-dark quartz has a dendritic texture (Fig. 5e), suggesting that it propagated along sub-micron cracks and dislocations and may possibly record some degree of dissolution-reprecipitation process of the primary quartz.

Fig. 5. Cathodoluminescence and SEM petrography of the albitized facies. (a) Pink albitized granite near the top of the profile. Albitized plagioclase grains display non-luminescent albitized cores (Ab2) and preserve a primary Na-rich CL-yellow rim (Ab1) in contact with a K-feldspar grain with primary CL-blue zones (Kfs1) and CL-turbid microclinized areas (Kfs2). (b) CL-yellow primary plagioclase (Pl1) partially pseudomorphosed by non-luminescent secondary albite (Ab2) penetrating along twin planes and micro fractures. (c) CL-image of very strongly albitized red granite at the top of the profile. Patches of secondary CL-orange calcite (Cal2) inside non-luminescent albitized plagioclase (Ab2) and chloritized biotite (Chl2a). Chloritized biotite also shows significant yellow apatite inclusions (Ap) compared with primary biotite. (d) BSE-image of clusters of synchysite-(Ce) ‘sticks’ inside the secondary...
porosity of albitized plagioclase ($Ab_2$) and microclinized orthoclase ($Kfs_2$). (e) SEM-CL picture of igneous quartz grain from the upper part of the profile showing a dendritic net of CL-dark secondary quartz ($Qtz_2$). Patches of primary quartz ($Qtz_1$) are preserved. (f) BSE-image showing alteration of monazite in the reaction front approximately indicated by the pink line. Left, monazite pseudomorphosed by secondary monazite ($Mnz_2$) and apatite ($Ap_2$) and accompanied by euhedral synchysite (Syn2) and titanite (Tit2). Right, primary monazite grains ($Mnz_1$) mostly preserved but showing some pseudomorphic secondary monazite ($Mnz_2$) in the boundaries. Chl2a: Chloritized biotite; $Kfs_2$: Microclinized orthoclase.

Authigenic synchysite-(Ce) [Ca(Ce, La)(CO$_3$)$_2$F] is the dominant REE-mineral in the red-stained albitized rocks (Fig. 4) and its abundance decreased from the top to the bottom of the profile. It usually occurs in clusters of 5-15 µm stick-shaped crystals inside the secondary micron-sized porosity of the albitized plagioclase, microclinized orthoclase and chloritized biotite (Fig. 5d), strongly suggesting coeval formation with these secondary minerals. Synchysite-(Ce) is mostly Th-poor (0 - 4.68 wt% Th [CO$_3$]) with 33 to 54 wt% of $LREE_2$O$_3$ and 1.6 to 5.5 wt% of $Y_2$O$_3$ + $HREE_2$O$_3$. The Ca content (wt. % CaCO$_3$) of Synchysite-(Ce) decreases from 29-32% at the top of the profile (n= 9) to 22-23% at the bottom (n= 10).

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

The alteration of all silicates and non-silicates, namely albitization of Ca-plagioclase, microclinization of orthoclase, chloritization of biotite, and precipitation of secondary CL-dark quartz, iron oxides and REE-minerals, decreases from the top to the bottom of the profile (Fig. 4). In the same context, the succession of mineral alteration adjacent to fractures decreases in intensity towards the cores of the granite blocks. Decimetre-thick alteration zones occur adjacent to the major fractures, with restricted millimetre-thick zones walls adjacent to secondary fractures, and less along micro-cracks. These relationships point clearly to the influence of fluid circulation. As well, albitization was not associated with a volume change, i.e. the texture and fabric of the altered rocks is not significantly different from that of the unaltered rocks, at least at a macroscopic level.
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$_{39.99}$ | Or$_{84.96}$ | Ab$_{97.99}$ | Or$_{56.99}$ |
| Roc de Frausa | Ab$_{60.74}$ | Ab$_{39.99}$ | Or$_{74.98}$ | Ab$_{97.99}$ | Or$_{57.93}$ |

Geochemical characteristics of the alteration

Mass balance

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

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

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

| rock        | n | 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    |

Petrographical observations of the red-stained albitized rocks show that albitization of plagioclase, microclinization of K-felspar, and chloritization of biotite are intimately linked to the precipitation of secondary synchysite-(Ce), apatite, epidote, calcite and hematite that probably recycled some of the ions released by the major reactions. Consistent with the albitization of primary plagioclase, the amount of Na in the albitized rock presents a mass increase of about +91%, and a Ca loss of -60% (Fig. 6). By considering the atomic mass of Na and Ca, this means that only about half of the Ca released by replacement of plagioclase by albite has been removed from the system. The remnant Ca was likely
recycled into secondary synchysite-(Ce), apatite, epidote, and calcite. The K content presents a significant reduction of -43% (Fig. 6), which is consistent with the systematic biotite chloritization and some K-feldspar albitization. A fraction of the K is probably retained by the secondary K-feldspar lenses within chloritized biotite and micron-size patches of perthite in the albitized plagioclase. Mg presents a significant increase of +30% (Fig. 6). The Si content increases by about +17%, which agrees with the overall albitization of plagioclase (Fig. 6). Al released during albitization of plagioclase may have been consumed during chloritization of biotite and the formation of secondary K-feldspar. However, the albitization reflects an overall increase in Al of +7%. The Fe content remains stable (Fig. 6). The Fe released during chloritization of biotite was probably retained to form the secondary Fe-oxides. The amount of Ti decreased about -5% (Fig. 6), most of it probably released during chloritization of biotite and partly retained in secondary titanite. The variation in Mn shows a loss of -2% (Fig. 6). The loss of P was about -19% (Fig. 6), mostly due to the dissolution of monazite in the albitized profile. Some of the P participated in the formation of secondary fluorapatite in combination with F released during chloritization of biotite.

![Fig. 6. Weight variation (%)](image)

Positive variation indicates an increase in the element concentration in the albitized facies with respect to the unaltered rocks.

**δ¹⁸O composition**

Primary minerals in the unaltered rocks

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

In the leucogranite of the Guilleries Massif, the zoned plagioclase has δ¹⁸O values ranging from 8.52 to 9.51‰ in the Ca-bearing cores and 11.14 to 11.93‰ in the Na-rich rims (Table 4), showing a positive
correlation of δ¹⁸O values with increasing sodic composition (Fig. 7a). Primary K-feldspar grains have δ¹⁸O values ranging from 10.42 to 11.65‰ (Table 4), without any correlation with the primary K-feldspar composition (Fig. 7b). Primary quartz has a δ¹⁸O composition between 6.4 and 9.60‰ (Table 4). In the Tagamanent area (see Fig. 2b), the δ¹⁸O of the K-feldspar phenocrysts is between 10.6 and 10.8‰, close to the mean value of the primary matrix K-feldspar grains in the Guilleries samples.

Table 4. δ¹⁸O (‰) of feldspars and quartz in the Guilleries and Roc de Frausa Massifs

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

In the porphyritic granite of the Roc de Frausa Massif, δ¹⁸O values for the primary plagioclase range 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 positive correlation of δ¹⁸O values with the increase of sodium content (Fig. 7a). The primary K-feldspar grains in the granitic matrix have δ¹⁸O values ranging from 11.50 to 12.39‰ (Table 4) and do not show any correlation with the K-feldspar composition (Fig. 7b). In the porphyritic granite of Hortmoier area, primary K-feldspar phenocrysts have steady δ¹⁸O values ranging from 11.4 to 11.6‰, near the mean value of the primary matrix K-feldspar grains in the Roc de Frausa samples.

In the Guilleries, Roc de Frausa and Hormoier, the δ¹⁸O compositions of the primary feldspars are consistent with high δ¹⁸O crustal-derived magmas and follow the expected higher values in δ¹⁸O composition in the alkali feldspars characterized by Anorthite δ¹⁸O < K-feldspar ≈ Albite δ¹⁸O (Bindeman, 2008).

The oxygen isotope fractionation between primary plagioclase and K-feldspar (Δ¹⁸O<sub>Ab-Kfs</sub>) were about +0.5‰ and -0.5‰ for the Guilleries and Roc de Frausa, respectively, suggesting that, within error, primary feldspars formed under equilibrium conditions (Fig. 8a). The oxygen isotope fractionation between primary quartz and primary plagioclase (Δ¹⁸O<sub>Qtz-Pl</sub>) are negative, with values about -3 and -4‰ for the Guilleries and Roc de Frausa, respectively (Fig. 8b). In the case of the quartz and primary K-feldspar (Δ¹⁸O<sub>Qtz-Kfs</sub>) fractionation, values are also negative about -3 and -5‰ for the Guilleries and Roc de Frausa, respectively (Fig. 8c). These negative fractionation values of plagioclase and K-feldspar with
With respect to quartz are reversed and indicate that the feldspars and quartz formed under disequilibrium conditions.

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

Secondary minerals of the red-stained albitized rocks

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

Albitized plagioclase from Guilleries has $\delta^{18}$O ranging from 10.31 to 11.60‰ (Table 4), representing an average increase about +2‰ with respect to the $\delta^{18}$O of the primary Ca-bearing plagioclase cores (Fig. 7a). At the Roc de Frausa, $\delta^{18}$O values for albitized plagioclase range from 11.14 to 12.75‰ (Table 4), an average increase about +2.5‰ compared to the primary Ca-rich plagioclase cores (Fig. 7a).
The microclinized orthoclase of Guilleries has $\delta^{18}O$ values ranging from 11.76 to 13.81‰ (Table 4), an average increase about +1.5‰ compared with the primary orthoclase (Fig. 7b). At Roc de Frausa, the $\delta^{18}O$ composition of microclinized orthoclase ranges from 12.31 to 13.96‰ (Table 4), an average increase about +1‰ compared to the primary orthoclase (Fig. 7b).

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

The $\delta^{18}O$ values of secondary feldspars and quartz in both massifs indicate disequilibrium fractionation values ($\Delta^{18}O$) for the mineral pairs. The oxygen isotope fractionation between secondary albite and microclinized orthoclase ($\Delta^{18}O_{Ab2-Kfs2}$) presents disequilibrium values about -1.8‰ and -1.6‰ for the Guilleries and Roc de Frausa, respectively (Fig. 8a). In the Roc de Frausa samples, the oxygen isotope fractionation between CL-dark secondary quartz and albitized plagioclase ($\Delta^{18}O_{Qtz2-Ab2}$) is about 0.4‰ (Fig. 8b), and between CL-dark secondary quartz and microclinized orthoclase ($\Delta^{18}O_{Qtz2-Kfs2}$) is about -1.2‰ (Fig. 8c).
Fig. 8. $\delta-\delta$ plots of primary and secondary mineral pairs of each massif. (a) Primary plagioclase vs. primary K-feldspar and secondary albite vs. secondary microclinized K-feldspar. (b) Primary plagioclase vs. primary quartz (grey) and albitized plagioclase vs. CL-dark quartz (pink). (c) Primary K-feldspar vs. primary quartz (grey) and microclinized orthoclase vs. CL-dark quartz (pink). The equilibrium fractionations at equilibrium of each mineral pair were calculated for 200 and 800 ºC using the equations of Zheng (1993).

Geochronology

**K-Ar dating of K-feldspar phenocrysts**

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

In the red albitized rocks, brown K-feldspar phenocrysts from albitized fracture walls (see Fig. 3e), represent a degree of microclinization of 30-40% and yielded K-Ar ages of 244.5 ± 6, 237.6 ± 6, and 230.7 ± 6 Ma (2σ). The textural similarities and the overlapping of the three ages within the 2σ range
support a probable K-Ar resetting event during the Early Triassic. Given that these microclinized brown
K-feldspar phenocrysts occur near the reaction front (see Fig. 3e) and are accompanied by partially
albitized plagioclase and chloritized biotite, these Early Triassic dates are considered to constrain the age
of the alteration in these red fracture facies in the lower part of the albitized profile.

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

**Monazite U-Th-Pb<sub>total</sub> dating**

EPMA U-Th-Pb<sub>total</sub> dating was carried out on primary monazite grains in the unaltered rocks and on
pseudomorphic secondary monazite associated with the reaction front in the red-stained albitized rocks.
In the Guilleres Massif (Fig. 9a), the deconvolution of the histogram of the U-Th-Pb<sub>total</sub> analyses
(n = 117) yielded two significant ages of 251.2 ± 12 and 295.2 ± 14 Ma (2σ), with a relative misfit of
0.925. The histogram deconvolution of the analyses (n = 80) of the Roc de Frausa Massif (Fig. 9b) also
indicates the existence of two significant ages of 254 ± 14 and 298 ± 12 Ma (2σ), presenting a relative
misfit of 0.966.
Fig. 9. Deconvoluted histograms of the U-Th-Pb\textsubscript{total} monazite dates. (a) Guilleries Massif. (b) Roc de Frausa Massif. Grey vertical lines= Carboniferous – Permian ages. Pink vertical lines= Permian-Triassic ages. The two graphs (a, b) use the same X scale.

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

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


**Discussion**

**Age of the red-stained albitized profile**

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

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

All the age determinations using independent methods are coherent and point to the albitization and related alteration having developed during the Late Permian to Early Triassic, while the Variscan granites in NE Spain were exposed at the landsurface (López-Gómez et al., 2005; Linol et al., 2009; Galán-Abellán et al., 2013). Thus, the red-stained albitization relates to the Triassic palaeosurface, and its geopetal organization indicates that alteration of the granites most probably occurred under the influence of palaeogeography, climate, weathering, and groundwater.
δ¹⁸O fluid-rock exchange during albitization

The minerals in both the unaltered and red albitized rocks have δ¹⁸O values that implicate fluid-rock oxygen-isotope exchange processes during albitization. For example:

1. All secondary phases in the red-stained albitized rocks (albitized plagioclase, microclinized orthoclase and CL-dark quartz) have higher δ¹⁸O values compared to their primary counterparts in the unaltered rocks.

2. The reactions follow this sequence: (a) albitization of plagioclase, (b) microclinization of orthoclase and (c) formation of CL-dark quartz, and partially overlapped over time. The δ¹⁸O values of the secondary phases are in disequilibrium, suggesting that the minerals re-equilibrated with fluid with a changing δ¹⁸O and/or temperature throughout the reaction sequence.

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

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

\[ \delta^{18}O_f = \delta^{18}O_i + \frac{R}{W} \times (\delta^{18}O_m^i - \delta^{18}O_m^f) \]  

(1)

\( \delta^{18}O_i \) and \( \delta^{18}O_f \) being the initial and final oxygen isotope compositions of fluid, respectively, \( R \) and \( W \) the percentage of oxygen atoms in the rock (or mineral) and water, respectively, and \( \delta^{18}O_m^i \) and \( \delta^{18}O_m^f \) the oxygen isotope composition of the initial and final minerals, respectively.

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

\[ 1000 \ln \alpha_{Ab-H_2O} = \frac{4.33 \times 10^6}{T^2} - \frac{6.15 \times 10^3}{T} + 1.98 \]  

(2)
\[ 1000 \ln \alpha_{Kfs-H2O} = \frac{4.32}{T^2} \times 10^6 - \frac{6.27}{T} \times 10^3 + 2.00 \]  
\[ 1000 \ln \alpha_{Qtz-H2O} = \frac{4.48}{T^2} \times 10^6 - \frac{4.77}{T} \times 10^3 + 1.71 \]  

Where \( T \) is the equilibrium temperature and 1000ln\( \alpha \sim (\delta^{18}O_{w_i} - \delta^{18}O_{w}) \) the oxygen isotope fractionation between mineral and fluid, being \( \delta^{18}O_{w} \) determined by Eq. 1.

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

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

The rock to water (R/W) oxygen mass ratio is also a key factor for an estimation of the isotopic evolution of the fluid. Reactions arising directly at fracture walls, where solution may be renewed by circulation, may correspond to relative low R/W ratios, whereas those occurring away from the fractures, at the reaction front within primary crystals in an almost closed system, most likely correspond to higher R/W.
ratios. To determine a minimum and conservative estimate of the $\delta^{18}$O evolution of water, calculations were carried out applying R/W values of 0.5 and 1, considered to be high ($\geq$1) water to rock ratios (Taylor, 1977).

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

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

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

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

(2) An open system, in which fluid is renewed by circulation. The calculation (Eq. 1) considered concomitant mineral alterations and with the same initial fluid composition for each reaction. It corresponds to exchanges with surrounding systems, allowing imports and exports of chemical elements. After calculation of the resulting oxygen isotope composition of fluid for each reaction, the corresponding
temperatures were calculated using Eq. (2), (3) and (4) for albitization of plagioclase, microclinization of K-feldspar and the CL-dark quartz formation, respectively.

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

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

| Mineral reaction                  | R/W oxygen mass ratio | Initial δ¹⁸O fluid ‰ | Final δ¹⁸O 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                    |
| Concomitant reactions # open system                   |                       |                      |                   |                        |
| 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                    |

**Palaeoenvironmental setting of the albitization**

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

In addition, Triassic palaeoenvironments are known for their giant salt deposits connected with lagunal evaporitic environments (Hay et al., 2006; Brookfield, 2008; Bourquin et al., 2011) and the frequency of halite moulds in transgressive epicontinental and continental clastic deposits (Courel, 1982; Galán-Abellán and Martínez, 2018). It is possible that in continental settings halite may have been derived via
aeolian processes from marine-derived saline lakes and saltflats together with red desert dust typical of Triassic red sandstone deposits (Ruffell and Hounslow, 2006). Leaching of the salt accumulated in the landscape would have provided Na-rich solutions depleted in K relative to marine brines (Fig. 11a).

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

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

These unique settings of Triassic palaeogeography are considered to be responsible for the albitization of granitic rocks in Triassic landscapes that are recognized and dated in several basement massifs in Western Europe, i.e. French Massif Central affecting as well Carboniferous and Permian graben deposits (Yerle and Thiry, 1979; Schmitt et al., 1984; Clément, 1986; Schmitt, 1992), the Morvan Massif (Ricodel et al.,
A question remains about the depth at which the alteration leading to albitization occurred. Reaction temperatures calculated from the oxygen isotope composition of minerals and hypotheses about the oxygen isotope composition of reactant fluids and their circulation led to an estimate of the mean temperature of albitization and associated reactions of about 55°C. Based on this temperature, an estimate of the mean depth at which alteration occurred can be made by applying a geothermal gradient and a surface temperature. A surficial temperature could be set to 30°C in consideration of the high palaeotemperature proposed for the Permian-Triassic boundary (Retallack, 1999; Joachimski et al., 2012) and a geothermal gradient for crystalline basement in a stable tectonic context could be set at about 25–30°C/km. Under such conditions, albitization may have taken place at about 1 km depth.

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

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

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

δ¹⁸O isotope data show that the secondary phases of the red-stained albitized facies (i.e. albitized plagioclase, microclinized orthoclase and CL-dark quartz) are δ¹⁸O enriched with respect to their primary counterparts in unaltered rocks. Calculation of the oxygen isotope equilibrium temperature between minerals and albitizing fluids was undertaken by testing minima and maxima range values of initial oxygen isotope composition of fluid and rock to fluid mass ratios consistent with fluid flow rates in main and restricted fractures. This led to an estimate that albitized plagioclase, microclinized orthoclase and CL-dark quartz formed between 45 and 65°C. These temperatures are far less than 200 to 400ºC typically assigned to late-magmatic and hydrothermal albitization processes. Instead, the low temperature range accords with the geological settings and age dating that correlates the red-stained albitized profile with the Triassic palaeosurface. It is possible that the albitized profile may have developed a few hundred meters beneath the Triassic palaeosurface and was subsequently exposed at the surface after erosion of the uppermost weathering mantles.

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

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

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**Data Availability**

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

[dataset] Parcerisa Duocastella, D. [et al.]. (2016). Geostandards of the Valentí Masachs Geology Museum [Dataset]. 1 v. Universitat Politècnica de Catalunya. DOI: 10.5821/data-2117-10344-

[https://upcommons.upc.edu/handle/2117/103444].

[dataset] Fàbrega, C. [et al.]. (2018). Geochemical data of albitized profiles in Europe [Dataset]. 1 v. Universitat Politècnica de Catalunya. DOI: 10.5821/data-2117-114114-

[https://upcommons.upc.edu/handle/2117/114114].

**References**

Aagaard P, Egeberg PK, Saigal GC (1990) Diagenetic albitization of detrital K-feldspars in Jurassic, Lower Cretaceous and Tertiary clastic reservoir rocks from offshore Norway; II, Formation water chemistry and kinetic considerations. J Sediment Res 60:575

Ague JJ, van Haren JLM (1996) Assessing metasomatic mass and volume changes using the bootstrap, with application to deep crustal hydrothermal alteration of marble. Econ Geol 91:1169–1182. doi: 10.2113/gsecongeo.91.7.1169
Aguilar C, Liesa M, Castineiras P, Navidad M (2014) Late Variscan metamorphic and magmatic evolution in the eastern Pyrenees revealed by U-Pb age zircon dating. J Geol Soc London 171:181–192. doi: 10.1144/jgs2012-086

Aguilar C, Liesa M, Štípská P, Schulmann K, Muñoz JA, Casas JM (2015) P-T-t-d evolution of orogenic middle crust of the Roc de Frausa Massif (Eastern Pyrenees): a result of horizontal crustal flow and Carboniferous doming? J Metamorph Geol 33:273–294. doi: 10.1111/jmg.12120

Algeo TJ, Twitchett RJ (2010) Anomalous Early Triassic sediment fluxes due to elevated weathering rates and their biological consequences. Geol 38:1023–1026. doi: 10.1130/G31203.1

Anadón P, Cabrera L, Colombo F, Marzo M, Riba O (1986) Syntectonic Intraformational Unconformities in Alluvial Fan Deposits, Eastern Ebro Basin Margins (NE Spain). In: Foreland Basins. Blackwell Publishing Ltd., Oxford, UK, pp 259–271

Baker JH (1985) Rare earth and other trace element mobility accompanying albitization in a Proterozoic granite, W. Bergslagen, Sweden. Mineral Mag 49:107–115. doi: 10.1180/minmag.1985.049.350.17

Barth SR (2000) Geochemical and boron, oxygen and hydrogen isotopic constraints on the origin of salinity in groundwaters from the crystalline basement of the Alpine Foreland. Appl Geochemistry 15:937–952. doi: 10.1016/S0883-2927(99)00101-8

Battiau-Queney Y (1997) Preservation of old palaeosurfaces in glaciated areas: examples from the French western Alps. Geol Soc London, Spec Publ 120:125–132. doi: 10.1144/GSL.SP.1997.120.01.08

Beinlich A, Klemd R, John T, Gao J (2010) Trace-element mobilization during Ca-metasomatism along a major fluid conduit: Eclogitization of blueschist as a consequence of fluid–rock interaction. Geochim Cosmochim Acta 74:1892–1922. doi: 10.1016/j.gca.2009.12.011

Benton MJ, Twitchett RJ (2003) How to kill (almost) all life: The end-Permian extinction event. Trends Ecol Evol 18:358–365. doi: 10.1016/S0169-5347(03)00093-4

Bernet M, Bassett K (2005) Provenance Analysis by Single-Quartz-Grain SEM-CL/Optical Microscopy. J Sediment Res. doi: 10.2110/jsr.2005.038

Bindeman I (2008) Oxygen Isotopes in Mantle and Crustal Magmas as Revealed by Single Crystal Analysis. Rev Mineral Geochemistry 69:445–478. doi: 10.2138/rmg.2008.69.12

Boles JR (1982) Active albitization of plagioclase, Gulf Coast Tertiary. Am J Sci 282:165–180

Boulvais P, Ruffet G, Cornichet J, Mermet M (2007) Cretaceous albitization and dequartzification of Hercynian peraluminous granite in the Salvezines Massif (French Pyrénées). Lithos 93:89–106

Bourquin S, Bercovici A, López-Gómez J, Diez JB, Broutin J, Ronchi A, Durand M, Arche A, Linol B, Amour F (2011) The Permian-Triassic transition and the onset of Mesozoic sedimentation at the northwestern peri-Tethyan domain scale: Palaeogeographic maps and geodynamic implications. Palaeoecolog Palaeoclimatol Palaeoecol 299:265–280

Brookfield ME (2008) Palaeoenvironments and palaeoecotones of the arid to hyperarid intracontinental latest Permian- late Triassic Solway basin (U.K.). Sediment Geol 210:27–47

Cahileneau M (1986) The hydrothermal alkali metasomatism effects on granitic rocks: Quartz dissolution and related subsolidus changes. J Petrol 27:945–965

Cherniak DJ, Pyle JM (2008) Th diffusion in monazite. Chem Geol 256:52–61. doi: 10.1016/j.chemgeo.2008.07.024
Cherniak D., Watson EB, Grove M, Harrison TM (2004) Pb diffusion in monazite: a combined RBS/SIMS study. Geochim Cosmochim Acta 68:829–840. doi: 10.1016/j.gca.2003.07.012

Clément J.-Y. (1986) Minéralogie, pétrologie et géochimie du Permien de Lodève (Hérault, France). Diagenèse précoce, altération feldspathisante et mise en place des minéralisations uranifères. ENSMP, Mém Sci de la Terre 2: 136 p.

Cocherie A, Albarede F (2001) An improved U-Th-Pb age calculation for electron microprobe dating of monazite. Geochim Cosmochim Acta 65:4509–4522. doi: 10.1016/S0016-7037(01)00753-0

Cocherie A, Legendre O, Peucat JJ, Kouame LAN (1998) Geochronology of polygenetic monazites constrained by in situ electron microprobe Th-U-total lead determination: Implications for lead behaviour in monazite. Geochim Cosmochim Acta. doi: 10.1016/S0016-7037(98)00171-9

Coombs DS (1954) The nature and alteration of some Triassic sediments from Southland, New Zealand. Trans R Soc New Zealand 82:65–109

Courel L (1982) Les facies de transgression du trias sur la bordure nord-est du Massif Central français. Geol Rundschau 71:773–781

Dinarès-Turell J, Diez JB, Rey D, Arnal I (2005) “Buntsandstein” magnetostratigraphy and biostratigraphic reappraisal from eastern Iberia: Early and Middle Triassic stage boundary definitions through correlation to Tethyan sections. Palaeogeogr Palaeoclimatol Palaeoecol 229:158–177. doi: 10.1016/j.palaeo.2005.06.036

Engvik AK, Putnis A, Fitz Gerald JD, Austrheim H (2008) Albitization of granitic rocks: the mechanism of replacement of oligoclase by albite. Can Mineral 46:1401–1415. doi: 10.3749/canmin.46.6.1401

Erwin DH (1993) The great Paleozoic crisis: life and death in the Permian. Columbia University Press, New York, US

Fàbrega C, Parcerisa D, Gómez-Gras D (2013) Multiple Feldspar replacement in Hercynian granites of the Montseny-Guilleries Massif (Catalan Coastal Ranges, NE Spain). Geophys Res Abstr 15:

Fàbrega C, Parcerisa D, Gómez-Gras D, Travé A, Franke C, Gurenko A (2016) Composició isotòpica de l’oxigen (18O/16O) en els feldspats i el quars dels granitoides hercinians: Guileries-Montseny i Pirineus Orientals. In: Vilà M, Herms I, Cirés J (eds) Geoquímica ambiental a Catalunya. Recull d’articles. Monografies tècniques de l’Institut Cartogràfic i Geològic de Catalunya, núm. 5. Institut Cartogràfic i Geològic de Catalunya, Barcelona, Spain, pp 83–95 (in Catalan)

Fàbrega C, Parcerisa D, Rossell JM, Gurenko A, Franke C (2017) Predicting instrumental mass fractionation (IMF) of stable isotope SIMS analyses by response surface methodology (RSM). J Anal At Spectrom 32:731–748. doi: 10.1039/C6JA00397D

Fàbrega C, Parcerisa D, Gómez-Gras D, Travé A, Thiry M, Franke C, Gurenko A, Solé J (2018) Geochemical data of albitized profiles in Europe [Dataset] URL: https://upcommons.upc.edu/handle/2117/102354

Fallourd S, Poujol M, Boulvais P, Paquette JL, de Saint Blanquat M, Rémy P (2014) In situ LA-ICP-MS U-Pb titanite dating of Na-Ca metasomatism in orogenic belts: The North Pyrenean example. Int J Earth Sci 103:667–682
Parcerisa D, Casas L, Franke C, Gómez-Gras D, Lacasa G, Núñez JA, Thiry M (2010a) Geomorphological stability of Permo-Triassic albitized profiles - case study of the Montseny-Guilleries High (NE Iberia). Geophys Res Abstr 12: EGU2010-15607

Parcerisa D, Thiry M, Schmitt JM (2010b) Albitisation related to the Triassic unconformity in igneous rocks of the Morvan Massif (France). Int J Earth Sci 99:527–544. doi: 10.1007/s00531-008-0405-1

Parcerisa D, Franke C, Fàbrega C, Yao K, Thiry M (2013), Implications from paleomagnetic age constraints and petrology analyses on the reconstruction of the Triassic paleosurface in Europe – examples from Catalonia and the Polish Sudetes, Abstract GP12A-02 presented at 2013 Fall Meeting. AGU, San Francisco, Calif., US, 9-13 Dec.

Parcerisa D, Fàbrega C, Gurenko A, Franke C (2016) Geostandards of the Valentí Masachs Geology Museum [Dataset] URL: https://upcommons.upc.edu/handle/2117/103444

Parrish RR (1990) U–Pb dating of monazite and its application to geological problems. Can J Earth Sci. doi: 10.1139/e90-152

Parsons I, Lee MR (2009) Mutual replacement reactions in alkali feldspars I: microtextures and mechanisms. Contrib to Mineral Petrol 157:641–661. doi: 10.1007/s00410-008-0355-4

Parsons I, Magee CW, Allen CM, Shelley JMG, Lee MR (2009) Mutual replacement reactions in alkali feldspars II: trace element partitioning and geothermometry. Contrib to Mineral Petrol 157:663–687

Perez R, Boles JR (2005) An empirically derived kinetic model for albitization of detrital plagioclase. Am J Sci 305:312–343

Petersson J, Eliasson T (1997) Mineral evolution and element mobility during episyenitization (dequartzification) and albitization in the postkinematic Bohus granite, southwest Sweden. Lithos 42:123–146

Petersson J, Stephens MB, Mattsson H, Möller C (2012) Albitization and quartz dissolution in Paleoproterozoic metagranite, central Sweden - Implications for the disposal of spent nuclear fuel in a deep geological repository. Lithos 148:10–26. doi: 10.1016/j.lithos.2012.06.001

Petersson J, Fallick AE, Broman C, Eliasson T (2014) Imprints of multiple fluid regimes on episyenites in the Bohus granite, Sweden. Lithos 196–197:99–114

Plümper O, Putnis A (2009) The Complex Hydrothermal History of Granitic Rocks: Multiple Feldspar Replacement Reactions under Subsolidus Conditions. J Petrol 50:967–987. doi: 10.1093/petrology/egp028

Poujol M, Boulvais P, Kosler J (2010) Regional-scale Cretaceous albitization in the Pyrenees: evidence from in situ U-Th-Pb dating of monazite, titanite and zircon. J Geol Soc London 167:751–767. doi: 10.1144/0016-76492009-144

Putnis A (2002) Mineral replacement reactions: from macroscopic observations to microscopic mechanisms. Mineral Mag 66:689–708

Putnis A (2009) Mineral Replacement Reactions. Rev Mineral Geochemistry 70:87–124. doi: 10.2138/rmg.2009.70.3

Putnis A, Hinrichs R, Putnis CV, Golla-Schindler U, Collins LG (2007) Hematite in porous red-clouded feldspars: Evidence of large-scale crustal fluid-rock interaction. Lithos 95:10–18

Ramseyer K, Boles JR, Lichtner PC (1992) Mechanism of plagioclase albitization. J Sediment Petrol 62:349–456
Retallack GJ (1999) Postapocalyptic greenhouse paleoclimate revealed by earliest Triassic paleosols in the Sydney Basin, Australia. Geol Soc Am Bull 111:52–70

Ricordel C, Parcerisa D, Thiry M, Moreau MG, Gómez-Gras D (2007) Triassic magnetic overprints related to albitization in granites from the Morvan massif (France). Palaeogeogr Palaeoclimatol Palaeoecol 251:268–282. doi: 10.1016/j.palaeo.2007.04.001

Roberts MP, Pin C, Clemens JD, Paquette JL (2000) Petrogenesis of Mafic to Felsic Plutonic Rock Associations: the Calc-alkaline Querigut Complex, French Pyrenees. J Petrol 41:809–844. doi: 10.1093/petrology/41.6.809

Rogers DB, Dreiss SJ (1995) Saline groundwater in Mono Basin, California: 1. Distribution. Water Resour Res 31:3131–3150. doi: 10.1029/95WR02108

Röhling, H.G. (1991) A lithostratigraphic subdivision of the Lower Triassic in the Northwest German Lowlands and the German sector of the North Sea, based on gamma-ray and sonic logs. Geol Jb A119: 3–24.

Røyne A, Jamtveit B, Mathiesen J, Malthe-Sørenssen A (2008) Controls on rock weathering rates by reaction-induced hierarchical fracturing. Earth Planet Sci Lett 275:364–369. doi: 10.1016/j.epsl.2008.08.035

Ruffell A, Hounslow M (2006) Triassic: seasonal rivers, dusty deserts and saline lakes. In: Rawson PF, Brenchley P (eds) The Geology of England & Wales. Geological Society of London, pp 295–325

Rusk BG (2006) Intensity of quartz cathodoluminescence and trace-element content in quartz from the porphyry copper deposit at Butte, Montana. Am Mineral 91:1300–1312. doi: 10.2138/am.2006.1984

Rusk B, Reed M (2002) Scanning electron microscope–cathodoluminescence analysis of quartz reveals complex growth histories in veins from the Butte porphyry copper deposit, Montana. Geology 30:727. doi: 10.1130/0091-7613(2002)030<0727:SEMCAO>2.0.CO;2

Saha D, Dwivedi SN, Roy GK, Reddy D V. (2013) Isotope-based investigation on the groundwater flow and recharge mechanism in a hard-rock aquifer system: the case of Ranchi urban area, India. Hydrogeol J 21:1101–1115. doi: 10.1007/s10040-013-0974-3

Saigal GC, Morad S, Bjørlykke K, Egeberg PK, Aagaard P (1988) Diagenetic albitization of detrital K-feldspar in Jurassic, Lower Cretaceous, and Tertiary clastic reservoir rocks from offshore Norway, I. Textures and origin. J Sediment Petrol 58:1003–1013

Saighi O, Michelot JL, Filly A (2001) Isotopic characteristic of meteoric water and groundwater in Ahaggar massif (central Sahara)

Schmitt JM (1986) Albitisation triasique, hydrothermalisme jurassique et altération supèr-gène récente: métallogénie des gisements uranifères du Rouergue. Louis Pasteur University

Schmitt JM (1992) Triassic albitization in southern France: an unusual mineralogical record from a major continental paleosurface. In: Schmitt JM, Gall Q (eds) Mineralogical and geochemical records of paleoweathering. Paris, ENSMP, Mem Sci Terre. ENSMP, Mémoires des Sciences de la Terre, Paris, pp 115–131

Schmitt JM, Baubron JC, Bonhomme MG (1984) Pétrographie et datations K-Ar des transformations minérales affectant le gîte uranifère de Bertholène (Aveyron-France). Miner Depos 19:123–131
Scotese CR, Schettino A (2017) Late Permian–Early Jurassic Paleogeography of Western Tethys and the Atlantic Margins. Elsevier, pp 57–95

Simmons CT, Fenstemaker TR, Sharp JM (2001) Variable-density groundwater flow and solute transport in heterogeneous porous media: approaches, resolutions and future challenges. J Contam Hydrol 52:245–275. doi: 10.1016/S0169-7722(01)00160-7

Simon-Coinçon R (1999) Palaeolandscape reconstruction of the south-western Massif Central (France). Palaeoweathering, Palaeosurfaces Relat. Cont. Depos. 27:225–243

Solé de Porta, N., Calvet, F., Torrentó L (1987) Análisis Palinologico del Triassico de los Catalanides (NE España). Cuad Geol Ibérica 11:237–254

Solé J (2009) Determination of K-Ar ages in milligram samples using an infrared laser for argon extraction. Rapid Commun Mass Spectrom 23:3579–3590. doi: 10.1002/rcm.4280

Solé J, Enrique P (2001) X-ray fluorescence analysis for the determination of potassium in small quantities of silicate minerals for K-Ar dating. Anal Chim Acta. doi: 10.1016/S0003-2670(01)01060-1

Steiger RH, Jäger E (1977) Subcommission on geochronology: Convention on the use of decay constants in geo- and cosmochronology. Earth Planet Sci Lett 36:359–362. doi: 10.1016/0012-1057(77)90060-7

Sun Y, Joachimski MM, Wignall PB, Yan C, Chen Y, Jiang H, Wang L, Lai X (2012) Lethally Hot Temperatures During the Early Triassic Greenhouse. Science (80- ) 338:366–370. doi: 10.1126/science.1224126

Taylor HP (1977) Water/rock interactions and the origin of H2O in granitic batholiths: Thirtieth William Smith lecture. J Geol Soc London 133:509–558. doi: 10.1144/gsjs.133.6.0509

Thiry M, Schmitt JM, Simon-Coinçon R (1999) Problems, progress and future research concerning palaeoweathering and palaeosurfaces. In: Thiry M, Simon-Coinçon R (eds) Palaeoweathering,
Palaeosurfaces and Related Continental Deposits. Blackwell Science. Special Publications of the International Association of Sedimentologists, Oxford, pp 3–17

Thiry M, Théveniaut H, Simon-Coinçon R, Prognon C, Lenoir F, Lagroix F (2014) Persistent paléosurfaces in the basement of French Massif Central: geodynamic implications. In: Diagénèse: avancées récentes et perspectives. Association des Sédimentologistes Français (ASF), Orsay (France), pp 113–117

Trusheim, F. (1961) Über Diskordanzen im mittleren Buntsandstein Norddeutschlands zwischen Weser und Ems. Erdöl-Zeitschrift 77: 361–367.

Vià M, Pin C, Enrique P, Liesa M (2005) Telescoping of three distinct magmatic suites in an orogenic setting: Generation of Hercynian igneous rocks of the Albera Massif (Eastern Pyrenees). Lithos 83:97–127. doi: 10.1016/j.lithos.2005.01.002

Williams ML, Jercinovic MJ, Goncalves P, Mahan K (2006) Format and philosophy for collecting, compiling, and reporting microprobe monazite ages. Chem Geol 225:1–15. doi: 10.1016/j.chemgeo.2005.09.009

Williams ML, Jercinovic MJ, Harlov DE, Budzyń B, Hetherington CJ (2011) Resetting monazite ages during fluid-related alteration. Chem Geol. doi: 10.1016/j.chemgeo.2011.01.019

Witkowski FW, Blundell DJ, Gutteridge P, Horbury AD, Oxtoby NH, Qing H (2000) Video cathodoluminescence microscopy of diagenetic cements and its applications. Mar Pet Geol 17:1085–1093. doi: 10.1016/S0264-8172(00)00055-6

Wojdyr M (2010) Fityk: a general-purpose peak fitting program. J Appl Crystallogr 43:1126–1128. doi: 10.1107/S0021889810030499

Wolburg, J. (1968) Vom zyklischen Aufbau des Buntsandsteins. Neues Jb Geol. Paläontol. Mh. 9: 535–559.

Wooding RA, Tyler SW, White I (1997) Convection in groundwater below an evaporating Salt Lake: 1. Onset of instability. Water Resour Res 33:1199–1217. doi: 10.1029/96WR03533

Worden RH, Walker FDL, Parsons I, Brown WL (1990) Development of microporosity, diffusion channels and deuteric coarsening in perthitic alkali feldspars. Contrib to Mineral Petrol 104:507–515. doi: 10.1007/BF00306660

Yao KFE (2013) Albition and oxidation of the granitoid rocks related to the Triassic paleosurface in the Sudetes (SW Poland). École Nationale Supérieure des mines de Paris

Yao KFE, Franke C, Thiry M, Paweł A, Szuszkiewicz A, Turniak K (2011) Albitionization as record of the Triassic Paleosurface in the Sudetic Crystalline basement (Poland). Geophys Res Abstr 13: EGU2011-5930

Yerle JJ, Thiry M (1979) Albitisations et minéralisations uranifères dans le socle et les sédiments permohouillers du bassin de Brousses-Broquiés (Aveyron, France). Bull du BRGM Ser 2 4:275–290

Zheng Y-F, Hoefs J (1993) Carbon and oxygen isotopic covaritations in hydrothermal calcites. Miner Depos 28. doi: 10.1007/BF00196332

Zheng Y-F (1993) Calculation of oxygen isotope fractionation in anhydrous silicate minerals. Geochim Cosmochim Acta 57:1079–1091. doi: 10.1016/0016-7037(93)90042-U