Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Textural-chemical changes and deformation conditions registered by phyllosilicates in a fault zone (Pic de Port Vieux thrust, Pyrenees)



Ahmed Abd Elmola^{a,*}, Delphine Charpentier^a, Martine Buatier^a, Pierre Lanari^b, Patrick Monié^c

^a UMR Chrono-Environnement, Université de Bourgogne Franche-Comté, 16 Route de Gray, F-25030 Besançon, France

^b Institute of Geological Sciences, University of Bern, Baltzestrasse 1 + 3, CH-3012 Bern, Switzerland

^c Géosciences Montpellier, UMR-CNRS 5243, Université de Montpellier, F-34095 Montpellier, France

ARTICLE INFO

Keywords: Phyllosilicates Pyrenees Thrust fault Chlorite K-white mica Fluid-rock interactions

ABSTRACT

Synkinematic phyllosilicates in fault zones can be used to deduce the deformation mechanisms and the conditions of fault activity, as their chemical composition, crystal structure and texture can record the different stages of deformation and fluid-rock interactions. The Pic de Port Vieux, a second-order thrust related to the major Gavarnie thrust in the southern central part of the Pyrenees Axial Zone, juxtaposes Triassic pelites of the hanging wall and Cretaceous limestones of the footwall. In order to investigate the mineralogical and geochemical changes and constrain the deformation conditions of thrusting, characterization of phyllosilicates was performed along a transect in the fault hanging wall pelites.

The Triassic pelites are mainly composed of quartz, calcite, phyllosilicates (chlorite and K-white mica) and \pm hematite. The core fault zone thickness is estimated to be about one meter of intensively foliated green pelites, whereas the damage zone is composed of several meters of red pelites. XRD data demonstrated that the difference in color is related to hematite which is only present in the damage zone. Phyllosilicates of the damage zone are mainly inherited/diagenetic K-white mica and chlorite. In the core zone, newly formed chlorite is abundant and preferentially located in veins. It is enriched in Fe compared to the chlorite of the red pelites. The well-defined foliation in the core zone is overlaid by preferentially oriented muscovite grains which have homogeneous compositions, with less Na and relatively more Fe than mica from the red pelites. Newly formed chlorite and muscovite in the core zone are synkinematic to the fault activity. They are both related to deformation processes and fluid rock interactions. Kübler index measurements and chlorite thermometry show that synkinematic phyllosilicates have registered a temperature of 270°C \pm 23°C for the damage zone and $285^{\circ}C \pm 28^{\circ}C$ for the core zone which are corresponding to lower-anchizone/epizone grade conditions. Numerical modelling with the geochemical modelling program PhreeqC was performed to determine the favorable conditions for the mineralogical change between red and green pelites. It suggests that the main critical parameter favoring hematite dissolution and chlorite precipitation in the core zone, is the redox conditions. According to the model, the chemical changes in the core zone occurred due to interactions with highly reductive fluids. In addition, the hematite dissolution maybe the source of iron for newly formed phyllosilicates in the core zone that are more iron rich compared to those from the red pelites.

1. Introduction

Phyllosilicates are major constituents of fault zones in a broad range of geological contexts and particularly in sedimentary environments (Blatt et al., 1980). During the evolution of sedimentary basins, phyllosilicates record changes in their composition, crystal structure and texture in response to burial diagenesis, tectonic activity, and interactions with fluids. Consequently they are used to decipher the basin evolution history, deformation mechanisms, P-T conditions and the timing of various geologic events (Jiang, 2012). For example, illite/

http://dx.doi.org/10.1016/j.clay.2017.05.008

muscovite has been commonly used to quantify diagenetic and lowgrade metamorphic conditions (Frey, 1987; Kisch et al., 2004; Kübler, 1964, 1967, 1968; Kübler and Jaboyedoff, 2000; Warr and Cox, 2016; Warr and Ferreiro Mählmann, 2015). Temperature estimation from chlorite composition as well is a very often used method; recently the thermodynamic modelling approach has been proposed and developed by Bourdelle et al. (2013), Inoue et al. (2009), Lanari et al. (2012, 2014c) and Vidal et al. (2005, 2006, 2016) among others.

In fault zones, phyllosilicates may form contemporaneously with fault activity as deformation and fluid/rock interactions promote the



^{*} Corresponding author at: 16 Route de Gray, F-25030 Besançon, France. *E-mail address:* ahmed.abd_elmola@univ-fcomte.fr (A. Abd Elmola).

Received 24 February 2017; Received in revised form 5 May 2017; Accepted 9 May 2017 0169-1317/ @ 2017 Elsevier B.V. All rights reserved.

growth of synkinematic phyllosilicates during faulting episodes (Duvall et al., 2011). There are several formation mechanisms for those minerals in fault zones: (1) direct precipitation from fluids in veins or (2) alteration from less stable minerals or (3) recrystallization of detrital clay minerals as a result of shearing, comminution, pressure solutions and dissolution/recrystallization processes. Newly formed phyllosilicates in fault zone can be a good proxy for the estimation of variable parameters related to deformation. For example, they can provide the ages of different fault episodes based on their isotopic composition (Bui et al., 2017; Clauer, 2013; Lanari et al., 2014a; Rolland et al., 2009; Sanchez et al., 2011; Torgersen et al., 2015). Moreover, they are a useful tool for characterizing fluid-rock interactions that occurred in the fault zone (e.g. Lacroix et al., 2011). All this information can assist in reconstruction of the basin history and improve understanding of the fault behavior (Buatier et al., 2012; Faulkner et al., 2010; Niwa et al., 2005; Pei et al., 2015).

Following the evolution of tectonic activities is one of the challenging topics in particular in sedimentary basins due to multiple exhumations, uplifting, multistage of activation, mixing sediments of different ages and variable fluid influxes of different origins. The Pyrenees orogen is one of the best areas to study thrust faults and deformation/sedimentation relationships because it has well exposed deformation structures and exceptionally well preserved syntectonic sedimentary rocks (Teixell, 1996). The focus of the present study is the Pic de Port Vieux thrust (PPVT) fault located in the southern central part of the Axial Zone of the Pyrenees. The fault is a suitable candidate for the present study as it is a complex thrust with multistage deformation and fluid circulations at low-grade metamorphic conditions (Grant, 1992). Six deformation stages have been identified by Banks et al. (1991), Grant (1989) and McCaig et al. (2000). Previous studies on the PPVT focused mainly on synkinematic veins and suggested that deformation PT conditions are about 250-300°C and 1.5–2 kbar (Grant, 1992) corresponding to a burial depth of 5–7.5 km. They demonstrated that fluids have been buffered by host rock composition and would originate from buried Triassic sediments (McCaig et al., 2000). Trincal et al. (2015) thoroughly characterized oscillatory zoning chlorite from veins, but the behavior and the mechanisms of deformation of phyllosilicates in the PPVT core zone have never been studied. Therefore, the focus of the present study is phyllosilicates from the fault zone to determine the deformation conditions and geochemical changes attributed to thrust activity. For that purpose a transect along the fault hanging wall was investigated to (1) characterize the phyllosilicates, comparing their mineralogy, texture and chemical composition as a function of distance from the fault contact; (2) define their origin and mechanisms of their formation in the fault zone; (3) estimate the deformation conditions from their crystallinity and chemical compositions; (4) understand the key-parameters that control the mineralogical changes in the fault zone.

2. Geological setting and sample location

The Pyrenees orogen is a doubly-vergent orogenic wedge formed by the convergence of the Iberian and European plates during the Late Cretaceous to early Miocene periods (Choukroune et al., 1990; Roest and Srivastava, 1991). Three main structural zones constitute this orogeny (Fig. 1A). First, the North-Pyrenean zone corresponds to a Mesozoic extensional basin system inverted and transported northward by the Pyrenean compression. Secondly, the Axial Zone (the core zone of the range) corresponds to the inner part of the south-vergent thrust belt. It exposes the most deeply exhumed rocks, a series of pre-Cambrian through Carboniferous basement thrust sheets initially stacked during Variscan orogenesis (Masini et al., 2014; Muñoz, 1992; Zwart, 1986). Thirdly, the South Pyrenean fold and thrust belt comprises a deformed Mesozoic succession detached on Triassic evaporites and overlain by *syn*-deformational Tertiary sediments (Metcalf et al., 2009; Teixell et al., 2016).

The PPVT fault is located in the south-western part of the Pyrenean Axial Zone. The fault is a second-order thrust related to the major thrust in the area, which is the Gavarnie thrust. The latter involves a minimum southward displacement of 11.5 km of Upper Paleozoic strata on Variscan to Lower Paleozoic basement covered with Permo-Triassic and Upper Cretaceous strata (Grant, 1989). Stratigraphic correlation suggests a Priabonian-Rupelian age for Gavarnie thrust activity (Teixell, 1996) and a Priabonian age (36.5 \pm 1.4 Ma) based on ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ radiometric dating (Rahl et al., 2011). The PPVT emplacement, which folded and deformed the overlying Gavarnie thrust, is thought to occur later (Fig. 1B, C and D). However, it is not excluded that both thrusts are related to the same global tectonic event and should have a similar age. The PPVT occurs in the footwall of the Gavarnie thrust, with a minimum southward displacement of 0.85 km (Grant, 1990). The PPVT footwall has a 10 m thick layer of Upper Cretaceous dolomitic limestones progressively transformed into mylonitic limestones near the fault contact. The hanging wall consists of lower Triassic red pelites and sandstones that turned to be intensely foliated green pelites close to the fault contact. The hanging wall of PPVT is the focus of the present study as no phyllosilicate is present in the fault footwall. The damage zone of the hanging wall features numerous fractures affecting several meters thick of red pelites, whereas the core zone is composed of a 0.6 m thick layer of intensely foliated green pelites. Therefore, a vertical transect along the hanging wall was investigated to characterize the mineralogical and geochemical changes induced by deformation and fluids that are attributed to the fault activity. The GPS coordinates for the transect location are 42°43'40.52" N and 0° 9'44.67" E. Eight samples were collected along the transect in the Triassic pelites, covering the green core zone and the red damage zone (Fig. 2A and B).

3. Analytical methods

3.1. Bulk composition and phyllosilicates mineralogy

The samples were analyzed at the Université de Bourgogne Franche-Comté by using a Bruker D8 Advance diffractometer system, Cu-Ka radiation equipped with a fast LynxEye linear detector. Samples were hand ground to < 50 μ m and the < 16 μ m fraction obtained by sedimentation was submitted to ultra-centrifugation in order to extract the < 2 μ m fractions. For the bulk powder samples, the X-ray diffractograms were acquired between 5 and 70°20 at a step size of 0.02, a number of steps 3450, a time/step 1 s at 40 kV and 40 mA. While for the < 2 μ m fractions, oriented specimens preparation were analyzed in air dried conditions between 5 and 30°20 at a step size of 0.01, a number of steps 2228 and time/step 0.5 s. No expandable or interstratified minerals were found confirmed by ethylene-glycol saturation and after heating at 550°C.

3.2. Petrographic and geochemical characterizations

3.2.1. Scanning electron microscope (SEM)

The analyses by SEM were performed at the FEMTO-ST Institute (Université de Bourgogne Franche-Comté). Microstructures and mineral assemblages were analyzed with a JEOL JSM5600 (SEM) equipped with Secondary Electron (SEI), backscatter electron (BSE) and Energy Dispersive X-ray Spectroscopy (EDX) detectors.

3.2.2. Electron probe micro-analyzer (EPMA)

Quantitative chemical analyses of chlorite and K-white mica were performed using an electron probe micro-analyzer (EPMA) JEOL 8200 at the Institute of Geological Sciences (University of Bern). Total number of 169 spot analyses for chlorite and 50 analyses for mica from both the damage and core fault zones were performed. The following natural and synthetic standards have been used: orthoclase (SiO₂, K₂O), anorthite (Al₂O₃, CaO) albite (Na₂O), almandine (FeO), forsterite (MgO), tephroite (MnO) and ilmenite (TiO₂). The analyses



Fig. 1. (A) Structural map of the Pyrenees with the location of the study area (modified from Teixell et al. (2000). (B), (C) Photograph and sketch respectively showing the Pic de Port Vieux culmination, modified from Grant (1989). (D) Stratigraphic log for the Pic de Port Vieux outcrop, modified from Grant (1990) and Trincal et al. (2015).

were performed at 15 keV accelerating voltage, 10 nA specimen current and 40 s dwell time (including 2×10 s of background measurement). Quantitative X-ray maps were carried out to check the variation of chemistry in each mineral phase and the relationships with the microstructures. The maps were acquired using the wavelength dispersive spectrometers (WDS) at 15 KeV accelerating voltage, 10 nA specimen current, dwell time of 200 ms and 1 µm spot size. The X-ray maps were classified and standardized into maps of oxide weight percentage concentrations using the program XMapTools 2.3.1 (Lanari et al., 2014b).

3.3. Deformations conditions

3.3.1. Kübler index (KI)

The Kübler Index (KI) was measured on muscovite (001) at 10 Å for five samples in oriented preparations of the $< 2 \mu m$ fraction to determine the metamorphic grade conditions. Interlaboratory variations have been reduced by following the recommendations of Kisch (1991) and using the widely applied standardized Crystallinity Index Scale (CIS) procedure recommendations for measurements. The calibration of the crystallinity results to CIS scale was achieved by measuring the crystallinity of the four standards proposed by Warr and Rice (1994). A regression analysis allows a correction to be made by using the equation: KI _(CIS) = 1.52 * KI (my lab) - 0.0121. The evaluation of metamorphic conditions boundaries was performed by using the boundaries of the anchizone originally defined by Kübler (1967) at IC values of $0.25^{\circ}2\theta$ and $0.42^{\circ}2\theta$. In order to be compatible with the original Anchizone boundaries of Kübler (1967), the CIS values were calibrated to the traditional Kübler-Kisch scale by using the equation: Kübler Index_(CIS) = $1.1523 * \text{Kübler Index}_{(Basel lab)} + 0.036$ which is presented in the Fig. 1 of Warr and Ferreiro Mählmann (2015).

3.3.2. Chlorite thermometer

Temperatures of chlorite crystallization in the current study were estimated through multi-equilibrium thermodynamic calculations using the method and solid solution models of Vidal et al. (2006, 2005) by the program ChLMICAEQUI (Lanari, 2012; Lanari et al., 2012). This method is based on thermodynamic calculations of equilibrium conditions for chlorite whose composition is expressed as the activities of end-member components of known thermodynamic properties (Berman, 1991; Vidal



Fig. 2. The Pic de Port Vieux outcrop, (A) Photograph showing the hanging wall and footwall of Pic de Port Vieux thrust. (B) Transect along the hanging wall with the sample locations.



Fig. 3. X-ray diffraction patterns for randomly oriented preparations of bulk powder for five representative samples along the transect in the hanging wall of the Pic de Port Vieux. Chl = chlorite, Mus = muscovite, Hm = hematite and Qz = Quartz. The 104 reflection of hematite and the 060 reflections of phyllosilicates are highlighted by a dashed rectangle in the figure.

et al., 2001). In addition, the calculation of XFe^{3+} which is equal to $(Fe^{3+}/\Sigma Fe)_{chl}$ was approximated by the numerical method of Vidal et al. (2005, 2006). This method is based on the achievement of convergence of four reactions (chlorite + quartz and internal chlorite equilibria). 89 spot analyses of newly formed chlorite were performed on the damage zone and 80 spot analyses on the core zones and used for chlorite thermometry.

3.4. Fluid/rock interaction modelling

In order to understand the chemical reactions that occurred between fluids and rocks in the PPVT, modelling of fluid/rock interactions was performed. The version 2.15 of PhreeqC software (Parkhurst, 1995; Parkhurst and Appelo, 1999) was used for speciation of the solution and mineral saturation index calculations with respect to the solution. Mineral dissolution (under-saturation) is characterized by a negative saturation index and its precipitation (supersaturation) is characterized by a positive saturation index. Equilibrium batch reactions were performed to determine the stable rock composition at the chosen conditions and to compare it with the observed composition (EPMA analyses).

4. Results

The hanging wall is composed of Triassic pelites and sandstones at the outcrop scale and has been divided into two zones based on their lithology (Fig. 2). The core fault zone is intensely foliated, contains numerous mineralized veins and is characterized by a green color observed up to one meter perpendicular to the main thrust. The second zone is the damage zone that is composed of several meters of red pelites. In addition, secondary normal faults are observed in this damage zone marked by green color (a few centimeters in width) inside the red pelites.

4.1. Mineralogy

XRD results of the bulk powder samples from the damage and core zones revealed similar mineralogical compositions with mainly K-white mica, quartz, chlorite, calcite, minor rutile and apatite (Fig. 3). The only difference is the absence of hematite in the core fault zone as indicated by the disappearance of hematite reflections peaks, the most intense peak for hematite (104) at 2.70 Å is highlighted in Fig. 3. Reflections at 1.50 Å and 1.55 Å are corresponding to phyllosilicates 060 reflections, they confirm the presence of di-octahedral phase (di-white mica) and tri-octahedral phase (chlorite) respectively. XRD patterns of $< 2 \,\mu m$ for five representative samples along the pelitic transect are presented in Fig. 4. The K-white mica is characterized by reflections at 10.02 Å, 5.00 Å and 3.33 Å corresponding to 001, 002, and 003 basal reflections respectively. Reflections at 14.16 Å, 7.08 Å, 4.73 Å and 3.54 Å are corresponding to 001, 002, 003 and 004 reflections of chlorite. The 002 and 004 reflections of chlorite are more intense compared to 001 and 003 reflections suggesting the presence of a Fe-rich chlorite (Brown and Brindley, 1980; Moore and Reynolds, 1997). The intensity of K-white mica and chlorite peaks increases gradually toward the fault contact (Fig. 4) indicating a phyllosilicate enrichment toward the core fault zone.

4.2. Petrographic observations

In order to compare the textural and microstructural features of the core and damage zones, two representative samples (PPV12-05 from the core zone and PPV12-07 from the damage zone) were investigated in details. At the rock chip and thin section scales (Fig. 5), there are several textural and mineralogical differences between these two samples:

- The change of pelite color from red to green toward the fault contact; SEM images, EDS analyses beside XRD results confirmed that the color change is related to hematite that is presents only in the damage zone.
- The presence of more mineralized veins and veinlets within the pelitic matrix of the core zone compared to the damage zone (Fig. 5A and B). Those veins are composed mainly of quartz + chlorite ± calcite, they are folded and crosscut each other suggesting several stages of deformation. Moreover there is a strong foliation and a well-defined cleavage marked by the preferential orientation of K-white mica in the core zone compared to the randomly-oriented texture in the damage zone (Fig. 5C and D).
- The matrix of the damage zone sample contains more quartz grains with random orientation and larger grain size (Fig. 5E). While in the matrix of the core zone sample, quartz grains become less abundant and display elongated shape and smaller grain size formed by pressure solution mechanisms. The decrease in quartz content in the fault core zone is balanced by K-white mica enrichment (Fig. 5F).

SEM-BSE images with higher magnification for samples PPV12-07(damage zone) and PPV12-05 (core zone) are illustrated in Fig. 6. In the damage zone, chlorite is mainly located in the matrix as elongated large grains (50 μ m) suggesting a detrital origin (Fig. 6A) and also appears as stacks with mica (Fig. 6C). Moreover, chlorite also occurs locally inside rare veins (Fig. 6E). K-white mica is present in the matrix of the damage zone sample as large elongated grains (probably of detrital origin) (Fig. 6A) and as randomly-oriented coarse stacks with chlorite (diagenetic). Their grain size ranges from 30 to 80 μ m and only few smaller grains can be observed in this matrix.

Conversely, in the core zone sample, newly formed chlorite is



Fig. 4. X-ray diffraction patterns for oriented preparations $< 2 \mu m$ fractions (untreated, air dried conditions), for five representative samples along transect in the hanging wall of the Pic de Port Vieux. Chl = chlorite, Mus = muscovite, Qz = Quartz and Rt = rutile.



Fig. 5. Photographs illustrating the differences in textural and microstructural features between samples PPV12-07 and PPV12-05. (A), (B) Rock chip scans showing the difference in color and the presence of more veins in the PPV12-05 sample. (C), (D) Optical microscope pictures in cross-polarized light. The quartz grains in the matrix of sample PPV12-07 have a random orientation and large grain size. Toward the fault contact those grains became smaller and more elongate following the shearing direction indicated by dashed lines in the picture (D). There is enrichment in muscovite (characterized by bright 2nd order colors) in the matrix of the PPV12-05 sample. The change in the quantity and grain size of quartz are shown in SEM-BSE images in (E) and (F) images. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

abundant and preferentially located in veins (Fig. 6F) The chlorite/mica stacks are folded, kinked and display smaller grain size (Fig. 6D) compared to the large stacks in the damage zones (Fig. 6C). The well-defined cleavage in the core zone sample is underlined by preferentially oriented K-white mica with a smaller grain size ($< 5 \mu$ m) compared to larger mica from the damage zone. Mica grains that have step like shaped boundaries with quartz grains in the core zone suggest that a significant recrystallization process occurred along this strongly deformed zone (Fig. 6B).

4.3. Chemical composition variation of phyllosilicates

4.3.1. Chlorite

EPMA analyses were performed on newly formed chlorite from both the damage zone (sample PPV12-07) and the core zone (sample PPV12-05). Structural formulas were calculated on a 14 oxygen basis and some representative analyses are listed in Table 1, then plotted in (Fe + Mg) – Si – Al^(total) ternary diagram and in Fe/(Fe + Mg) vs. Si diagram (Fig. 7A). Newly formed chlorite from both the damage and the core zone is situated between clinochlore-daphnite, sudoite and amesite end-members. Si values vary from 2.68 to 2.87 apfu, Al^{total} from 2.61 to 2.87 apfu, Fe from 1.59 to 2.23 apfu and Mg from 2.08 to 2.80 apfu. (Si_{2.78} Al_{1.22})O₁₀ (Al_{1.52} Mg_{2.57} Fe_{1.73}) (OH)₈ is an average structural formula for newly formed chlorite from the damage zone (based on 89 analyses) while the average structural formula for chlorite from the core zone is (Si_{2.77} Al_{1.23})O₁₀ (Al_{1.53} Mg_{2.33} Fe_{1.97}) (OH)₈ (based on 80 analyses). The only difference observed between chlorite from the damage and core zones is that, close to the fault contact (the green pelite zone) newly formed chlorite has relatively more Fe (1.80 to 2.23 apfu) compared to newly formed chlorite from the damage zone which has an Fe content that varies from 1.59 to 1.85 apfu.

4.3.2. K-white mica

EPMA analyses were achieved on K-white micas from both the damage zone (sample PPV12-07) and the core zone (sample PPV12-05) and are presented in Table 2. In the damage zone, analyses for both large mica (10 analyses) and small mica (10 analyses) were performed. The structural formulas have been calculated on the basis of 11 oxygens. The results are then plotted in a M + -4Si - R2 + ternary diagram (Meunier and Velde, 1989) and in a Na/(Na + K) vs. Si



Fig. 6. Backscattered electron images (BSE) for samples PPV12-07(damage zone) and PPV12-05 (core zone). Qz refer to quartz, Ch = chlorite, Mus = muscovite, Hm = hematite, Ca = calcite and Rt = rutile. (A) and (B) images of the matrix of the damage zone and the core zone. Recrystallized muscovite in the matrix of the core zone presented in image (B) characterized by the step like shaped on the boundary with quartz grains. The chlorite-muscovite stacks are presented in images (C) and (D), in the core zone those stacks are folded, broken and have smaller grain size (highlighted by black dashed lines in the image (D)). (E) and (F) images showing part of vein with newly formed chlorite.

diagram (Fig. 7B). Mica compositions from both samples are located close to muscovite end member with a small trend toward celadonite. As Si content varies between 3.11 and 3.30 apfu, it suggests that muscovite is the dominant end member; so hereafter muscovite will be used to describe K-white mica within the present paper. Altotal content varies between 2.50 and 2.72 apfu, K from 0.80 to 0.93 apfu and Na from 0.02 to 0.14 apfu. There is a small Tschermak substitution with Mg values between 0.10 and 0.20 apfu and Fe between 0.06 and 0.16 apfu. Muscovite from the core zone displays homogenous composition with an average structural formula of (Si3.18 Alo.82) O10 (Al1.79 Mg_{0.12} Fe_{0.13} Ti_{0.01}) (OH)₂ K_{0.91} Na_{0.03}. Conversely, muscovite from the damage zone displays higher dispersion in composition, due to Na-K substitution in interlayer space and also divalent cation substitutions in the octahedral sheet. The large and small muscovite grains in the damage zone have different composition; large grains have lower Si, Fe, Mg contents and a higher Na/(Na + K) ratio in the interlayer space, whereas small grains have higher Si, Fe, Mg contents and a lower Na/

(Na + K) ratio in the interlayer space as illustrated in a Na/(Na + K) vs. Fe plot (Fig. 7B). Large muscovite grains have the following average structural formula, $(Si_{3.14} Al_{0.86}) O_{10} (Al_{1.86} Mg_{0.08} Fe_{0.07} Ti_{0.01}) (OH)_2 K_{0.84} Na_{0.10}$. The small muscovite grains structural formula is $(Si_{3.26} Al_{0.74})O_{10} (Al_{1.74} Mg_{0.16} Fe_{0.13}) (OH)_2 K_{0.91} Na_{0.03}$ similar to the average composition of mica from the core zone.

SEM-BSE images and compositional maps of muscovite Na₂O wt% are presented in Fig. 8 for samples PPV12-07(damage zone) and PPV2-05(core zone) respectively. The random coarse muscovite aggregates are shown in SEM-BSE image beside the large chlorite in the matrix of the damage zone (Fig. 8A); in the core zone muscovite grains are smaller and follow the foliation direction in the matrix. In addition, smaller grains of chlorite are located in the veins (Fig. 8B). The most important compositional variation of muscovite is derived from the maps of Na₂O (in wt%, see Fig. 8C and D). The maps show that larger grains have higher Na₂O (1%–2%) than the smaller grains (0.1%–0.5%). In addition, Na is higher in muscovite from the damage

Table 1

Calculated chlorite structural formula of some representative analyses from the damage zone and core zone of the Pic de Port Vieux respectively. Calculated temperature using chlorite thermometry for each analysis is presented in the table.

Damage zone	Tetrahedra	al layer			Octahed	ral layer						
Sample PPV12-07	Si	Al ^(IV)	Al ^(VI)	Mg	Fe	Ti	Mn	ΣOcta	K	Na	Ca	T °C
1	2.81	1.19	1.50	2.54	1.77	0.00	0.00	5.82	0.02	0.00	0.00	246
2	2.78	1.22	1.49	2.64	1.73	0.00	0.00	5.86	0.00	0.00	0.00	276
3	2.81	1.19	1.44	2.68	1.73	0.00	0.00	5.86	0.00	0.01	0.01	262
4	2.78	1.22	1.46	2.70	1.69	0.00	0.01	5.86	0.00	0.01	0.01	277
5	2.80	1.20	1.49	2.63	1.71	0.00	0.00	5.84	0.00	0.01	0.00	258
6	2.74	1.26	1.47	2.60	1.80	0.00	0.01	5.88	0.01	0.00	0.01	307
7	2.87	1.13	1.51	2.68	1.59	0.00	0.00	5.79	0.01	0.00	0.01	218
8	2.85	1.15	1.52	2.64	1.63	0.00	0.00	5.79	0.02	0.01	0.01	227
9	2.81	1.19	1.42	2.80	1.64	0.00	0.00	5.87	0.00	0.00	0.00	264
10	2.76	1.24	1.52	2.56	1.75	0.00	0.00	5.84	0.01	0.00	0.00	279
11	2.73	1.27	1.50	2.52	1.64	0.00	0.00	5.87	0.01	0.00	0.01	282
12	2.73	1.25	1.54	2.40	1.67	0.00	0.00	5.80	0.01	0.00	0.01	202
13	2.83	1.17	1.54	2.50	1.07	0.00	0.00	5.83	0.00	0.00	0.01	204
15	2.74	1.20	1.59	2.51	1.72	0.00	0.00	5.85	0.00	0.00	0.00	273
16	2.70	1.22	1.50	2.55	1.83	0.00	0.00	5.88	0.00	0.00	0.01	268
17	2.78	1.22	1.53	2.55	1.75	0.00	0.00	5.83	0.01	0.00	0.00	259
18	2.78	1.22	1.58	2.47	1.76	0.00	0.00	5.82	0.00	0.00	0.00	303
19	2.73	1.27	1.54	2.54	1.76	0.00	0.00	5.85	0.00	0.00	0.00	273
20	2.77	1.23	1.51	2.60	1.72	0.00	0.00	5.84	0.00	0.01	0.00	317
21	2.72	1.28	1.55	2.55	1.75	0.00	0.00	5.86	0.00	0.00	0.00	231
22	2.83	1.17	1.57	2.49	1.72	0.00	0.00	5.79	0.00	0.00	0.01	250
23	2.79	1.21	1.60	2.40	1.78	0.00	0.00	5.79	0.00	0.00	0.01	242
24	2.81	1.19	1.59	2.40	1.80	0.00	0.00	5.79	0.01	0.00	0.01	289
25	2.74	1.26	1.56	2.50	1.76	0.00	0.01	5.83	0.01	0.01	0.00	257
26	2.79	1.21	1.52	2.54	1.77	0.00	0.00	5.84	0.00	0.00	0.00	238
27	2.83	1.17	1.49	2.67	1.67	0.00	0.00	5.83	0.00	0.00	0.00	251
28	2.81	1.19	1.50	2.59	1.74	0.00	0.00	5.83	0.00	0.01	0.00	268
29	2.75	1.25	1.54	2.54	1.76	0.00	0.01	5.83	0.01	0.01	0.00	279
30	2.78	1.22	1.50	2.62	1.68	0.00	0.02	5.82	0.00	0.00	0.00	310
Core zone	Tetrahedra	al laver			Octahed	ral laver						
Core zone Sample PPV12-05	Tetrahedra Si	al layer Al ^(IV)	A1 ^(VI)	Mg	Octahed Fe	ral layer Ti	Mn	ΣOcta	К	Na	Са	T °C
Core zone Sample PPV12-05 1	Tetrahedra Si 2.68	al layer Al ^(IV) 1.32	Al ^(VI) 1.54	Mg 2.29	Octahed Fe 2.03	ral layer Ti 0.00	Mn 0.00	ΣOcta 5.87	K 0.00	Na 0.01	Ca 0.01	T °C 288
Core zone Sample PPV12-05 1 2	Tetrahedra Si 2.68 2.74	al layer Al ^(IV) 1.32 1.26	Al ^(VI) 1.54 1.58	Mg 2.29 2.24	Octahed Fe 2.03 1.99	ral layer Ti 0.00 0.00	Mn 0.00 0.01	ΣOcta 5.87 5.82	K 0.00 0.00	Na 0.01 0.00	Ca 0.01 0.01	T °C 288 338
Core zone Sample PPV12-05 1 2 3	Tetrahedra Si 2.68 2.74 2.74	al layer Al ^(IV) 1.32 1.26 1.26	Al ^(VI) 1.54 1.58 1.56	Mg 2.29 2.24 2.29	Octahed Fe 2.03 1.99 1.99	ral layer Ti 0.00 0.00 0.00	Mn 0.00 0.01 0.00	ΣOcta 5.87 5.82 5.84	K 0.00 0.00 0.00	Na 0.01 0.00 0.00	Ca 0.01 0.01 0.01	T °C 288 338 289
Core zone Sample PPV12-05 1 2 3 4	Tetrahedra Si 2.68 2.74 2.74 2.74 2.70	al layer Al ^(IV) 1.32 1.26 1.26 1.30	Al ^(VI) 1.54 1.58 1.56 1.55	Mg 2.29 2.24 2.29 2.28	Octahed Fe 2.03 1.99 1.99 2.02	ral layer Ti 0.00 0.00 0.00 0.00	Mn 0.00 0.01 0.00 0.00	ΣOcta 5.87 5.82 5.84 5.86	K 0.00 0.00 0.00 0.00	Na 0.01 0.00 0.00 0.00	Ca 0.01 0.01 0.01 0.01	T °C 288 338 289 277
Core zone Sample PPV12-05 1 2 3 4 5	Tetrahedra Si 2.68 2.74 2.74 2.70 2.70 2.74	al layer Al ^(IV) 1.32 1.26 1.26 1.30 1.26	Al ^(VI) 1.54 1.58 1.56 1.55 1.54	Mg 2.29 2.24 2.29 2.28 2.32	Octahed Fe 2.03 1.99 1.99 2.02 1.97	ral layer Ti 0.00 0.00 0.00 0.00 0.00	Mn 0.00 0.01 0.00 0.00 0.01	ΣOcta 5.87 5.82 5.84 5.86 5.83	K 0.00 0.00 0.00 0.00 0.00	Na 0.01 0.00 0.00 0.00 0.00	Ca 0.01 0.01 0.01 0.01 0.01	T °C 288 338 289 277 261
Core zone Sample PPV12-05 1 2 3 4 5 6	Tetrahedra Si 2.68 2.74 2.74 2.74 2.70 2.74 2.75	al layer Al ^(IV) 1.32 1.26 1.26 1.30 1.26 1.25	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59	Mg 2.29 2.24 2.29 2.28 2.32 2.23	Octahed Fe 2.03 1.99 1.99 2.02 1.97 1.98	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00	Mn 0.00 0.01 0.00 0.00 0.01 0.00	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.83	K 0.00 0.00 0.00 0.00 0.00 0.01	Na 0.01 0.00 0.00 0.00 0.00 0.01	Ca 0.01 0.01 0.01 0.01 0.01 0.01	T °C 288 338 289 277 261 252
Core zone Sample PPV12-05 1 2 3 4 5 6 7	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78	al layer Al ^(TV) 1.32 1.26 1.26 1.30 1.26 1.25 1.22	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.32 2.32	Octahed Fe 2.03 1.99 1.99 2.02 1.97 1.98 1.93	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.01 0.00 0.00	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81	K 0.00 0.00 0.00 0.00 0.00 0.01 0.01	Na 0.01 0.00 0.00 0.00 0.00 0.01 0.00	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01	T °C 288 338 289 277 261 252 225
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.24	al layer Al ^(TV) 1.32 1.26 1.26 1.30 1.26 1.25 1.22 1.21	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.32 2.32 2.30	Octahed Fe 2.03 1.99 2.02 1.97 1.98 1.93 1.93 1.95	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.81	K 0.00 0.00 0.00 0.00 0.00 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.01 0.00 0.00	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01	T °C 288 338 289 277 261 252 225 236
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9	Tetrahedra Si 2.68 2.74 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84	al layer Al ^(TV) 1.32 1.26 1.26 1.30 1.26 1.25 1.22 1.21 1.16	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56 1.55	Mg 2.29 2.24 2.29 2.28 2.32 2.23 2.32 2.32 2.30 2.30 2.30	Octahed Fe 2.03 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.82	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.81 5.79 5.70	K 0.00 0.00 0.00 0.00 0.01 0.01 0.02 0.01	Na 0.01 0.00 0.00 0.00 0.01 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10	Tetrahedra Si 2.68 2.74 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76	al layer Al ^(IV) 1.32 1.26 1.26 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56 1.55 1.56 1.55	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.32 2.30 2.36 2.36 2.29 2.31	Octahed Fe 2.03 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.92	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.81 5.79 5.78 5.78	K 0.00 0.00 0.00 0.00 0.01 0.01 0.02 0.01 0.01	Na 0.01 0.00 0.00 0.00 0.01 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 266 272 261
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77	al layer Al ^(IV) 1.32 1.26 1.26 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56 1.55 1.56 1.55 1.57 1.58	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.32 2.30 2.36 2.29 2.31 2.43	Octahed Fe 2.03 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.93 1.84	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.81 5.79 5.78 5.82 5.82	K 0.00 0.00 0.00 0.00 0.01 0.01 0.02 0.01 0.01	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13	Tetrahedra Si 2.68 2.74 2.74 2.70 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78	al layer Al ^(IV) 1.32 1.26 1.26 1.30 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56 1.55 1.56 1.55 1.57 1.58 1.54 1.55	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.32 2.30 2.36 2.30 2.36 2.29 2.31 2.43 2.36	Octahed Fe 2.03 1.99 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.01 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.81 5.79 5.78 5.82 5.82 5.82	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.77 2.78	al layer Al ^(IV) 1.32 1.26 1.26 1.30 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.21	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56 1.55 1.56 1.55 1.57 1.58 1.54 1.55 1.53	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.32 2.30 2.36 2.29 2.31 2.43 2.36 2.46	Octahed Fe 2.03 1.99 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.01 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.83 5.80 5.81 5.81 5.81 5.79 5.78 5.82 5.82 5.82 5.82 5.81	K 0.00 0.00 0.00 0.00 0.01 0.01 0.02 0.01 0.01	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.77 2.78 2.79 2.84 2.77 2.78 2.79	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56 1.55 1.56 1.55 1.57 1.58 1.54 1.55 1.57 1.58 1.54	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.32 2.30 2.36 2.29 2.31 2.43 2.36 2.43 2.36 2.46 2.33	Octahed Fe 2.03 1.99 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.79 5.78 5.82 5.82 5.82 5.82 5.82 5.81 5.81	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 264
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.81 2.76 2.77 2.78 2.83 2.79 2.80	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21 1.20	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56 1.55 1.57 1.58 1.57 1.58 1.54 1.55 1.57 1.58 1.54 1.55 1.54 1.55 1.58 1.58 1.58 1.59	Mg 2.29 2.24 2.29 2.32 2.32 2.32 2.32 2.30 2.36 2.36 2.31 2.43 2.36 2.43 2.36 2.46 2.33 2.29	Octahed Fe 2.03 1.99 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81 1.90 1.91	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.79 5.78 5.82 5.82 5.82 5.82 5.82 5.81 5.81 5.79	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 268
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.81 2.76 2.77 2.78 2.83 2.79 2.83 2.79 2.80 2.77	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21 1.20 1.23	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56 1.55 1.57 1.58 1.54 1.55 1.57 1.58 1.54 1.55 1.53 1.58 1.59 1.58 1.59 1.58	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.30 2.36 2.36 2.31 2.43 2.36 2.43 2.36 2.44 2.33 2.36 2.43 2.36	Octahed Fe 2.03 1.99 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81 1.90 1.81 1.90 1.81	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.79 5.78 5.82 5.82 5.82 5.82 5.82 5.81 5.81 5.79 5.83	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 261 235 250 244 268 284
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.83 2.79 2.83 2.79 2.83 2.79 2.80 2.77 2.77	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21 1.20 1.23 1.23 1.23	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56 1.55 1.57 1.58 1.54 1.55 1.54 1.55 1.54 1.55 1.53 1.58 1.58 1.59 1.58 1.55 1.54 1.55 1.56 1.55 1.57 1.58 1.58 1.55 1.54 1.55 1.57 1.58 1.55 1.54 1.55 1.58 1.58 1.58 1.58 1.58 1.58 1.58 1.58 1.58 1.58 1.58 1.58 1.58 1.58 1.58 1.58 1.58 1.58 1.58	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.32 2.30 2.36 2.29 2.31 2.43 2.36 2.43 2.36 2.43 2.36 2.46 2.33 2.29 2.38 2.38	Octahed Fe 2.03 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81 1.90 1.91 1.86 1.89	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.79 5.82 5.82 5.82 5.82 5.82 5.81 5.81 5.81 5.79 5.82 5.82	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.01 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.01 0.00 0.01 0.00 0.01	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 264 264 264 264 264 288 4289
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.83 2.79 2.80 2.77 2.80 2.77 2.76	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21 1.20 1.23 1.23 1.23 1.23 1.24	$\begin{array}{c} Al^{(VI)}\\ 1.54\\ 1.58\\ 1.56\\ 1.55\\ 1.54\\ 1.59\\ 1.55\\ 1.56\\ 1.55\\ 1.56\\ 1.55\\ 1.57\\ 1.58\\ 1.54\\ 1.55\\ 1.53\\ 1.58\\ 1.59\\ 1.58\\ 1.59\\ 1.58\\ 1.55\\ 1.49\end{array}$	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.30 2.36 2.29 2.31 2.43 2.43 2.43 2.43 2.43 2.43 2.36 2.46 2.33 2.29 2.38 2.38 2.38 2.39	Octahed Fe 2.03 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81 1.90 1.91 1.86 1.89 1.98	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.79 5.78 5.82 5.82 5.82 5.82 5.81 5.81 5.81 5.79 5.82 5.82 5.82 5.82 5.82 5.82 5.82 5.82	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.01 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 264 264 264 268 289 262
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20	Tetrahedra Si 2.68 2.74 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.83 2.79 2.80 2.77 2.80 2.77 2.76 2.77 2.76 2.75	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21 1.20 1.23 1.23 1.23 1.23 1.24 1.25	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56 1.55 1.57 1.58 1.54 1.55 1.53 1.54 1.55 1.53 1.58 1.58 1.58 1.58 1.55 1.49 1.49 1.48	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.32 2.30 2.36 2.29 2.31 2.43 2.36 2.46 2.33 2.29 2.38 2.38 2.38 2.39 2.33	Octahed Fe 2.03 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81 1.90 1.81 1.90 1.91 1.86 1.89 1.98 2.04	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.79 5.78 5.82 5.82 5.82 5.82 5.81 5.81 5.81 5.79 5.82 5.82 5.82 5.82 5.82 5.82 5.82 5.82	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 264 264 264 268 284 284 289 262 273
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.83 2.79 2.80 2.77 2.78 2.83 2.79 2.80 2.77 2.76 2.77 2.76 2.75 2.79	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21 1.20 1.23 1.23 1.23 1.23 1.24 1.25 1.21	$\begin{array}{c} A1^{(VI)}\\ 1.54\\ 1.58\\ 1.56\\ 1.55\\ 1.54\\ 1.59\\ 1.55\\ 1.56\\ 1.55\\ 1.56\\ 1.55\\ 1.57\\ 1.58\\ 1.54\\ 1.55\\ 1.53\\ 1.58\\ 1.58\\ 1.58\\ 1.59\\ 1.58\\ 1.55\\ 1.49\\ 1.48\\ 1.50\end{array}$	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.30 2.36 2.29 2.31 2.43 2.36 2.46 2.33 2.29 2.31 2.43 2.36 2.46 2.33 2.29 2.38 2.38 2.39 2.33 2.31	Octahed Fe 2.03 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81 1.90 1.81 1.90 1.91 1.86 1.89 1.98 2.04 2.04	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.79 5.78 5.82 5.82 5.82 5.82 5.81 5.81 5.81 5.81 5.81 5.81 5.82 5.82 5.82 5.82 5.82 5.82 5.82 5.82	K 0.00 0.00 0.00 0.01 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 264 264 264 264 264 284 284 284 284 284 284 284 284 284 28
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.83 2.79 2.83 2.79 2.80 2.77 2.76 2.77 2.76 2.75 2.79 2.70	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21 1.20 1.23 1.23 1.23 1.24 1.25 1.21 1.23	$\begin{array}{c} Al^{(VI)}\\ 1.54\\ 1.58\\ 1.56\\ 1.55\\ 1.54\\ 1.59\\ 1.55\\ 1.56\\ 1.55\\ 1.56\\ 1.55\\ 1.57\\ 1.58\\ 1.54\\ 1.55\\ 1.53\\ 1.58\\ 1.59\\ 1.58\\ 1.59\\ 1.58\\ 1.55\\ 1.49\\ 1.48\\ 1.50\\ 1.48\end{array}$	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.32 2.30 2.36 2.29 2.31 2.43 2.36 2.46 2.33 2.29 2.38 2.38 2.38 2.39 2.33 2.31 2.34	Octahed Fe 2.03 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81 1.90 1.81 1.90 1.91 1.86 1.89 1.98 2.04 2.04 2.04 2.03	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.83 5.80 5.81 5.81 5.79 5.78 5.82 5.82 5.82 5.82 5.82 5.81 5.81 5.79 5.82 5.81 5.81 5.79 5.82 5.81 5.81 5.81 5.81 5.81 5.82 5.82 5.82 5.82 5.82 5.82 5.82 5.82	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 268 244 264 264 264 289 262 273 292 290
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 20 21 22 23	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.83 2.79 2.80 2.77 2.78 2.83 2.79 2.80 2.77 2.76 2.77 2.76 2.75 2.79 2.77 2.75 2.79 2.77 2.75	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21 1.20 1.23 1.23 1.23 1.24 1.25 1.21 1.23 1.25	$\begin{array}{c} Al^{(V1)}\\ 1.54\\ 1.58\\ 1.56\\ 1.55\\ 1.54\\ 1.59\\ 1.55\\ 1.56\\ 1.55\\ 1.57\\ 1.58\\ 1.57\\ 1.58\\ 1.57\\ 1.58\\ 1.59\\ 1.58\\ 1.59\\ 1.58\\ 1.59\\ 1.58\\ 1.59\\ 1.58\\ 1.59\\ 1.58\\ 1.59\\ 1.58\\ 1.59\\ 1.48\\ 1.50\\ 1.48\\ 1.50\\ 1.48\\ 1.45\\ $	Mg 2.29 2.24 2.29 2.32 2.32 2.32 2.30 2.36 2.36 2.29 2.31 2.43 2.36 2.43 2.29 2.31 2.43 2.29 2.38 2.39 2.38 2.39 2.33 2.31 2.34 2.34 2.38	Octahed Fe 2.03 1.99 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81 1.90 1.91 1.86 1.89 1.91 1.86 1.89 1.98 2.04 2.04 2.03 2.04	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.81 5.82 5.82 5.82 5.82 5.82 5.82 5.81 5.81 5.81 5.81 5.81 5.81 5.81 5.82 5.82 5.82 5.82 5.82 5.82 5.82 5.82	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 268 284 268 284 289 262 273 290 317
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.83 2.79 2.83 2.79 2.80 2.77 2.77 2.76 2.75 2.75 2.79 2.75 2.75 2.75 2.76	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21 1.20 1.23 1.23 1.23 1.24 1.25 1.21 1.23 1.25 1.24	$\begin{array}{c} Al^{(V1)} \\ 1.54 \\ 1.58 \\ 1.56 \\ 1.55 \\ 1.54 \\ 1.59 \\ 1.55 \\ 1.56 \\ 1.55 \\ 1.57 \\ 1.58 \\ 1.57 \\ 1.58 \\ 1.54 \\ 1.55 \\ 1.53 \\ 1.58 \\ 1.59 \\ 1.58 \\ 1.59 \\ 1.58 \\ 1.59 \\ 1.58 \\ 1.59 \\ 1.48 \\ 1.50 \\ 1.48 \\ 1.45 \\ 1.45 \\ 1.45 \end{array}$	Mg 2.29 2.24 2.29 2.32 2.32 2.32 2.30 2.36 2.36 2.36 2.31 2.43 2.36 2.43 2.36 2.46 2.33 2.29 2.38 2.38 2.38 2.39 2.33 2.31 2.34 2.38 2.38 2.38	Octahed Fe 2.03 1.99 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81 1.90 1.81 1.90 1.81 1.90 1.81 1.90 1.91 1.86 1.89 1.98 2.04 2.04 2.04 2.04 2.04	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.81 5.82 5.82 5.82 5.82 5.81 5.81 5.79 5.82 5.81 5.81 5.79 5.82 5.82 5.82 5.82 5.82 5.82 5.82 5.82	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 264 268 284 289 262 273 290 317 283
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 24	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.83 2.79 2.83 2.79 2.80 2.77 2.76 2.77 2.76 2.75 2.79 2.77 2.75 2.79 2.77 2.75 2.79	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21 1.20 1.23 1.23 1.23 1.23 1.24 1.25 1.21 1.23 1.25 1.24 1.25	$\begin{array}{c} Al^{(VI)} \\ 1.54 \\ 1.58 \\ 1.56 \\ 1.55 \\ 1.54 \\ 1.59 \\ 1.55 \\ 1.56 \\ 1.55 \\ 1.57 \\ 1.58 \\ 1.57 \\ 1.58 \\ 1.54 \\ 1.55 \\ 1.53 \\ 1.58 \\ 1.59 \\ 1.58 \\ 1.59 \\ 1.58 \\ 1.59 \\ 1.58 \\ 1.59 \\ 1.58 \\ 1.59 \\ 1.49 \\ 1.48 \\ 1.45 \\ 1.45 \\ 1.45 \\ 1.45 \\ 1.45 \\ 1.45 \\ 1.49 \\ 1.49 \\ 1.48 \\ 1.45 \\ 1.45 \\ 1.45 \\ 1.45 \\ 1.45 \\ 1.45 \\ 1.49 \\ 1.49 \\ 1.48 \\ 1.45 \\ 1.45 \\ 1.45 \\ 1.45 \\ 1.49 \\ 1.48 \\ 1.45$	Mg 2.29 2.24 2.29 2.23 2.32 2.32 2.30 2.36 2.36 2.30 2.36 2.31 2.43 2.36 2.43 2.36 2.43 2.36 2.46 2.33 2.29 2.38 2.38 2.38 2.39 2.33 2.31 2.34 2.38 2.38 2.38 2.38 2.38	Octahed Fe 2.03 1.99 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81 1.90 1.81 1.90 1.81 1.90 1.81 1.80 1.91 1.86 1.89 1.98 2.04 2.04 2.04 2.04 2.04 2.04	ral layer Ti 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.81 5.82 5.82 5.82 5.82 5.82 5.81 5.81 5.81 5.81 5.81 5.82 5.82 5.82 5.82 5.82 5.82 5.82 5.82	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 264 264 264 284 289 262 273 292 290 317 283 263
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.83 2.79 2.83 2.79 2.80 2.77 2.76 2.77 2.76 2.75 2.79 2.77 2.75 2.76 2.72 2.75 2.76 2.72 2.75	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21 1.20 1.23 1.23 1.23 1.23 1.24 1.25 1.21 1.23 1.23 1.24 1.25 1.24 1.28 1.25	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56 1.55 1.57 1.58 1.54 1.55 1.53 1.54 1.55 1.53 1.58 1.59 1.58 1.55 1.55 1.58 1.55 1.55 1.54 1.55 1.54 1.55 1.55 1.54 1.55 1.55 1.54 1.55 1.55 1.55 1.54 1.55 1.55 1.54 1.55 1.55 1.55 1.55 1.54 1.55 1.55 1.55 1.55 1.55 1.55 1.55 1.55 1.55 1.55 1.55 1.55 1.55 1.54 1.55 1.55 1.55 1.54 1.55 1.55 1.55 1.55 1.54 1.55 1.55 1.54 1.55 1.55 1.55 1.54 1.55 1.55 1.54 1.55 1.55 1.55 1.54 1.55 1.55 1.55 1.54 1.55 1.55 1.54 1.55 1.55 1.54 1.55 1.55 1.54 1.55 1.55 1.56 1.55 1.55 1.56 1.55 1.55 1.56 1.55 1.55 1.55 1.55 1.55 1.49 1.48 1.45 1.55 1.49 1.45 1.45 1.45 1.45 1.55 1.49 1.45 1.45 1.45 1.45 1.55 1.49 1.55 1.45 1.45 1.45 1.45 1.45 1.55 1.49 1.51 1.55 1.49 1.51 1.55 1.45 1.45 1.45 1.45 1.55 1.55 1.49 1.51 1.55 1.45 1.45 1.45 1.55 1.45 1.45 1.45 1.55 1.55 1.45 1.45 1.45 1.45 1.55 1.55 1.45 1.45 1.45 1.55 1.55 1.45 1.45 1.45 1.55 1.55 1.45 1.45 1.45 1.55 1.55 1.45 1.45 1.55 1.45 1.45 1.55 1.45 1.55 1.45 1.55 1.45 1.55 1.45 1.45 1.55 1.55 1.45 1.45 1.55 1.55 1.45 1.45 1.55 1.55 1.55 1.55 1.55 1.55	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.30 2.36 2.29 2.31 2.43 2.36 2.43 2.36 2.43 2.36 2.43 2.33 2.29 2.33 2.33 2.38 2.39 2.33 2.31 2.34 2.38 2.38 2.38 2.38 2.38 2.38 2.38 2.35 2.32	Octahed Fe 2.03 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81 1.90 1.81 1.90 1.91 1.86 1.89 1.98 2.04 2.04 2.04 2.04 2.04 2.04 2.04 2.04	ral layer Ti 0.00 0.0	Mn 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.0	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.79 5.82 5.82 5.82 5.82 5.82 5.81 5.81 5.79 5.82 5.81 5.81 5.79 5.82 5.82 5.82 5.82 5.84 5.86 5.86 5.84 5.85 5.88 5.88 5.88 5.88	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 264 264 264 264 264 264 264 264 264
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.83 2.79 2.83 2.79 2.83 2.79 2.80 2.77 2.75 2.76 2.75 2.79 2.77 2.75 2.76 2.72 2.75 2.76 2.72 2.75 2.76 2.72 2.75 2.76 2.72 2.75 2.76 2.77 2.75 2.76 2.77 2.75 2.79 2.77 2.77 2.77 2.77 2.77 2.77 2.77	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21 1.20 1.23 1.22 1.17 1.21 1.20 1.23 1.23 1.24 1.25 1.21 1.23 1.25 1.24 1.25 1.24 1.28 1.25	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56 1.55 1.57 1.58 1.54 1.55 1.57 1.58 1.54 1.55 1.53 1.58 1.55 1.59 1.58 1.55 1.59 1.58 1.55 1.59 1.58 1.55 1.54 1.55 1.54 1.55 1.57 1.58 1.54 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.55 1.56 1.55 1.57 1.58 1.55 1.54 1.55 1.57 1.58 1.55 1.54 1.55 1.57 1.58 1.55 1.54 1.55 1.54 1.55 1.57 1.58 1.54 1.55 1.54 1.55 1.57 1.58 1.54 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.57 1.58 1.55 1.54 1.55 1.57 1.58 1.55 1.54 1.55 1.54 1.55 1.57 1.58 1.55 1.54 1.55 1.55 1.57 1.58 1.55 1.57 1.58 1.55 1.57 1.58 1.55 1.49 1.48 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.48 1.45	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.30 2.36 2.29 2.31 2.43 2.36 2.43 2.36 2.43 2.36 2.43 2.33 2.39 2.33 2.38 2.39 2.38 2.39 2.38 2.39 2.38 2.39 2.38 2.39 2.38 2.39 2.38 2.39 2.38 2.39 2.38 2.39 2.38 2.39 2.38 2.39 2.38 2.39 2.38 2.39 2.38 2.39 2.39 2.30 2.30 2.30 2.30 2.30 2.30 2.30 2.30	Octahed Fe 2.03 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81 1.90 1.81 1.90 1.91 1.86 1.89 1.98 2.04 2.04 2.04 2.04 2.04 2.04 2.04 2.04	ral layer Ti 0.00 0.0	Mn 0.00 0.01 0.00 0.	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.79 5.78 5.82 5.82 5.82 5.82 5.82 5.81 5.81 5.79 5.82 5.81 5.81 5.79 5.82 5.82 5.81 5.81 5.79 5.82 5.82 5.81 5.81 5.81 5.82 5.86 5.86 5.86 5.88	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.01 0.00 0.01 0.00 0.01 0.00 0.01 0.00 0.00 0.00 0.00 0.01 0.000000	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 264 264 264 264 264 264 264 264 264
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28	Tetrahedra Si 2.68 2.74 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.83 2.79 2.84 2.81 2.76 2.77 2.78 2.83 2.79 2.80 2.77 2.75 2.76 2.75 2.79 2.77 2.75 2.76 2.75 2.76 2.75 2.76 2.75 2.76 2.75 2.76 2.77 2.75 2.76 2.77 2.75 2.76 2.77 2.75 2.76 2.77 2.77 2.77 2.75 2.76 2.77 2.77 2.77 2.77 2.77 2.77 2.77	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21 1.20 1.23 1.22 1.17 1.21 1.23 1.23 1.24 1.25 1.21 1.25 1.24 1.25 1.24 1.25 1.21 1.24	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56 1.55 1.57 1.58 1.54 1.55 1.57 1.58 1.54 1.55 1.53 1.58 1.59 1.58 1.55 1.59 1.58 1.55 1.49 1.48 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.55 1.56 1.55 1.57 1.58 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.57 1.58 1.54 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.57 1.58 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.57 1.58 1.55 1.57 1.58 1.55 1.55 1.49 1.48 1.45 1.45 1.45 1.45 1.45 1.48 1.45 1.45 1.45 1.45 1.45 1.55 1.57 1.58 1.55 1.57 1.58 1.55 1.57 1.58 1.55 1.57 1.58 1.55 1.57 1.58 1.55 1.57 1.58 1.55 1.49 1.48 1.45 1.55 1.47 1.51 1.55 1.55 1.55 1.49 1.55 1.45 1.45 1.45 1.55 1.45 1.45 1.45 1.55 1.55 1.55 1.55 1.55 1.55	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.32 2.30 2.36 2.29 2.31 2.43 2.43 2.43 2.43 2.43 2.43 2.43 2.44 2.33 2.29 2.33 2.31 2.38 2.39 2.33 2.31 2.34 2.38 2.35 2.32 2.31 2.32 2.31 2.34 2.38 2.35 2.32 2.31 2.34 2.38 2.35 2.32 2.31 2.34 2.38 2.38 2.39 2.33 2.31 2.34 2.38 2.39 2.33 2.31 2.32 2.32 2.32 2.32 2.32 2.32	Octahed Fe 2.03 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81 1.90 1.81 1.90 1.91 1.86 1.89 1.98 2.04 2.04 2.04 2.04 2.04 2.04 2.04 2.04	ral layer Ti 0.00 0.0	Mn 0.00 0.01 0.00 0.	ΣOcta 5.87 5.82 5.84 5.86 5.83 5.80 5.81 5.81 5.79 5.78 5.82 5.82 5.82 5.82 5.82 5.81 5.81 5.79 5.82 5.81 5.81 5.79 5.82 5.82 5.82 5.81 5.81 5.81 5.79 5.82 5.82 5.82 5.82 5.82 5.82 5.82 5.81 5.81 5.81 5.79 5.78 5.82 5.82 5.82 5.82 5.82 5.82 5.82 5.81 5.81 5.81 5.82 5.86 5.86 5.88	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 264 264 264 264 264 264 264 264 264
Core zone Sample PPV12-05 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30	Tetrahedra Si 2.68 2.74 2.74 2.70 2.74 2.75 2.78 2.79 2.84 2.81 2.76 2.77 2.78 2.83 2.79 2.80 2.77 2.78 2.83 2.79 2.80 2.77 2.75 2.76 2.75 2.79 2.77 2.75 2.76 2.72 2.75 2.79 2.75 2.76 2.72 2.75 2.79 2.75 2.76 2.72 2.75 2.76 2.72 2.75 2.76 2.72 2.75 2.76 2.77 2.75 2.76 2.77 2.77 2.75 2.76 2.77 2.77 2.77 2.77 2.77 2.77 2.77	al layer Al ^(TV) 1.32 1.26 1.26 1.26 1.25 1.22 1.21 1.16 1.19 1.24 1.23 1.22 1.17 1.21 1.20 1.23 1.22 1.17 1.21 1.20 1.23 1.23 1.23 1.24 1.25 1.21 1.24 1.25 1.21 1.21 1.24 1.25	Al ^(VI) 1.54 1.58 1.56 1.55 1.54 1.59 1.55 1.56 1.55 1.57 1.58 1.54 1.55 1.57 1.58 1.54 1.55 1.53 1.58 1.59 1.58 1.55 1.49 1.48 1.45 1.48 1.45 1.45 1.49 1.45 1.45 1.41 1.45 1.41 1.45 1.41 1.45 1.41 1.45 1.41 1.45 1.41 1.45 1.41 1.45 1.41 1.45 1.44 1.55 1.55 1.54 1.54 1.55 1.54 1.54 1.55 1.54 1.55 1.54 1.54 1.55 1.54 1.54 1.55 1.54 1.54 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.54 1.55 1.57 1.58 1.55 1.54 1.55 1.55 1.57 1.58 1.55 1.57 1.58 1.55 1.57 1.58 1.55 1.57 1.58 1.55 1.57 1.58 1.55 1.57 1.58 1.55 1.49 1.48 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.45 1.47 1.45 1.47 1.51 1.47 1.51 1.51 1.42	Mg 2.29 2.24 2.29 2.28 2.32 2.32 2.30 2.36 2.29 2.31 2.43 2.36 2.46 2.33 2.36 2.46 2.33 2.39 2.38 2.39 2.33 2.31 2.34 2.38 2.39 2.33 2.31 2.34 2.38 2.35 2.32 2.31 2.28 2.31 2.28 2.30 2.31 2.32 2.31 2.32 2.31 2.32 2.33 2.33	Octahed Fe 2.03 1.99 2.02 1.97 1.98 1.93 1.95 1.88 1.92 1.93 1.84 1.90 1.81 1.90 1.91 1.86 1.89 1.98 2.04 2.04 2.04 2.04 2.04 2.04 2.04 2.04	ral layer Ti 0.00 0.0	Mn 0.00 0.01 0.00 0.	ΣOcta 5.87 5.82 5.84 5.86 5.80 5.81 5.81 5.79 5.78 5.82 5.82 5.82 5.81 5.81 5.79 5.82 5.81 5.81 5.79 5.82 5.86 5.88	K 0.00 0.00 0.00 0.00 0.01 0.01 0.01 0.0	Na 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.0	Ca 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	T °C 288 338 289 277 261 252 225 236 272 268 261 235 250 244 264 264 264 264 264 264 264 264 264

zone compared to those from the core zone. Moreover, the compositional maps demonstrate that Na_2O is higher in the core of the grains compared to the rims of the grains which suggests alteration from detrital mica/illite with paragonitic substitution into muscovite. An-

other possibility is alteration from detrital feldspar into muscovite during diagenesis and fault deformation.



Fig. 7. Ternary and di-diagrams for chemical analyses of chlorite and micas from the core zone (sample PPV12-05) and the damage zone (sample PPV12-07). (A) Fe + Mg-Si-Al^(total) ternary diagrams and Fe/(Fe + Mg) vs. Si plot for chlorite. (B) M + -4Si-R²⁺ ternary diagrams (Meunier and Velde, 1989) and Na/(Na + K) vs. Fe plot for muscovite. $M^+ = Na^+ + K^+ + 2Ca^{2+}$, 4Si = (Si/4) and $R^{2+} = (Mg + Fe + Mn)$ and Di-Tri is (dioctahedral-trioctahedral substitutions). Chlorite and muscovite initial and average compositions obtained by modelling at high reductive conditions are highlighted with the star icon.

4.4. Deformation conditions

The Kübler index was measured on five samples along the hanging wall transect. The KI values of muscovite (001) range from $0.20^{\circ} 2\theta$ to $0.26^{\circ} 2\theta$ (Kübler-Kisch scale) see Supplementary Table 1. These values are corresponding to lower -anchizone/epizone grade conditions.

The average temperature estimated by chlorite thermometry (through multi-equilibrium thermodynamic calculations) is presented in (Table 3). The temperature in the damage zone ranges between 218°C to 317°C with an average value of 270°C \pm 23°C. The core zone temperature is between 225°C and 359°C with an average value 285°C \pm 28°C. The redox conditions can be evaluated by assessing the variation of XFe³⁺. In red pelites XFe³⁺ values are between 11% and 44% with an average value of 25% and standard deviation of \pm 7%. In green pelites the values are relatively lower, they range from 3 to 34% with an average value of 16% and standard deviation of \pm 7%. This indicates less Fe³⁺ is stored in chlorite of the green pelite. Such as variation can be linked to changes in P-T conditions or in the oxidation state (Lanari et al., 2014c; Trincal et al., 2015; Vidal et al., 2006).

4.5. Fluid/rock interactions modelling

4.5.1. Conditions

In the PPVT, the Triassic red pelites transformed into green pelites in the core fault zone due to dissolution of hematite in the core zone. In order to better understand their mineralogical changes, a simulation of the fluid/rock interactions was performed.

The Triassic red pelites compositions was used as an initial

composition and the relative proportion of each mineral is presented in Table 4 (data are from Trincal, 2014). The chemical compositions of detrital chlorite and muscovite from the red pelites matrix are based on the EPMA analyses of the present study. The newly formed chlorite that is present in a few veins in the red pelites is excluded during this simulation.

As it is not possible to analyze the pore fluids in the Triassic pelites, a first simulation was performed to simulate their composition. The initial pore fluid was assumed to be at equilibrium with the red pelites minerals before thrusting at 270°C (burial diagenetic conditions). The pore fluid composition (Table 5) was obtained by simulating interactions between the red pelites and low charge fluid (rain water data from Apello and Postma, 2005). The equilibrium was reached by dissolving very small quantities of the detrital minerals. Then the mineralogical changes were simulated by batch reactions between the pore fluids (previously calculated) and the initial red pelites composition at 285°C (temperature which was estimated by chlorite thermometry in the green pelites). To test the impact of redox condition change, a series of calculations were performed at various redox conditions (from reduction potential (Eh) = 0.420 V to Eh = -0.841 V). The precipitation possibility was tested for iron oxi/hydroxides (hematite, goethite, and magnetite), iron sulfur and sulfates (pyrite, gypsum and anhydrite), phyllosilicates (muscovite, celadonite, illite, annite, paragonite, pyrophyllite and phlogopite), chlorite solid-solutions (amesite, chamosite, clinochlore and daphnite) and other initial minerals (such as, calcite and quartz).

4.5.2. Modelling results

The calculated composition of the resulting interstitial fluids in

Table 2

Calculated muscovite structural formula from the damage zone and core zone of the Pic de Port Vieux respectively.

Damage zone	Tetrahedr	al layer		Octahedral layer Interlayer								
Sample PPV12-07	Si	Al ^(IV)	Al ^(VI)	Mg	Fe	Ti	Mn	ΣOcta	К	Na	Ca	ΣInterlayer
Large muscovite												
1	3.21	0.79	1.81	0.10	0.12	0.00	0.00	2.04	0.85	0.07	0.00	0.92
2	3.14	0.86	1.86	0.08	0.07	0.01	0.00	2.03	0.84	0.10	0.00	0.94
3	3.22	0.78	1.78	0.12	0.13	0.01	0.00	2.04	0.80	0.12	0.00	0.92
4	3.18	0.82	1.82	0.10	0.11	0.01	0.00	2.04	0.84	0.10	0.00	0.94
5	3.16	0.84	1.86	0.08	0.08	0.01	0.00	2.03	0.81	0.14	0.00	0.95
6	3.15	0.85	1.85	0.09	0.06	0.02	0.00	2.03	0.88	0.09	0.00	0.97
7	3.16	0.84	1.86	0.09	0.07	0.02	0.00	2.04	0.88	0.07	0.00	0.95
8	3.12	0.88	1.84	0.09	0.07	0.02	0.00	2.03	0.90	0.09	0.00	0.99
9	3.14	0.86	1.86	0.09	0.07	0.02	0.00	2.03	0.86	0.11	0.00	0.97
10	3.24	0.76	1.73	0.14	0.12	0.02	0.00	2.01	0.89	0.10	0.00	0.99
Small muscovite												
11	3.19	0.81	1.79	0.12	0.14	0.00	0.00	2.04	0.92	0.03	0.00	0.95
12	3.23	0.77	1.74	0.13	0.16	0.01	0.00	2.04	0.93	0.02	0.00	0.96
13	3.29	0.71	1.71	0.20	0.13	0.00	0.00	2.04	0.92	0.01	0.00	0.93
14	3.30	0.70	1.77	0.13	0.13	0.00	0.00	2.03	0.84	0.04	0.00	0.88
15	3.26	0.74	1.74	0.16	0.14	0.00	0.00	2.04	0.91	0.03	0.00	0.93
16	3.16	0.84	1.81	0.11	0.10	0.01	0.01	2.03	0.90	0.06	0.00	0.96
17	3.26	0.74	1.73	0.17	0.13	0.00	0.00	2.03	0.93	0.02	0.00	0.95
18	3.20	0.80	1.78	0.12	0.12	0.01	0.00	2.04	0.90	0.04	0.00	0.94
19	3.18	0.82	1.86	0.10	0.08	0.01	0.00	2.04	0.82	0.06	0.00	0.88
20	3.28	0.72	1.77	0.14	0.13	0.00	0.00	2.04	0.84	0.04	0.00	0.89
Core zone	Tetrahedr	al laver			Octahed	Iral laver			Interlay	or.		
Sample PPV12-05	Si	Al ^(IV)	A1 ^(VI)	Mø	Fe	Ti	Mn	ΣOcta	K	Na	Ca	ΣInterlayer
1	3 1 9	0.81	1 78	0.13	0.13	0.01	0.00	2.05	0.90	0.03	0.00	0.93
2	3.22	0.78	1.76	0.13	0.15	0.01	0.00	2.04	0.92	0.03	0.00	0.95
3	3.18	0.82	1.80	0.10	0.12	0.01	0.00	2.04	0.91	0.03	0.00	0.94
4	3.19	0.81	1.79	0.11	0.13	0.00	0.00	2.04	0.92	0.03	0.00	0.94
5	3.23	0.77	1.75	0.16	0.15	0.01	0.00	2.06	0.88	0.02	0.00	0.90
6	3.19	0.81	1.81	0.12	0.11	0.01	0.00	2.04	0.91	0.03	0.00	0.94
7	3.15	0.85	1.82	0.10	0.13	0.01	0.00	2.05	0.90	0.03	0.00	0.93
8	3.19	0.81	1.77	0.13	0.15	0.01	0.00	2.06	0.90	0.03	0.00	0.93
9	3.13	0.87	1.83	0.11	0.11	0.02	0.00	2.07	0.92	0.02	0.00	0.94
10	3.16	0.84	1.80	0.11	0.14	0.01	0.00	2.05	0.91	0.03	0.00	0.95
11	3.14	0.86	1.82	0.12	0.12	0.01	0.00	2.07	0.89	0.04	0.00	0.93
12	3.13	0.87	1.84	0.10	0.11	0.02	0.00	2.07	0.89	0.04	0.00	0.93
13	3.11	0.89	1.82	0.11	0.13	0.01	0.00	2.07	0.92	0.02	0.00	0.94
14	3.14	0.86	1.82	0.11	0.12	0.01	0.00	2.06	0.91	0.03	0.00	0.93
15	3.17	0.83	1.79	0.12	0.13	0.01	0.01	2.06	0.90	0.03	0.00	0.93
16	3.17	0.83	1.79	0.13	0.13	0.00	0.00	2.05	0.92	0.03	0.00	0.95
17	3.15	0.85	1.78	0.14	0.14	0.00	0.00	2.06	0.91	0.02	0.00	0.93
18	3.20	0.80	1.81	0.12	0.12	0.01	0.00	2.06	0.87	0.02	0.00	0.90
19	3.22	0.78	1.79	0.12	0.13	0.02	0.00	2.05	0.90	0.03	0.00	0.94
20	3.20	0.80	1.78	0.11	0.13	0.01	0.00	2.04	0.91	0.03	0.00	0.94
21	3.19	0.81	1.80	0.11	0.11	0.01	0.00	2.03	0.93	0.03	0.00	0.96
22	3.20	0.80	1.78	0.13	0.11	0.01	0.00	2.03	0.92	0.03	0.00	0.95
23	3.21	0.79	1.76	0.14	0.14	0.01	0.01	2.05	0.89	0.04	0.00	0.93
24	3.19	0.81	1.81	0.10	0.13	0.01	0.00	2.04	0.92	0.02	0.00	0.94
25	3.23	0.77	1.76	0.14	0.14	0.01	0.00	2.05	0.89	0.05	0.00	0.93
26	3.15	0.85	1.80	0.12	0.13	0.02	0.00	2.07	0.93	0.02	0.00	0.95
27	3.19	0.81	1.76	0.14	0.15	0.01	0.00	2.06	0.91	0.02	0.00	0.93
28	3.18	0.82	1.79	0.11	0.13	0.01	0.00	2.05	0.93	0.02	0.00	0.95
29	3.17	0.83	1.80	0.11	0.13	0.01	0.00	2.05	0.92	0.03	0.00	0.95
30	3.19	0.81	1.80	0.11	0.11	0.01	0.00	2.03	0.90	0.04	0.00	0.94

equilibrium with the red pelite mineralogy is given in Table 5. The mineralogical transformations of red pelite minerals at various redox conditions were calculated and illustrated in Fig. 9A. According to the model, the same calcite content is predicted when modifying the redox conditions. Furthermore, muscovite seems to be slightly under-saturated whatever the redox conditions. At oxidative to low reductive conditions quartz content increases compared to the initial pelite composition. However at moderate to high reducing conditions, quartz content does not change. The observed change during the simulation concerns iron bearing minerals as illustrated in Fig. 9B. The increase in the reducing conditions promotes an increase in hematite dissolution

and this dissolution is complete at Eh < 0.410 V. Magnetite is the ironrich mineral predicted for precipitation in the system when going to higher reducing conditions. However at Eh = -0.819 V magnetite is progressively replaced by chlorite which is the only iron bearing phase predicted to precipitate in extreme reducing conditions (Eh = -0.819 V).

The chlorite and muscovite compositions as a combination of different end members are displayed in Fig. 10. During the simulation, the noticeable change is the variation in proportion of the different end members at high reducing conditions. In Fig. 10A, chamosite, daphnite, clinochlore and amesite correspond to the four end-members of chlorite



Fig. 8. (A) and (B) SEM-BSE images for the damage zone sample PPV12-07 and the core zone sample PPV12-05 respectively. (C) and (D) Quantitative maps showing Na₂O wt% in muscovite for the samples PPV12-07 and PPV12-05 respectively.

Table 3

Illustrating number of analyses of chlorite that have been used in temperature estimation using chlorite thermometry, the average estimated temperature, $XFe^{3+} = (Fe^{3+/}\Sigma Fe)_{chl}$ and the standard deviation for both damage and core zone samples respectively.

Samples	No. of analyses	T °C Vidal	St.dev.	XFe ^{3 +} (%)	St.dev.
PPV12-07(damage	89	270	23	25	7
PPV12-05(core zone)	80	285	28	16	7

Table 4

The initial red pelites composition (data are from Trincal, 2014) which was used as input data for the modelling. The quantity of each phase is presented as a number of moles.

Sample PPV12-07

Phase	Moles in initial assemblage
Calcite	9.69
Quartz	56.4
Rutile	1.00
Hematite	2.32
Total mica	10.8
Mica end-members	
Muscovite	6.58
Annite	0.25
Illite	2.24
Celadonite	0.76
Paragonite	1.01
Total chlorite	1.46
Chlorite end-members	
Amesite	0.53
Clinochlore	0.39
Daphnite	0.54

Table 5 The composition of the pore fluids that result from equilibrium between low charge fluid and the red pelite

mineralogy

Initial fluid composition				
Molality				
Al	6.07E-04			
С	3.18E-05			
Ca	3.28E-05			
Cl	1.30E-05			
Fe	1.00E-12			
K	3.20E-05			
Mg	6.71E-11			
Na	1.62E-03			
S	2.90E-05			
Si	7.36E-03			
Ti	2.26E-10			

that were used to calculate the composition of chlorite. When increasing the reducing conditions a decrease in the proportion of amesite (Mg-rich end member) and an increase in the proportion of daphnite and chamosite (Fe-rich end members) is observed. The composition of chlorite formed after total hematite dissolution (without magnetite) at Eh < -0.830 V, has the following structural formula (Si_{2.85} Al_{1.15}) O₁₀ (Al_{1.14} Mg_{2.41} Fe_{2.44}) (OH)₈.

Illite, celadonite, annite, paragonite and muscovite are the end members used for mica composition simulation. The average muscovite composition is slightly modified when increasing the reducing conditions with the presence of iron instead of magnesium (Fig. 10B), which is simulated by annite component precipitation. The muscovite average structural formula calculated from modelling results at Eh < -0.830 V is (Si_{3.00}Al_{1.00}) O₁₀ (Al_{1.81} Fe_{0.28}) (OH)₂ K_{0.90} Na_{0.10}.



Fig. 9. The simulation results at different redox condition. The first column in the left represents the input data and the others column are corresponding to the minerals quantities obtained by the model at different reducing conditions. (A) Showing the simulation for all the minerals and (B) is zooming for iron rich minerals.

5. Discussion

5.1. Mineralogical and textural changes attributed to fault activity

In the present study, the variations in texture, mineralogy and chemistry between the damage zone and core fault zone deepen our understanding of the impact of deformation and fluid circulation on phyllosilicates.

The core zone of the PPVT is clearly different from the damage zone; it is characterized by a change in pelite color from red to green toward the fault contact, attributed to the dissolution of hematite. The parameters and conditions of that process will be discussed in the following. The second remarkable difference is the presence of numerous veins and veinlets of quartz + chlorite \pm calcite in the core fault zone which can be observed even at the chip rock scale. These veins are associated with the fractures and micro-fractures opening and attributed to fluid circulation coeval to the fault movement (Grant, 1990). Pelites from the core zone have been affected by several stages of deformation and fluid circulation as shown by the distribution of several vein generations that crosscut each other, as well their folded and deformed shape.

Quartz dissolution by pressure solution was observed in the matrix of the core zone and is characterized by smaller grain size and elongation of the grains compared to quartz present in the damage zone. Furthermore, the core zone shows a well-developed foliation, enrichment in phyllosilicates and a pervasive cleavage with preferential orientation of muscovite that facilitated the circulation of the fluids. The results of the present study indicate that deformation and fluid circulation in the fault zone are connected and are related to the same tectonic event. These observations suggest aseismic behavior of the PPVT fault with a pressure solution creep mechanism that involves coupling deformation and recrystallizations in the presence of fluids (e.g. Hadizadeh et al., 2012; Richard et al., 2014). Moreover, this deformation mechanism is consistent with the results from the footwall obtained by Trincal et al., (2016); who suggested that mylonitisation that occurred in core zone of the limestone is related to both mechanical grain size reduction processes and interaction with fluids.

Similarly, Gratier et al. (2013) and Janssen et al. (2016) demonstrated the same mechanism through the dissolution of soluble minerals (feldspars, quartz and calcite) and passive concentration of phyllosilicates in the presence of fluids in active faults from the Western Alps and the San Andreas. In addition, they suggested that fracturing can accelerate pressure solution by developing diffusion shortcut (e.g. Gratier et al., 2011; Lockner et al., 2011). In the present study, the same diffusion process was observed and appears clearly in the fractures within the red pelites and is indicated by the development of green zones around the veins.

5.2. Origin and deformation conditions of phyllosilicates in the PPVT

Many recent studies have focused on phyllosilicates in fault zones (e.g. Alpine Fault, Warr and Cox, 2001; Moab Fault, Solum et al., 2005; Carbonera Fault, Solum and van der Pluijm, 2009; San Andreas Fault, Wenk et al., 2010; Bogd fault, Buatier et al., 2012; Chelungpu fault, Janssen et al., 2016; JFAST fault, Kameda et al., 2015) to study their origin and the deformation conditions. They demonstrated that phyllosilicates in fault zone can be formed by various mechanisms; the passive concentration of clays by pressure solution and dissolution-recrystallization mechanisms (e.g. Buatier et al., 2012; Lacroix et al., 2011), the precipitation of synkinematic clays as a result of fluid rock interactions (e.g. Haines and van der Pluijm, 2008; Wibberley et al., 2008; Wibberley and McCaig, 2000) or mechanical incorporation (e.g. (Egholm et al., 2008; Fisher and Knipe, 2001; Loveless et al., 2011). Phyllosilicates that were observed in the PPVT are chlorite and muscovite. Based on their texture and chemistry, we can discuss their origin in the fault zone.

5.2.1. Chlorite

In the damage zone, chlorite is observed mainly in the matrix and in a few veins, while in the core zone, chlorite is abundant in the numerous veins and veinlets. The presence of chlorite in veins suggests that it is mainly formed by direct precipitation from fluids, whereas the large chlorite grains located in the matrix are probably inherited and a result of diagenetic reactions. The chlorite/muscovite stacks that are present in the damage zone indicate that chlorite formed through micachloritization. Those stacks have been commonly described in sediments that have undergone diagenesis and low-grade metamorphism (Jiang and Peacor, 1994; Milodowski and Zalasiewicz, 1991; Randive et al., 2015). They are formed by alteration of detrital biotite into chlorite through a layer-by-layer transformation and then muscovite progressively fills the chlorite cleavages (Bartier et al., 1998; Li et al., 1994). The association of titanium oxide to chlorite in the fault zone matrix confirmed that the alteration of biotite might have occurred in the PPVT (Eggleton and Banfield, 1985; Parry and Downey, 1982; Ren, 2012; Veblen and Ferry, 1983). In the core fault zone those stacks have been subjected to size reduction and a folding, reflecting more impact by shearing mechanisms compared to the damage zone.

The proportion of inherited chlorite in the matrix decreases toward the fault contact and its grain size decreases, while newly formed chlorite is more abundant in the core zone compared to the damage zone. The only observed difference is that, in the core fault zone chlorite is more Fe-rich and has a homogenous composition compared to chlorite from the damage zone. All these features suggest that newly formed chlorite is synkinematic to the fault activity and probably precipitated from iron rich fluids in the core zone.



Fig. 10. The quantities of the different end members expected by modelling for chlorite and mica are shown in (A) and (C) respectively. The first column in the left is corresponding to the input composition. (B) and (D) are presenting the cation contents in chlorite and mica at Eh = -0.830: -0.841 respectively.

5.2.2. Muscovite

Muscovite is present in the matrix of both damage and core fault zones in three form: randomly oriented coarse aggregates (1), elongated large grains (2), and as smaller grains with sharp grain boundaries (3). All of them have a composition close to muscovite end-member. The large grains of muscovite are mainly observed in the damage zone and probably have a detrital origin. Na₂O content is higher in the core of those grains compared to the rims suggesting either transformation or alteration of detrital mica (with high paragonite content) or from detrital feldspars and the excess Na moved away with the fluids.

Muscovite that has a smaller grain size with well-defined grain boundaries displays homogenous composition and contains less Na in the interlayer space. Close to the fault contact this muscovite contains relatively more Fe and less Na compared to muscovite from the damage zone. The step like shape grain boundary of those grains with quartz indicates dissolution/recrystallization mechanism though the recrystallization/growth of muscovite and the dissolution of quartz.

Based on these results, the newly formed phyllosilicates in the fault core zone are considered as synkinematic and related to deformation processes/fluid circulations coeval with the activity of the PPVT. This is in agreement with previous studies of Cavailhes et al. (2013) and Leclère et al. (2012) among others who found a correlation between fluid-flow and abundance of newly formed phyllosilicates.

5.2.3. Deformation conditions of PPVT activity

As mentioned above, muscovite and chlorite are synkinematic to the fault activity, hence they are a good thermometer for obtaining the deformation conditions of the PPVT. According to (KI) values that range between 0.20 and $0.26^{\circ}20$, the PPVT has experienced deformation under lower-anchizone/epizone grade conditions (sub-greenschist to greenschist facies), where the anchizone grade boundaries are defined

at 0.25 to 0.42°20 (Kübler, 1967).

Thermodynamic calculations from synkinematic chlorite chemistry suggest that fault deformation occurred under average temperatures of 270°C in the damage zone and 285°C in the fault core zone. Those results are consistent with previous estimates deduced from fluid inclusions in quartz veins of the same outcrop that suggested a temperature range of 250°C–300°C (Banks et al., 1991; Grant, 1990; McCaig et al., 2000). This temperature is also in agreement with a stable isotope study on quartz and chlorite from the same geological area with a mean temperature value of 320 \pm 30°C (Lacroix and Vennemann, 2015).

5.3. Key-parameters that control mineralogical changes in the fault zone

Based on the petrographic observation and geochemistry data, there are several parameters that appear to control the mineralogical changes in the PPVT fault zone. The pressure solution and recrystallization processes play a major role in deformation in the core zone. Moreover, the existence of numerous veins in the core zone corroborates the strong influence of fluid circulations.

However, the parameters that control the hematite dissolution/Ferich phyllosilicates formation and induce the color change in the core zone were not clearly identified. Increasing the temperature does not allow dissolution of hematite in the core zone and the chlorite formation temperatures from both the green pelites and red pelites are similar within analytical uncertainty. However, it well known that to mobilize Fe, interaction with reducing fluids is required (Busigny and Dauphas, 2007). In addition, the decrease of XFe^{3+} in newly formed chlorite from the core zone (green pelites) of the PPVT shows a change in the oxidation state of Fe.

Based on the results of numerical modelling of the present study, the

dissolution of hematite is due to interaction with reducing fluids. Hematite dissolution was described in the Entrada Sandstone (United States) and was explained by the interaction with reducing brine involving an iron reduction (Wigley et al., 2012 and 2013). Furthermore, the modelling results indicate that hematite dissolution can be a source of iron for the newly formed phyllosilicates in the core zone. The chemical composition of chlorite and muscovite obtained by the modelling at high reductive conditions is in agreement with the composition calculated by EPMA analyses regarding iron content (Fig. 7). However Na content in muscovite calculated by the model is a bit different; this can be explained by the modelling limitation due to lack of mica end members in the database or by the variation in the initial white mica composition in the red pelites which arises from their different detrital origin and subsequent diagenesis.

6. Conclusion

The characterization of phyllosilicates (chlorite and muscovite) in the PPVT fault helps to better understand their origin, deduce the deformation conditions and the chemical evolution during deformation in the fault zone. The majority of chlorite and muscovite grains are inherited and affected by burial diagenesis in the red pelite damage zone, while in the green pelite core zone, they are mainly newly formed and are synkinematic to the fault activity. Chlorite preferentially formed in veins through direct precipitation from fluids, while muscovite formed through recrystallization of inherited minerals. Newly formed chlorite and muscovite in the green pelites have more Fe compare to those from the red pelites.

Based on the crystallinity and chemical composition of those synkinematic phyllosilicates, the deformation in the PPVT occurred under lower-anchizone/epizone conditions (sub-greenschist to greenschist facies) with an average temperature of 270°C and 285°C in the damage zone and core zone respectively. The strong foliation and enrichment of phyllosilicates in the core zone as well as the numerous generations of deformed veins reveal the strong impact of deformation and fluid circulation.

The change in the pelites color from red to green toward the fault contact is related to hematite dissolution and the enrichment of newly formed chlorite in the core zone. Modelling of fluid-sediment interactions shows that the redox condition is the main parameter that controls the chemical changes in the core fault zone. It suggests that highly reductive fluids may have dissolved hematite by bleaching the red pelites in the core fault zone and precipitated Fe-rich chlorite, thus inducing the green color in the core zone. Moreover, it demonstrates that those mineralogical changes in the core zone occurred at extreme reducing conditions. The results suggest that deformation and fluid circulation in the PPV thrust zone are connected processes and are related to different stages of fault activation.

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.clay.2017.05.008.

Acknowledgements

This work was supported by the INSU program (Tellus-syster). Access to SEM facilities of the MIMENTO center was made through the cooperative projects in the French Renatech network. The author would like to sincerely thank Vincent Trincal for collecting the samples, Didier Convert-Gaubier for the preparation of the thin sections, Nicolas Carry for organizing the illustrations and Virginie Moutarlier for her help during XRD analysis. Finally, many thanks for the reviewers (Fernando Nieto García and Sebastian Potel); your valuable comments and suggestions have led to a significant improvement on the quality of this paper.

References

- Apello, A.C.A.J., Postma, D., 2005. Geochemistry, Groundwater and Pollution. Balkema Publ. Amst, Neth.
- Banks, D.A., Da Vies, G.R., Yardley, B.W.D., McCaig, A.M., Grant, N.T., 1991. The chemistry of brines from an Alpine thrust system in the Central Pyrenees: an application of fluid inclusion analysis to the study of fluid behaviour in orogenesis. Geochim. Cosmochim. Acta 55, 1021–1030. http://dx.doi.org/10.1016/0016-7037(91)90160-7.
- Bartier, D., Buatier, M., Lopez, M., Potdevin, J.L., Chamley, H., Arostegui, J., 1998. Lithological control on the occurrence of chlorite in the diagenetic Wealden complex of the Bilbao anticlinorium (Basco-Cantabrian Basin, Northern Spain). Clay Miner. 33, 317–332.
- Berman, R.G., 1991. Thermobarometry using multi-equilibrium calculations; a new technique, with petrological applications. Can. Mineral. 29, 833–855.
- Blatt, H., Middleton, G.V., Murray, R., 1980. Origin of sedimentary rocks. In: Prentice Hall in Englewood Cliffs, second ed. Prentice-Hall, Englewood Cliffs, N.J..
- Bourdelle, F., Parra, T., Beyssac, O., Chopin, C., Vidal, O., 2013. Clay minerals as geothermometer: a comparative study based on high spatial resolution analyses of illite and chlorite in Gulf Coast sandstones (Texas, U.S.A.). Am. Mineral. 98, 914–926. http://dx.doi.org/10.2138/am.2013.4238.
- Brown, G.T., Brindley, G.W., 1980. X-ray diffraction procedures for clay mineral identification. In: Crystal Structures of Clay Minerals and Their X-ray Identification.
- Buatier, M.D., Chauvet, A., Kanitpanyacharoen, W., Wenk, H.R., Ritz, J.F., Jolivet, M., 2012. Origin and behavior of clay minerals in the Bogd fault gouge, Mongolia. J. Struct. Geol. 34, 77–90. http://dx.doi.org/10.1016/j.jsg.2011.10.006.
- Bui, H.B., Ngo, X.T., Khuong, T.H., Golonka, J., Nguyen, T.D., Song, Y., Itaya, T., Yagi, K., 2017. Episodes of brittle deformation within the Dien Bien Phu Fault zone, Vietnam: evidence from K-Ar age dating of authigenic illite. Tectonophysics 695, 53–63. http://dx.doi.org/10.1016/j.tecto.2016.12.006.
- Busigny, V., Dauphas, N., 2007. Tracing paleofluid circulations using iron isotopes: a study of hematite and goethite concretions from the Navajo Sandstone (Utah, USA). Earth Planet. Sci. Lett. 254, 272–287. http://dx.doi.org/10.1016/j.epsl.2006.11.038.
- Cavailhes, T., Sizun, J.-P., Labaume, P., Chauvet, A., Buatier, M., Soliva, R., Mezri, L., Charpentier, D., Leclère, H., Travé, A., Gout, C., 2013. Influence of fault rock foliation on fault zone permeability: the case of deeply buried arkosic sandstones (Grès d'Annot, southeastern France). AAPG Bull. 97, 1521–1543. http://dx.doi.org/10. 1306/03071312127.
- Choukroune, P., Pinet, B., Roure, F., Cazes, M., 1990. Major Hercynian thrusts along the ECORS Pyrenees and Biscay lines. Bull. Soc. Géol. Fr. VI 313–320. http://dx.doi.org/ 10.2113/gssgfbull.VI.2.313.
- Clauer, N., 2013. The K-Ar and ⁴⁰Ar/³⁹Ar methods revisited for dating fine-grained Kbearing clay minerals. Chem. Geol. 354, 163–185. http://dx.doi.org/10.1016/j. chemgeo.2013.05.030.
- Duvall, A.R., Clark, M.K., van der Pluijm, B.A., Li, C., 2011. Direct dating of Eocene reverse faulting in northeastern Tibet using Ar-dating of fault clays and lowtemperature thermochronometry. Earth Planet. Sci. Lett. 304, 520–526. http://dx. doi.org/10.1016/j.epsl.2011.02.028.
- Eggleton, R.A., Banfield, J.F., 1985. The alteration of granitic biotite to chlorite. Am. Mineral. 70, 902–910.
- Egholm, D.L., Clausen, O.R., Sandiford, M., Kristensen, M.B., Korstgård, J.A., 2008. The mechanics of clay smearing along faults. Geology 36, 787–790. http://dx.doi.org/10. 1130/G24975A.1.
- Faulkner, D.R., Jackson, C.A.L., Lunn, R.J., Schlische, R.W., Shipton, Z.K., Wibberley, C.A.J., Withjack, M.O., 2010. A review of recent developments concerning the structure, mechanics and fluid flow properties of fault zones. J. Struct. Geol. 32, 1557–1575. http://dx.doi.org/10.1016/j.jsg.2010.06.009.
- Fisher, Q.J., Knipe, R.J., 2001. The permeability of faults within siliciclastic petroleum reservoirs of the North Sea and Norwegian Continental Shelf. Mar. Pet. Geol. 18, 1063–1081. http://dx.doi.org/10.1016/S0264-8172(01)00042-3.
- Frey, M., 1987. Very Low-grade Metamorphism of Clastic Sedimentary Rocks. Blackie Glasg.
- Grant, N., 1989. Deformation and Fluid Processes in Thrust Sheets from the Central Pyrenees. University of Leeds, Lond.
- Grant, N., 1990. Episodic discrete and distributed deformation: consequences and controls in a thrust culmination from the central Pyrenees. J. Struct. Geol. 12835–12850. http://dx.doi.org/10.1016/0191-8141(90)90058-7.
- Grant, N., 1992. Post-emplacement extension within a thrust sheet from the central Pyrenees. J. Geol. Soc. Lond. 149775–149792. http://dx.doi.org/10.1144/gsjgs.149. 5.0775.
- Gratier, J.-P., Richard, J., Renard, F., Mittempergher, S., Doan, M.-L., Toro, G.D., Hadizadeh, J., Boullier, A.-M., 2011. Aseismic sliding of active faults by pressure solution creep: evidence from the San Andreas Fault Observatory at Depth. Geology 39, 1131–1134. http://dx.doi.org/10.1130/G32073.1.
- Gratier, J.-P., Thouvenot, F., Jenatton, L., Tourette, A., Doan, M.-L., Renard, F., 2013. Geological control of the partitioning between seismic and aseismic sliding behaviours in active faults: evidence from the Western Alps, France. Tectonophysics 600, 226–242. http://dx.doi.org/10.1016/j.tecto.2013.02.013.
- Hadizadeh, J., Mittempergher, S., Gratier, J.-P., Renard, F., Di Toro, G., Richard, J., Babaie, H.A., 2012. A microstructural study of fault rocks from the SAFOD: implications for the deformation mechanisms and strength of the creeping segment of the San Andreas Rault. J. Struct. Geol. 42, 246–260. http://dx.doi.org/10.1016/j.jsg. 2012.04.011.
- Haines, S.H., van der Pluijm, B.A., 2008. Clay quantification and Ar-Ar dating of synthetic and natural gouge: application to the Miocene Sierra Mazatán detachment

fault, Sonora, Mexico. J. Struct. Geol. 30, 525–538. http://dx.doi.org/10.1016/j.jsg. 2007.11.012.

- Inoue, A., Meunier, A., Patrier-Mas, P., Rigault, C., Beaufort, D., Vieillard, P., 2009. Application of chemical geothermometry to low-temperature trioctahedral chlorites. Clay Clay Miner. 57, 371–382. http://dx.doi.org/10.1346/CCMN.2009.0570309.
- Janssen, C., Wenk, H.-R., Wirth, R., Morales, L., Kemnitz, H., Sulem, J., Dresen, G., 2016. Microstructures and their implications for faulting processes –insights from DGLab core samples from the Gulf of Corinth. J. Struct. Geol. 86, 62–74. http://dx.doi.org/ 10.1016/j.jsg.2016.03.008.
- Jiang, S., 2012. Clay minerals from the perspective of oil and gas exploration. In: Valaskova, M. (Ed.), Clay Minerals in Nature - Their Characterization, Modification and Application. InTech. http://dx.doi.org/10.5772/47790.
- Jiang, W.-T., Peacor, D.R., 1994. Formation of corrensite, chlorite and chlorite-mica stacks by replacement of detrital biotite in low-grade pelitic rocks. J. Metamorph. Geol. 12, 867–884. http://dx.doi.org/10.1111/j.1525-1314.1994.tb00065.x.
- Kameda, J., Shimizu, M., Ujiie, K., Hirose, T., Ikari, M., Mori, J., Oohashi, K., Kimura, G., 2015. Pelagic smectite as an important factor in tsunamigenic slip along the Japan Trench. Geology 43, 155–158. http://dx.doi.org/10.1130/G35948.1.
- Kisch, H.J., 1991. Illite crystallinity: recommendations on sample preparation, X-ray diffraction settings, and interlaboratory samples. J. Metamorph. Geol. 9, 665–670. http://dx.doi.org/10.1111/j.1525-1314.1991.tb00556.x.
- Kisch, H.J., Arkai, P., Brime, C., 2004. On the calibration of the illite Kubler index (illite "crystallinity"). Schweiz. Mineral. Petrogr. Mitt. 84, 323–331.
- Kübler, B., 1964. Les argiles, indicateurs de métamorphisme. Rev Inst Fr. Pétrol XIX 1093–1112.
- Kübler, B., 1967. La cristallinité de l'illite et les zones tout a fait superieures du métamorphisme. In: Étages Tecton. Colloq. Neuchâtel 1966 Baconniere Neuchâtel, pp. 105–121.
- Kübler, B., 1968. Evaluation quantitative du métamorphisme par la cristallinité d l'illite. Bull. Cent. Rech. Pau – S.N.P.A. 2, 385–397.
- Kübler, B., Jaboyedoff, M., 2000. Illite crystallinity. C. R. Acad. Sci. Ser. IIA-Earth Planet. Sci. 331, 75–89.
- Lacroix, B., Vennemann, T., 2015. Empirical calibration of the oxygen isotope fractionation between quartz and Fe–Mg-chlorite. Geochim. Cosmochim. Acta 149, 21–31. http://dx.doi.org/10.1016/j.gca.2014.10.031.
- Lacroix, B., Buatier, M., Labaume, P., Travé, A., Dubois, M., Charpentier, D., Ventalon, S., Convert-Gaubier, D., 2011. Microtectonic and geochemical characterization of thrusting in a foreland basin: example of the South-Pyrenean orogenic wedge (Spain). J. Struct. Geol. 33, 1359–1377. http://dx.doi.org/10.1016/j.jsg.2011.06.006.
- Lanari, P., 2012. Micro-cartographie P-T² dans les roches métamorphiques. Université de Grenoble, Applications aux Alpes et à l'Himalaya.
- Lanari, P., Guillot, S., Schwartz, S., Vidal, O., Tricart, P., Riel, N., Beyssac, O., 2012. Diachronous evolution of the alpine continental subduction wedge: evidence from P–T estimates in the Briançonnais Zone houillère (France – Western Alps). J. Geodyn. 56–57, 39–54. http://dx.doi.org/10.1016/j.jog.2011.09.006.
- Lanari, P., Rolland, Y., Schwartz, S., Vidal, O., Guillot, S., Tricart, P., Dumont, T., 2014a. P–T–t estimation of deformation in low-grade quartz-feldspar-bearing rocks using thermodynamic modelling and ⁴⁰Ar/³⁹Ar dating techniques: example of the Plan-de-Phasy shear zone unit (Briançonnais Zone, Western Alps). Terra Nova 26, 130–138. http://dx.doi.org/10.1111/ter.12079.
- Lanari, P., Vidal, O., De Andrade, V., Dubacq, B., Lewin, E., Grosch, E.G., Schwartz, S., 2014b. XMapTools: a MATLAB©-based program for electron microprobe X-ray image processing and geothermobarometry. Comput. Geosci. 62, 227–240. http://dx.doi. org/10.1016/j.cageo.2013.08.010.
- Lanari, P., Wagner, T., Vidal, O., 2014c. A thermodynamic model for di-trioctahedral chlorite from experimental and natural data in the system MgO–FeO–Al₂O₃–SiO₂–H₂O: applications to P–T sections and geothermometry.
- Contrib. Mineral. Petrol. 167. http://dx.doi.org/10.1007/s00410-014-0968-8.
 Leclère, H., Buatier, M., Charpentier, D., Sizun, J.-P., Labaume, P., Cavailhes, T., 2012.
 Formation of phyllosilicates in a fault zone affecting deeply buried arkosic sandstones: their influence on petrophysic properties (Annot sandstones, French
- external Alps). Swiss J. Geosci. 105, 299–312. http://dx.doi.org/10.1007/s00015-012-0099-z. Li, G., Peacor, D.R., Merriman, R.J., Roberts, B., van der Pluijm, B.A., 1994. TEM and
- AEM constraints on the origin and significance of chlorite-mica stacks in slates: an example from Central Wales, U.K. J. Struct. Geol. 16, 1139–1157. http://dx.doi.org/ 10.1016/0191-8141(94)90058-2.
- Lockner, D.A., Morrow, C., Moore, D., Hickman, S., 2011. Low strength of deep San Andreas fault gouge from SAFOD core. Nature 472, 82–85. http://dx.doi.org/10. 1038/nature09927.
- Loveless, S., Bense, V., Turner, J., 2011. Fault architecture and deformation processes within poorly lithified rift sediments, Central Greece. J. Struct. Geol. 33, 1554–1568. http://dx.doi.org/10.1016/j.jsg.2011.09.008.
- Masini, E., Manatschal, G., Tugend, J., Mohn, G., Flament, J.-M., 2014. The tectonosedimentary evolution of a hyper-extended rift basin: the example of the Arzacq–Mauléon rift system (Western Pyrenees, SW France). Int. J. Earth Sci. 103, 1569–1596. http://dx.doi.org/10.1007/s00531-014-1023-8.
- McCaig, A.M., Tritlla, J., Banks, D.A., 2000. Fluid flow patterns during Pyrenean thrusting. J. Geochem. Explor. 69, 539–543.
- Metcalf, J.R., Fitzgerald, P.G., Baldwin, S.L., Muñoz, J.-A., 2009. Thermochronology of a convergent orogen: constraints on the timing of thrust faulting and subsequent exhumation of the Maladeta Pluton in the Central Pyrenean Axial Zone. Earth Planet. Sci. Lett. 287, 488–503. http://dx.doi.org/10.1016/j.epsl.2009.08.036.
- Meunier, A., Velde, B., 1989. Solid solutions in I/S mixed-layer minerals and illite. Am. Mineral. 74, 1106–1112.

Milodowski, A.E., Zalasiewicz, J.A., 1991. The origin and sedimentary, diagenetic and

metamorphic evolution of chlorite-mica stacks in Llandovery sediments of central Wales, U.K. Geol. Mag. 128, 263–278. http://dx.doi.org/10.1017/ S0016756800022111.

- Moore, D.M., Reynolds, R.C., 1997. X-ray Diffraction and the Identification and Analysis of Clay Minerals.
- Muñoz, J.A., 1992. Evolution of a continental collision belt: ECORS-Pyrenees crustal balanced cross-section. Thrust Tecton. 235–246.
- Niwa, M., Tsukada, K., Tanaka, S., 2005. Kinematic analysis of sinistral cataclastic shear zones along the northern margin of the Mino Belt, central Japan. J. Asian Earth Sci. 24, 787–800. http://dx.doi.org/10.1016/j.jseaes.2004.05.002.
- Parkhurst, D.L., 1995. User's Guide to PHREEQC A Computer Program for Speciation, Reaction-path, Advective-transport, and Inverse Geochemical Calculations. (No. 95–4227.). (U.S. Geological Survey Water- Resources Investigations Report).
- Parkhurst, D.L., Appelo, C.A.J., 1999. User's Guide to PHREEQC (Version 2) A Computer Program for Speciation, Reaction-path, Advective-transport, and Inverse Geochemical Calculations. (No. 99–4259). (U.S. Geological Survey Water-Resources Investigations Report).
- Parry, W.T., Downey, L.M., 1982. Geochemistry of hydrothermal chlorite replacing igneous biotite. Clay Clay Miner. 30, 81–90.
- Pei, Y., Paton, D.A., Knipe, R.J., Wu, K., 2015. A review of fault sealing behaviour and its evaluation in siliciclastic rocks. Earth-Sci. Rev. 150, 121–138. http://dx.doi.org/10. 1016/j.earscirev.2015.07.011.
- Rahl, J.M., Haines, S.H., van der Pluijm, B.A., 2011. Links between orogenic wedge deformation and erosional exhumation: evidence from illite age analysis of fault rock and detrital thermochronology of syn-tectonic conglomerates in the Spanish Pyrenees. Earth Planet. Sci. Lett. 307, 180–190. http://dx.doi.org/10.1016/j.epsl. 2011.04.036.
- Randive, K.R., Korakoppa, M.M., Muley, S.V., Varade, A.M., Khandare, H.W., Lanjewar, S.G., Tiwari, R.R., Aradhi, K.K., 2015. Paragenesis of Cr-rich muscovite and chlorite in green-mica quartzites of Saigaon–Palasgaon area, Western Bastar Craton, India. J. Earth Syst. Sci. 124, 213–225.
- Ren, M., 2012. Distribution and origin of clay minerals during hydrothermal alteration of ore deposits. In: Valaskova, M. (Ed.), Clay Minerals in Nature - their Characterization, Modification and Application. InTech. http://dx.doi.org/10.5772/48312.
- Richard, J., Gratier, J.-P., Doan, M.-L., Boullier, A.-M., Renard, F., 2014. Rock and mineral transformations in a fault zone leading to permanent creep: Interactions between brittle and viscous mechanisms in the San Andreas Fault: fault rock changes leads to steady creep. J. Geophys. Res. Solid Earth 119, 8132–8153. http://dx.doi. org/10.1002/2014JB011489.
- Roest, W.R., Srivastava, S.P., 1991. Kinematics of the plate boundaries between Eurasia, Iberia, and Africa in the North Atlantic from the Late Cretaceous to the present. Geology 19, 613–616. http://dx.doi.org/10.1130/0091-7613(1991) 019<0613:KOTPRB>2.3.CO:2.
- Rolland, Y., Cox, S.F., Corsini, M., 2009. Constraining deformation stages in brittle-ductile shear zones from combined field mapping and 40Ar/39Ar dating: the structural evolution of the Grimsel Pass area (Aar Massif, Swiss Alps). J. Struct. Geol. 31, 1377–1394. http://dx.doi.org/10.1016/j.jsg.2009.08.003.
- 31, 1377–1394. http://dx.doi.org/10.1016/j.jsg.2009.08.003.
 Sanchez, G., Rolland, Y., Schneider, J., Corsini, M., Oliot, E., Goncalves, P., Verati, C., Lardeaux, J.-M., Marquer, D., 2011. Dating low-temperature deformation by 40Ar/ 39Ar on white mica, insights from the Argentera-Mercantour Massif (SW Alps). Lithos 125, 521–536. http://dx.doi.org/10.1016/j.lithos.2011.03.009.
- Solum, J.G., van der Pluijm, B.A., 2009. Quantification of fabrics in clay gouge from the Carboneras fault, Spain and implications for fault behavior. Tectonophysics 475, 554–562. http://dx.doi.org/10.1016/j.tecto.2009.07.006.
- Solum, J.G., van der Pluijm, B.A., Peacor, D.R., 2005. Neocrystallization, fabrics and age of clay minerals from an exposure of the Moab Fault, Utah. J. Struct. Geol. 27, 1563–1576. http://dx.doi.org/10.1016/j.jsg.2005.05.002.

Teixell, A., 1996. The Ansó transect of the southern Pyrenees: basement and cover thrust geometries. J. Geol. Soc. 153, 301–310.

- Teixell, A., Durney, D.W., Arboleya, M.L., 2000. Stress and fluid control on décollement within competent limestone. J. Struct. Geol. 22 (3), 349–371.
- Teixell, A., Labaume, P., Lagabrielle, Y., 2016. The crustal evolution of the west-central Pyrenees revisited: inferences from a new kinematic scenario. C. R. Geosci. 348, 257–267. From rifting to mountain building: the Pyrenean Belt. http://dx.doi.org/ 10.1016/j.crtc.2015.10.010.
- Torgersen, E., Viola, G., Zwingmann, H., Harris, C., 2015. Structural and temporal evolution of a reactivated brittle–ductile fault – part II: timing of fault initiation and reactivation by K–Ar dating of synkinematic illite/muscovite. Earth Planet. Sci. Lett. 410, 212–224. http://dx.doi.org/10.1016/j.epsl.2014.09.051.
- Trincal, V., 2014. Interactions fluide-roche, conditions physico-chimiques et transferts de matiere dans des zones de failles en milieux sedimentaires exemple de failles chevauchantes pyreneennes. Université de Bourgogne Franche-Comté.
- Trincal, V., Lanari, P., Buatier, M., Lacroix, B., Charpentier, D., Labaume, P., Muñoz, M., 2015. Temperature micro-mapping in oscillatory-zoned chlorite: application to study of a green-schist facies fault zone in the Pyrenean Axial Zone (Spain). Am. Mineral. 100, 2468–2483. http://dx.doi.org/10.2138/am-2015-5217.
- Trincal, V., Buatier, M., Charpentier, D., Lacroix, B., Lanari, P., Labaume, P., 2016. Fluidrock interactions related to metamorphic reducing fluid flow in meta-sediments: example of the Pic-de-Port-Vieux thrust (Pyrenees, Spain). Submitted to Contrib. Mineral. Petrol.
- Veblen, D.R., Ferry, J.M., 1983. A TEM study of the biotite-chlorite reaction and comparison with petrologic observations. Am. Mineral. 68, 1160–1168.
- Vidal, O., Parra, T., Trotet, F., 2001. A thermodynamic model for Fe-Mg aluminous chlorite using data from phase equilibrium experiments and natural pelitic assemblages in the 100 to 600 C, 1 to 25 kb range. Am. J. Sci. 301, 557–592.
- Vidal, O., Parra, T., Vieillard, P., 2005. Thermodynamic properties of the Tschermak solid

solution in Fe-chlorite: application to natural examples and possible role of oxidation. Am. Mineral. 90, 347–358. http://dx.doi.org/10.2138/am.2005.1554.

- Vidal, O., De Andrade, V., Lewin, E., Munoz, M., Parra, T., Pascarelli, S., 2006. P–Tdeformation-Fe3 +/Fe2 + mapping at the thin section scale and comparison with XANES mapping: application to a garnet-bearing metapelite from the Sambagawa metamorphic belt (Japan). J. Metamorph. Geol. 24, 669–683. http://dx.doi.org/10. 1111/j.1525-1314.2006.00661.x.
- Vidal, O., Lanari, P., Munoz, M., Bourdelle, F., De Andrade, V., 2016. Deciphering temperature, pressure and oxygen-activity conditions of chlorite formation. Clay Miner. 51, 615–633. http://dx.doi.org/10.1180/claymin.2016.051.4.06.
- Warr, L.N., Cox, S., 2001. Clay mineral transformations and weakening mechanisms along the Alpine Fault, New Zealand. Geol. Soc. Lond. Spec. Publ. 186, 85–101. http://dx. doi.org/10.1144/GSL.SP.2001.186.01.06.
- Warr, L.N., Cox, S.C., 2016. Correlating illite (Kübler) and chlorite (Árkai) "crystallinity" indices with metamorphic mineral zones of the South Island, New Zealand. Appl. Clay Sci. 164–174. (Clay mineral indices in palaeo-geothermal and hydrothermal studies 134, Part 3). http://dx.doi.org/10.1016/j.clay.2016.06.024.
- Warr, L.N., Ferreiro M\u00e4hlmann, R., 2015. Recommendations for K\u00fcbler index standardization. Clay Miner. 50, 283–286. http://dx.doi.org/10.1180/claymin.2015. 050 3 02

Warr, L.N., Rice, A.H.N., 1994. Interlaboratory standardization and calibration of day

mineral crystallinity and crystallite size data. J. Metamorph. Geol. 12, 141–152. http://dx.doi.org/10.1111/j.1525-1314.1994.tb00010.x.

- Wenk, H.-R., Kanitpanyacharoen, W., Voltolini, M., 2010. Preferred orientation of phyllosilicates: comparison of fault gouge, shale and schist. J. Struct. Geol. 32, 478–489. http://dx.doi.org/10.1016/j.jsg.2010.02.003.
- Wibberley, C.A.J., McCaig, A.M., 2000. Quantifying orthoclase and albite muscovitisation sequences in fault zones. Chem. Geol. 165, 181–196. http://dx.doi.org/10.1016/ S0009-2541(99)00170-9.
- Wibberley, C.A.J., Vielding, G., Toro, G.D., 2008. Recent advances in the understanding of fault zone internal structure: a review. Geol. Soc. Lond. Spec. Publ. 299, 5–33. http://dx.doi.org/10.1144/SP299.2.
- Wigley, M., Kampman, N., Dubacq, B., Bickle, M., 2012. Fluid-mineral reactions and trace metal mobilization in an exhumed natural CO₂ reservoir, Green River, Utah. Geology 40, 555–558. http://dx.doi.org/10.1130/G32946.1.
- Wigley, M., Dubacq, B., Kampman, N., Bickle, M., 2013. Controls of sluggish, CO₂promoted, hematite and K-feldspar dissolution kinetics in sandstones. Earth Planet. Sci. Lett. 362, 76–87. http://dx.doi.org/10.1016/j.epsl.2012.11.045.
- Zwart, H.J., 1986. The variscan geology of the Pyrenees. Tectonophysics 129, 9–27. The Geological Evolution of the Pyrenees. http://dx.doi.org/10.1016/0040-1951(86) 90243-X.