Microstructural vs compositional preservation and pseudomorphic replacement of muscovite in deformed metapelites from the Longmen Shan (Sichuan, China)

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ABSTRACT

Pressure-temperature-deformation (P-T-ε) paths for metamorphic rocks that experienced a complex deformation history commonly rely on the link between successive metamorphic assemblages and the different microstructures preserved at the sample scale. However, with changing P-T conditions, metamorphic minerals in a specific microstructure can chemically re-equilibrate. The direct link between deformation phases and mineral compositions for thermobarometry purposes can therefore be distorted. This study focuses on a series of garnet-biotite metapelites from the Longmen Shan (Sichuan, China) that preserve muscovite of different chemistry in distinct microstructures. To quantify the degree of re-equilibration of muscovite, a microstructural study was coupled with high-resolution chemical mapping. The chemical evolution of muscovite was modeled along a P-T loop previously constrained with phase equilibria calculations, semi-empirical and empirical thermobarometry. Results show that metapelites experienced a three-stage metamorphic history: (1) heating and burial up to 11 ± 2 kbar, 530 ± 20 °C, (2) minor decompression and heating up to 6.5 ± 1 kbar, 575 ± 10 °C and (3) decompression and cooling down to 4 ± 1 kbar, 380–450 °C. Muscovite partially re-equilibrated by pseudomorphic replacement during the three metamorphic stages, although it is mainly observed in prograde microstructures preceding the pressure peak. The main factors controlling the re-equilibration are the intensity of the deformation and the fluid availability during metamorphism. The P-T conditions of metamorphic assemblages thus reflect pulses of fluids release that enhanced mineral resorption and local replacement. Such micro-chemical behavior is probably relatively common in metapelites and questions the reliability of the P-T predictions based on relic phase chemistry, apparently preserved in microstructures that might have been affected by later re-equilibration.

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1. Introduction

Rocks that have experienced a multi-phased deformation history frequently exhibit complex meso and microstructures. In metapelites it is common to observe microstructures related to three to five deformation phases (i.e. Bell and Hickey, 1999; Cosgrove, 1976; Goswami et al., 2009; Huang et al., 2016; Worley et al., 1997) as it is the case in the internal domains of the Longmen Shan (Sichuan, China), at the eastern border of Tibetan plateau (Fig. 1 and Fig. 2a). In some favorable case a different metamorphic assemblage can be preserved in each microstructure. Pressure (P) and temperature (T) changes can be then quantified (e.g. Lanari et al., 2013, 2014b; Scheffer et al., 2016), and linked to deformation (ε) to derive P–T–ε paths (Parra et al., 2002; Vidal et al., 2006). This provides constraints on the large-scale geodynamic processes that drive metamorphism (Putnis and Timm, 2010). However, in the case of metapelites that have experienced a low to medium grade metamorphism (up to the amphibolite facies conditions) the prograde record in the matrix is often overprinted near the temperature peak. Consequently the majority of the studies focused on the P–T conditions of the peak assemblage (Boyle and Westhead, 1992; Huang et al., 2016) characterized by index minerals such as garnet, biotite, staurolite etc. Less attention has been paid to the evolution of the phyllolcite-rich matrix and to its chemistry, while it does record the long-lasting deformation history.

Recently, high-resolution quantitative compositional mapping has provided a picture of the complexity of the compositional zoning observed in the matrix minerals such as white mica (Scheffer et al., 2016). A similar complexity is observed in metapelites from the Longmen Shan (Sichuan, China) (Fig. 2b). Here metamorphism reaches amphibolite facies conditions (6–10 kbar, 550–600 °C, Dirks et al., 1994; Worley and Wilson, 1996) and evidences of a multi-phased deformation history...
Fig. 1. Structural and geological map of the studied area. (a) Inset represents the simplified structural map of the Tibetan plateau at Indian-Asian scale. Black frame indicates the location of the simplified structural map of the eastern border of the plateau modified from de Sigoyer et al. (2014). The red square delimits the studied area. WSZ: Wenchuan Shear Zone, BF: Beichuan fault, GF: Guanxian fault, Xb: Xuelongbao. (b) Geological map of the Tonghua area. Samples collected for this study are shown with white dots. The black line indicates the location of the cross section profile. (c) NW-SE directed geological cross section of the studied area, showing the intense deformation affecting the sedimentary series. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. (a) Optical image showing the different microstructures recorded in the matrix of a garnet-biotite metapelite from the Longmen Shan (see text). (b) X-ray map of the Si^4+ (pfu) content of white mica observed in the S1 and S2 cleavages of panel a. Different chemical domains are observed in the different microstructures.
are well preserved both in field (Harrowfield and Wilson, 2005) and microstructures (Worley and Wilson, 1996). Compositional maps reveal a significant zoning in composition within the matrix K-white mica (Fig. 2b).

Such observations call into question the validity of two major assumptions on which the construction of P–T paths often relies: (1) the continuous re-equilibration of the matrix minerals during metamorphism and (2) the link between the microstructural and the metamorphic record. It is therefore critical to understand which composition of white mica is stable for specific P–T conditions. Incomplete re-equilibration as suggested by Fig. 2b has important consequences on the interpretation of 40Ar/39Ar ages on mica (Villa, 2010; Lanari et al., 2014c) and the 87Rb/86Sr ages of mica and garnet, these last potentially affected by incomplete Rb and Sr re-equilibration among matrix minerals (Sousa et al., 2013). Although some petrological and geochronological studies have dealt with the problem of partial equilibration of the mineral assemblage (Dempster, 1992; Konrad-Schmolke et al., 2011) and the consequences on the age record (Mulch and Cosca, 2004; Mulch et al., 2002), this issue is commonly overseen.

In this study we investigated the relative timing and mechanisms K-white mica (Kwm) re-equilibration in a series of metapelites from the Longmen Shan (Sichuan, China) by coupling a detailed microstructural study with high-resolution quantitative compositional mapping and phase equilibrium modeling. P–T conditions of the successive metamorphic assemblages were reconstructed using empirical and semi-empirical thermobarometry, as well as multi-equilibrium and forward equilibrium models. Raman spectroscopy on carbonaceous material (RSCM) was used to retrieve the maximum temperature experienced by the organic-rich schists and thus to characterize the metamorphic peak. The combination of all methods provides a good framework to study the low to medium grade metamorphic area of the Longmen Shan and its regional tectonic implications.

2. A two end-member scenario for matrix re-equilibration in metapelites and modelling strategy

A two end-member scenario of matrix re-equilibration is presented in Fig. 3a and b to illustrate the consequences of replacement or preservation of Kwm in a typical garnet-biotite metapelite affected by several phases of metamorphism and deformation (Fig. 3c). An early S1 subvertical cleavage composed of muscovite (msA, red in Fig. 3a), chlorite and quartz grains is preserved in the matrix. S1 is folded and a new S2 crenulation cleavage develops parallel to microfold axial planes. The S2 cleavage is composed of elongated grains of muscovite (msB, yellow

![Fig. 3. Schematic sketch of the two end-member scenarios of matrix re-equilibration in a garnet-biotite metapelite affected by several deformation phases. (a) Scenario of total preservation: muscovite in each microstructure (S1, S2, P-shadows) preserves its original chemical composition. (b) scenario of total re-equilibration (with H2O in excess): muscovite completely re-equilibrated by dissolution-precipitation or pseudomorphic replacement during D3 and shows the same composition (msC) regardless its microstructural position. (c) Theoretical P–T path associated to the development of the microstructures imaged in panels a and b. T-peak: thermal peak. GS: greenschist facies conditions. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)]
in Fig. 3a). Garnet and biotite porphyroblasts are post S2 as they record both the S1 and S2 cleavages in their inclusion trails. The late muscovite (msC, light blue in Fig. 3a) grew in porphyroblasts pressure shadows (P-shadows), in equilibrium with chlorite and quartz. The two idealized end member scenarios are considered assuming either a complete preservation (Fig. 3a) or a complete compositional re-equilibration (Fig. 3b) of the muscovite. This example focuses on muscovite, as it is likely to be stable along the entire P–T loop with a continuous evolution of its composition, especially for Si4+ (in atoms per formula units, pfu) and X_{Mg} (Mg^{2+}/[Mg^{2+} + Fe^{2+}]). In the first scenario the matrix does not re-equilibrate resulting in the preservation of the original composition of muscovite related to each microstructure. The compositions of msA, msB and msC can be therefore used for thermobarometry (as in the studies of Parra et al., 2002; Vidal et al., 2006) to reconstruct the P–T–ε path. In the second scenario local equilibria are not preserved and a complete re-equilibration of the muscovite grains occurred during the latest metamorphic stage with the preservation of microstructures (Fig. 3b). In this case, regardless their microstructural position, all muscovite grains show the same chemistry of msC. Therefore they cannot be used to estimate any equilibrium conditions of the previous stages. The re-equilibration is achieved by different mechanisms such as pseudomorphic replacement or dissolution-precipitation (Putnis, 2009; Scheffer et al., 2016). The degree of re-equilibration depends on the burial and heating rates, deformation intensity and the amount and type of fluid available along the P–T path. It has been shown, indeed, that mineral reactions releasing a large amount of H$_2$O have a very limited thermal overstepping (high reaction affinity, Pattison and Tinkham, 2009).

Natural cases both end-member scenarios, together with intermediate ones are expected to occur. In some extreme cases, as we shall demonstrate, complete re-equilibration can be achieved for a given section of the P–T path, whereas only partial re-equilibration happens for a latest section, generating a mismatch between the deformation record and the P–T conditions.

The re-equilibration of the phyllosilicate-rich matrix in metapelite can significantly affect both thermobarometry and geochronology (Villa, 2010; Sousa et al., 2013), but in most of the studies, the matrix is considered to continuously re-equilibrate during the prograde path. However the compositional zoning observed in chlorite and K-white mica (Vidal et al., 2006; Scheffer et al., 2016 and Fig. 2b) witness of a more complex compositional record. To link the deformation stages to specific P–T conditions, it is necessary to use a modelling strategy that relates the observed mineral composition to pressure and temperature conditions. Combined with quantitative compositional mapping, this technique allows to understand the relative timing of re-equilibration of the phyllosilicate matrix. Thermobarometric methods based on equilibrium thermodynamics can be used to retrieve P–T conditions that are frozen-in by the rock as local equilibria (Berman, 1991; Powell and Holland, 2008). It has been early recognized that compositional zoning and mineral relics may record changes in P–T conditions (Atherton, 1968; Evans, 2004; Kohn, 2014; Marmo et al., 2002; Hsuwe, 1997). In this case, local disequilibria are established and maintained at the thin section scale. Thermobarometric methods based on equilibrium thermodynamics can then be used to retrieve P–T conditions of these local equilibria. The investigations must be restricted to local domains and require fractional crystallization models to approximate the changes in the reactive bulk composition (Lanari and Engl, 2017). Forward equilibration models calculated along a given P–T path have therefore been developed to compare the predicted and observed composition of the stable phases (Gaidies et al., 2008; Konrad-Schmolke et al., 2008; Robyr et al., 2014). However such a method requires a precise knowledge of the P–T path. In the following we therefore use a multi-method thermobarometric approach to retrieve the P–T path followed by metapelites from the Longmen Shan in order to investigate the timing and mechanisms of the muscovite re-equilibration.

### 3. Geologic setting

The Longmen Shan thrust belt (Sichuan, China) is situated at the eastern border of the Tibetan plateau at the boundary between the South China craton to the East and the Songpan-Ganze terrane to the West (Fig. 1a). Thermochronological data show that the belt underwent a phased of rapid exhumation since 30 Ma related to the India-Asia collision (Godard et al., 2009; Kirby et al., 2002; Wang et al., 2012). Metamorphic studies carried out in the Danba (Huang et al., 2003a, 2003b) and Xuelongbao areas (Dirks et al., 1994; Harrowfield and Wilson, 2005; Worley and Wilson, 1996) however revealed the occurrence of an early Mesozoic compressional event, associated to the closure of Paleotethys and the subsequent collision among North China, South China and Qiangtang blocks (de Sigoyer et al., 2014; Roger et al., 2010). This event, usually referred as the Indosinian orogeny, lasted from ca. 237 to ca. 185 Ma (Harrowfield and Wilson, 2005; Yan et al., 2011) and was characterized by multiple phases of deformation (Dirks et al., 1994; Worley and Wilson, 1996) during which the main metamorphic and structural characters of the Longmen Shan were acquired (Chen et al., 1995; Dirks et al., 1994; Harrowfield and Wilson, 2005; Worley and Wilson, 1996). In particular the internal meta-sedimentary units of the Songpan-Ganze terrain underwent an amphibolite facies metamorphism now observed in a 20–25 km wide band parallel to the belt, located in the hanging wall the Wenchuan shear zone (Anne et al., 1997; Dirks et al., 1994; Worley and Wilson, 1996; this study, Fig. 1). In the Xuelongbao area (Fig. 1a) P–T conditions of the metamorphic peak were estimated at 5–7 kbar, 550–600 °C by Dirks et al. (1994) and at approximately at 6 kbar, 600 °C by Worley and Wilson (1996). Close to the Wenchuan Shear Zone amphibolite facies rocks seem to be completely retrogressed under greenschist facies conditions (Worley and Wilson, 1996).

The studied area is located in the internal domains of the central Longmen Shan (West of the WSZ), North and North-east of the Tonghua crystalline massif (Fig. 1a and b). Here the Paleozoic sedimentary series of the Songpan-Ganze terrane consists of Cambrian meta-greywackes and mudstones over lain by massif Ordovician limestones and marbles and covered by a thick series of Silurian metapelites and organic-rich schists. Sedimentary units are folded in thin NE–SW directed anticlines and synclines (Fig. 1b and c) and exhibits a pervasive NW dipping cleavage striking N40°N. The Tonghua crystalline massif and its Neoproterozoic sedimentary cover are separated from the Paleozoic units to the North by a thrust oriented N40° and to the Silurian sediments to the South by the Wenchuan Shear Zone (Fig. 1b and c).

### 4. Sample description and petrography

#### 4.1. Sampling and sample description

A total of 14 samples were collected for this study along a NW-SE oriented cross section in the Cambrian and Silurian meta-sedimentary units (see Fig. 1 for sample location and Table 1 and Table 5 for sample geographic coordinates). Nine samples are organic-rich schists showing a high content of carbonaceous material, phyllosilicates in variable quantities and quartz grains. The carbonaceous material consists of flakes of more than 100 μm. Samples to13-4 and to13-7 are garnet-biotite-mica schists from the Silurian sedimentary unit with assemblages of Qz + wm + Bt + Grt + Chl + Ilm ± Pl ± Ab with allanite and apatite as accessory phases (mineral abbreviations after Whitney and Evans, 2010, apart from K-white mica = Kwm). At the outcrop lm09-221 the Cambrian sediments are composed of metagreywackes alternating with metapelitic levels. In metagreywackes a garnet-biotite bearing assemblage is preserved (Robert, 2011). In the metapelitic level, where sample ln09-221a has been collected, on the contrary, the amphibolitic assemblage is completely retrogressed under greenschist facies conditions. Garnet is observed as relics or is completely chloritized, while the main paragenesis is composed of Kwm + Chl +
Qz + Pl, with monazite as accessory phase. At the outcrop lm09-223 early microstructures are cross-cut by late metamorphic veins of quartz and calcite (in minor quantity). At thin section scale a single metamorphic assemblage of Kwm + Chl + Qz + Pl is observed.

4.2. Petrography and microstructures

In all collected samples three types of microstructures were observed and considered as the result of the superposition of three phases of ductile deformation (D1, D2, D3), as proposed by Worley and Wilson (1996). Since each microstructure is associated to a different metamorphic assemblage a first order relative chronology of the deformation history is derived from textures, inclusions, overlapping and crosscutting criteria. Metapelite to13-4 is the sample that best records the entire deformation history. For that it is used as a reference to describe the relative chronology of microstructures, which is not affected by the partial re-equilibration process discussed in this study.

(i) An early S1 cleavage, related to the first deformation phase D1, is observed and it is systematically overprinted by all the successive phases of deformation (Fig. 4a, b, d). The S1 cleavage is characterized by elongated chlorite and K-white mica intergrowths and quartz microlithons with grain size of 50–100 μm.

(ii) The second deformation phase D2 exhibits symmetric F2 microfolds deforming the S1 cleavage. A new cleavage S2 parallel to F2 fold axial planes developed to such an extent that S1 and S2 are approximately of equivalent importance in the rock (Fig. 4a). The S2 cleavage is underlined by 100–200 μm elongated grains of K-white mica, which develop at high angle (ca. 90°) relative to the S1 cleavage orientation (Fig. 4a and b). These characteristics are used to relate this sample to the third stage of the cleavage development succession defined by Bell and Rubenach (1983). Stretched along the S2 cleavage, elongated grains of 50–100 μm of biotite are observed. However the most evident expression of biotite in all studied samples is in euhedral porphyroblasts of 500 μm–2 mm large (representing ~10 vol% in sample to13-4), often showing surfaces crenulated according two different axes: F2 (related to D2) and F3 folds (related to D3 deformation phase) (Fig. 4b, c, e, f). Euhedral garnet porphyroblasts (~5% vol) of 800 μm–1 mm are also observed (Fig. 4d) sharing sharp rims with biotite porphyroblasts and are associated to ilmenite and allanite porphyroblasts >500 μm. Both biotite and garnet overprint the previous microstructures as shown by inclusion trails of Qz (in garnet) and Qz + Kwm (in biotite) oriented parallel to the S1 and S2 cleavage (Fig. 4d, f).

(iii) The third major deformation phase D3 is associated to the folding of the S2 cleavage and the shearing of garnet and biotite porphyroblasts, which are slightly turned. This phase leads to the development of P-shadows filled by elongated chlorite and Kwm grains of 200 μm (Fig. 4c, e, f). Such aggregates share irregular rims with garnet and biotite suggesting minor porphyroblast resorption. The associated sigmoid structures indicate a top-to-south-east sense of shear. Two families of elongated subehedral chlorite and Kwm porphyroblasts (up to 500 μm long) overprint all previous microstructures (Fig. 4c, g, h) and are disposed at a relative angle of ca. 60° (D3b phase).

Sample to13-7 shares similar features with sample to13-4 except that the early D2 is more pronounced. The S2 cleavage clearly predominates indeed on the S1, which is only recognizable in some relic fold hinges visible in backscatter (BSE) images (Fig. 4b). These characteristics are typical of the 4th stage of Bell and Rubenach (1983) cleavage evolution succession and suggest that to13-7 is more deformed than sample to13-4.

In samples lm09-221a and lm09-223 the presence of a unique greenschist stable assemblage as well as of phanomatous garnet porphyroblasts extensively chloritized (lm09-221a) suggest a more pervasive retrogression related to the proximity with the fault. Chlorite and Kwm are stretched in the very fine early cleavage which is crosscut by domains of larger grains of chlorite and Kwm 200–300 μm in size (lm09-223) or by Kwm porphyroblasts (lm09-221a) (Fig. 4g, h). The D3 deformation phase is particularly well expressed: relics of the S1 cleavage cannot be distinguished from the S2 cleavage anymore (Fig. 4c), biotite porphyroblasts are intensively crenulated and the S2 cleavage is folded to form kink structures (lm09-221a). These features indicate that these samples reached the 5th stage of Bell and Rubenach (1983). They are consequently more matures than the previous ones.

4.3. Petrographic interpretations

In the studied metapelites, the greenschist facies assemblage of Qz + wm + Chl + Ab is related to the deformation phases D1 and D2. These deformation phases are therefore linked to the prograde history (Fig. 3c), as classically proposed for prograde barrovian metamorphism (Arenas and Catalan, 2003; Weller et al., 2013; Worley et al., 1997). Biotite and garnet porphyroblasts overprint the S1 and the S2 cleavages but are at the same time slightly crenulated according to F2 microfolds (related to D2 deformation phase) (Fig. 4c, e). They are consequently classified as syn to post-D2 but they grew once the S2 cleavage developed (Fig. 3c). The textural equilibrium features such as the sharp boundaries observed among garnet and biotite in sample to13-4 suggest that they grew in chemical equilibrium. Biotite and garnet reflect the metamorphic peak under amphibolite facies conditions (Fig. 3c).

The late D3 deformation phase is associated to the development of an assemblage of Qz + wm + Chl that is related to the retrogression under greenschist facies conditions (Arenas and Catalan, 2003; Dirks et al., 1994) (Fig. 2a). The orientation of the late wm porphyroblasts is interpreted to reproduce the geometry of the microfolds associated to a late deformation event (D3b phase) (Fig. 4h). The large Kwm and chlorite grains in samples lm09-221 and lm09-223 are interpreted to be late since they overprint the fine composite S1-S2 cleavage.

In summary all studied samples record similar microstructures related to D1, D2 and D3. While some of them preserve index minerals associated to the early deformation phases (D1–D2), other better document the ones related to the retrogression (D3 and D3b).

5. Compositional mapping and mineral chemistry

5.1. Analytical method

High-resolution chemical analyses were performed with an electron probe microanalyzer (EPMA) JSM-6380 at the Institut des Sciences de la Terre (ISTerre) of the University of Grenoble Alpes.
Point analyses were acquired using 15 keV accelerating voltage and 12 nA beam current with a beam size of 2 μm for all studied samples. In order to investigate the link between compositional variability of metamorphic minerals and their microstructural position, compositional X-ray maps were also acquired for samples to13-4, to13-7 and lm09-223, using 15 keV accelerating voltage, 100 nA beam current and dwell times of 200 ms.

**Fig. 4.** Representative microstructures and associated metamorphic assemblages observed in the studied metapelites. On the right side a schematic interpretation of the chronology of microstructures is proposed. Abbreviations are from Whitney and Evans (2010), except wm = white mica. (a) Image under crossed polarized light of metapelite to13-4. A folded S1 cleavage is still recognizable among S2 cleavage domains. (b) Backscatter electron (BSE) image of the metapelite to13-7 showing the folded S1 chl-Kwm rich cleavage and the S2 Kwm-bearing cleavage overprinted by a biotite porphyroblast. (c) Porphyroblast of biotite cross cutting earlier microstructure in metapelite lm09-221. Biotite shows crenulated surfaces and Kwm porphyroblasts (zoom) overprint the early S1-S2 cleavage. (d) BSE image of a garnet porphyroblast in metapelite to13-7 showing quartz inclusions aligned along the S1 and S2 cleavage. Garnet is partly chloritized. (e) Porphyroblasts of biotite and ilmenite in sample to13-7. Chl + Kwm aggregates develop in porphyroblast P-shadows. (f) BSE image of chl + Kwm aggregates in the P-shadows of a biotite grain (sample to13-7). (g) Optical image of chl + Kwm large crystal domains superimposed to the S1-S2 chl-Kwm-bearing early cleavage (sample lm09-223). (h) BSE image of Kwm porphyroblasts overprinting all microstructures in sample to13-4. Chl is also observed associated to D3b Kwm in this same sample.
time of 200 ms. X-ray maps were then transformed into oxide weight percentage using the internal standard procedure implemented in the software XMAFTools 2.3.1 (Lanari et al., 2014a). XMAFTools was also used for classification purposes, to calculate mineral structural formulae and to display maps of the relative abundance of cations (in pfu) and end-members proportions.

5.2. Compositional variability of metamorphic minerals

Representative chemical analyses of index metamorphic minerals are listed in Table 2 for all analyzed samples. Both EPMA compositional maps and point analyses reveal the existence of three chemical groups of Kwm preserved in samples to13-4 and to13-7. They have typical muscovite composition (Xmp = 0.62–0.75) and show variations in Xmg, Na+ (pfu) and Si4+ (pfu) contents. The first group of muscovite (msA) has a Si4+ content of 3.2–3.25 (pfu), a Xmg of 0.54–0.61 (Fig. 6a,b) and a Na+ content of 0.08–0.13 (pfu). The second group of muscovite (msB) has a lower Xmg (0.43–0.6) and a lower Si4+ content between 3 and 3.15 (sample to13-7) and 3.13–3.22 pfu (sample to13-4) (Fig. 5a, b, c, d). The Na+ content of msB ranges between 0.13–0.2 pfu (sample to13-4) and 0.1–0.14 pfu (sample to13-7) (Fig. 5e, f). The third group of muscovite (msC) has a lower Xmg of 0.48–0.33 (fraction) and a Si4+ contents of 3–3.15 pfu (Fig. 5a, b, c, d, e). By contrast msC shows the highest Na+ contents of 0.29 (to13-4) and 0.19 (to13-7). In samples lm09-221a and lm09-223 only msC is observed.

Chlorite developed in S1 cleavage of samples to13-4 shows Si4+ contents of 2.55–2.7 (pfu) and Xmg of 0.46–0.50. Chlorite related to D3 presents a similar Si4+ content of 2.57–2.62 (pfu) and Xmg of 0.43–0.48 (Table 2). Similarly, in sample to13-7 chlorite in S1 cleavage shows a Si4+ (pfu) content of 2.59–2.65 for an Xmg of 0.45–0.48, while chlorite related to D3 has a Si4+ content of 2.5–2.7 (pfu) and a Xmg of 0.40–0.45. In samples lm09-221aa and lm09-223 the chemistry of chlorite is homogeneous regardless its microstructural position. Chlorite composition of sample lm09-221 clusters around a Si4+ (pfu) content of 2.66–2.67 for an Xmg of 0.41–0.43. Chlorite of sample lm09-223 shows a Si4+ (pfu) content of 2.61–2.62 for an Xmg of 0.40–0.41.

Ti in biotite slightly increases from the core (0.08–0.10 pfu) to the rims (0.12–0.14 pfu) of the biotite porphyroblasts suggesting an increasing temperature during its growth (Henry et al., 2005). In sample to13-4 small biotite grains are stretched in the S2 cleavage and have muscovite composition (Table 2 for all analyzed samples. Both EPMA compositional maps and point analyses reveal the existence of three chemical groups of Kwm preserved in samples to13-4 and to13-7. They have typical muscovite composition (Xmp = 0.62–0.75) and show variations in Xmg, Na+ (pfu) and Si4+ (pfu) contents. The first group of muscovite (msA) has a Si4+ content of 3.2–3.25 (pfu), a Xmg of 0.54–0.61 (Fig. 6a,b) and a Na+ content of 0.08–0.13 (pfu). The second group of muscovite (msB) has a lower Xmg (0.43–0.6) and a lower Si4+ content between 3 and 3.15 (sample to13-7) and 3.13–3.22 pfu (sample to13-4) (Fig. 5a, b, c, d). The Na+ content of msB ranges between 0.13–0.2 pfu (sample to13-4) and 0.1–0.14 pfu (sample to13-7) (Fig. 5e, f). The third group of muscovite (msC) has a lower Xmg of 0.48–0.33 (fraction) and a Si4+ contents of 3–3.15 pfu (Fig. 5a, b, c, d, e). By contrast msC shows the highest Na+ contents of 0.29 (to13-4) and 0.19 (to13-7). In samples lm09-221a and lm09-223 mostly preserve msC, while a little preservation of an early muscovite is observed in late larger muscovite grains (0.15).

In summary, although all samples record a similar number of deformation phases in their microstructures, only the metapelites to13-4 and to13-7 preserve the three chemical groups of muscovite (msA, msB, msC). Small differences are observed between the two samples, especially for to13-7 that shows higher surface fraction of msB and msC. Samples lm09-221aa and lm09-223 mostly preserve msC. A similar pattern is guessed for chlorite but it is not quantified here.

6. Thermobarometry

In order to constrain which chemical composition of muscovite (msA, msB, msC) has been stable during the successive P–T–c stages and to compare them with the observed compositions, it is firstly crucial to precisely constrain the P–T path followed by rock. In the following section, phase equilibria modelling is used to reconstruct the P–T path. The results are tested against the predictions from empirical and semi-empirical thermobarometers.

6.1. Phase equilibria

6.1.1. Methodology

Isochemical equilibrium phase diagrams were computed in a Na2O-CaO-K2O-FeO-MgO-MnO-Al2O3-SiO2-H2O-TiO2 system for metapelites to13-7 and to13-4 using THERIAK-DOMINO (Capitaní and Brown, 1987; de Capitani and Petrakakis, 2010) and the internally-consistent dataset of Berman (1988) (with subsequent updates collected in JUN92.bs and distributed with Theriax-Domino 03.01.2012). The following solution models where used: Berman (1990) for garnet; Fuhrman and Lindsley (1988) for feldspar; Meyer et al. (1997) for opal-hydrate; Keller et al. (2005) for white mica and ideal mixing models for amphibole (Mäder and Berman, 1992; Mäder et al., 1994), epidote and chlorite (Hunziker, 2003). Phases with no solid solution comprise titanite (sph), rutile, ilmenite and quartz.

For comparison purposes, similar isothermal equilibrium phase diagrams were calculated with the internally-consistent dataset of Holland and Powell (1998) and subsequent updates (tc55, distributed with Theriax-Domino 03.01.2012). A detailed comparison between the two datasets is provided in the supplementary material S1. For the following discussion, however, the Berman (1988) database was preferred since it best reproduces the observed stable assemblages and the measured Si4+ (pfu) and Xmg contents of muscovite.

The isothermal P–T phase diagrams were first made using the bulk-rock compositions obtained by ICP-OES (at SERM laboratory, Nancy, France) and listed in Table 4. A pure H2O fluid phase was considered in excess. Fe2+ was ignored since all the samples contained a significant amount of ilmenite suggesting highly reduced conditions (Diener and Powell, 2010; Weller et al., 2013). For each sample, the stable metamorphic assemblages predicted by the models were compared to those observed in thin sections. The optimal P–T conditions were then qualitatively estimated from garnet and micas isopleths as well as from garnet and biotite modes.

Two stages of garnet growth (core and rim) were also modeled using the program GmMgo (Lanari et al., 2017). This program searches the optimal P–T condition of garnet using a fractional crystallization model.

5.3. Degree of preservation

The extent at which the chemical groups of muscovite msA, msB, and msC are preserved in S1, S2 and S3-shadows was quantified with XMAFTools using the module Chem2D (Lanari et al., 2014a); results are reported in Table 3. The degree of preservation of ms in S1 (P), is calculated from the pixels fraction Xmx:

\[
P_{ij} = \frac{X_{mj}}{\sum_{i=1}^{n} X_{mj}}
\]

Muscovite in the S1 cleavage of sample to13-4 has 0.48 of msA that is restricted to the grain interiors. The remaining fraction of 0.52 has the chemistry of msB. MsB is also partially preserved in grains interiors of S2 cleavage but at lower extent (0.28) while msB largely dominates (0.71). A very small amount of msC (0.05) is observed in the S2 cleavage, while it constitutes the totality of the muscovite grown in porphyroblasts P-shadows and as post-tectonic porphyroblasts.
### Table 2
Representative mineral composition for analyzed samples. Mineral abbreviations are from Whitney and Evans (2010). $X_{\text{Mg}} = \text{Mg}/(\text{Mg} + \text{Fe})$.

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combined with Gibbs free energy minimization. The errors provided in Fig. 7 are estimated using the auto-refinement procedure provided in GrtMod and a residual variation ($C_0$) of ±1.5 corresponding to the uncertainty resulting from the EPMA chemical analyses (Lanari et al., 2017).

6.1.2. Results

For metapelites to13-4 and to13-7, the peak metamorphic assemblage of Grt + Ms + Chl (+Bt) is predicted to be stable at 520–550 °C (Fig. 6 and Fig. 7). The upper T limit is fixed by the staurolite-in reaction at 580 °C. In sample to13-7 the P–T conditions that best satisfy the garnet core isopleths and modes (ca. 4.5–5 vol%) yield at 11.5 ± 1 kbar, 530 ± 20 °C (Fig. 6a). The geometry of the garnet isopleths indicates that garnet grew rapidly along a prograde trajectory. MsA are predicted to be stable at these same P–peak conditions. As the growth of garnet porphyroblasts change the composition of the reacting system (Evans, 2004; Konrad-Schmolke et al., 2008), a fractionation of 5 vol% of garnet (estimated from the thin section) was introduced and results in an increase of the stability of biotite (Fig. 6b). The biotite mode of ca. 9 vol% that is observed in thin section is reached at 570 ± 10 °C, 6.5 ± 1 kbar. At the same P–T conditions the predicted $X_{Ms}$ content of biotite best matches the measured values in biotite rims. MsA are predicted to be stable at 8 ± 1.5 kbar, 550 ± 20 °C (blue dotted polygon in Fig. 6a). Garnet fractionation does not affect the P–T prediction of $X_{Ms}$ (Fig. 6b). 9 vol% of biotite was fractionated from the remaining bulk composition. The resulting phase diagram shows a larger stability field for chlorite (Fig. 6c). P–T conditions that best satisfy $X_{Ms}$ and chlorite $X_{Ms}$ and Si$_{4+}$ (pfu) isopleths yield at 380 ± 20 °C, 5.5 ± 1 kbar (red polygon in Fig. 6c). As no chloritoid is observed in thin sections the D3 greenschist assemblage is at slightly lower P–conditions, at 4.8 ± 0.5 kbar, 380 ± 20 °C (dark red polygon in Fig. 6c).

A similar approach was used for metapelite to13-4. In this case both biotite and garnet were predicted in equilibrium at P–peak conditions. The red polygon in Fig. 7a shows the P–T domain that best satisfies the garnet isopleths and the biotite and garnet modes observed in thin section (10 vol% and 5 vol% respectively). They yield at 11 ± 1 kbar, 530 ± 10 °C. MsA are predicted as these same P–T conditions. The results of the fractional crystallization model (GrtMod) predicts that garnet core grew at 11.6 kbar, 525 °C (5 vol% of garnet) and garnet rim at 12.2 kbar, 544 °C (1 vol%), confirming the prograde trajectory (Fig. 7a). The $X_{Ms}$ content of the small biotite grains in S2 cleavage is predicted at 9 ± 1 kbar, 515 ± 10 °C (see Fig. S1–4). The $X_{Ms}$ is predicted to be stable at 8 ± 1.5 kbar, 550 ± 20 °C. In phase diagrams where garnet and biotite were fractionated from the initial bulk, the Si$_{4+}$ (pfu) and $X_{Ms}$ contents of $X_{Ms}$ are best predicted at 4 ± 1 kbar, 390 ± 30 °C (Fig. 7b).

7. Additional thermobarometric constraints

7.1. Raman spectroscopy on carbonaceous material

The maximum temperature ($T_{max}$) experienced by the organic-rich sediments was estimated with the Raman Spectroscopy on Carbonaceous Material (RSCM) thermometer of Beyssac et al. (2002) with a relative accuracy of ±15 °C (Beyssac et al., 2002). RSCM was applied on polished thin sections following the procedure of Beyssac et al. (2002). Spectra were obtained using a Renishaw InVia Reflex microspectrometer at the Geosciences laboratory of Ecole Normale Supérieure (Paris, France) with laser power of 12 mW. Spectra were then processed with the PeakFit® software. The results are presented in Table 5.

$T_{max}$ values of the samples geographically very close to metapelites to13-4 and to13-7 (see Fig. 3) range between 502 °C (sample lm09-206) and 572 °C (±15 °C, sample lm145). $T_{max}$ for organic-rich schists collected very close to lm09-221 and lm09-223 yield at 522–
574 °C (±15 °C) (sample lm07-81-sample lm144), (Table 5). Sample lm09-221 shows a $T_{	ext{max}}$ of 535 ± 15 °C.

7.2. Garnet-biotite and Ti-in-biotite thermometry

Crystallization temperatures of garnet-biotite pairs were estimated using either the biotite-garnet thermometer (at the pressure peak conditions of 11 kbar, using the calibrations of Holdaway and Lee, 1977; Perchuk and Lavrent’eva, 1983; Thompson, 1976) for the sample to13-4, in which garnet and biotite were observed in textural equilibrium, or the Ti-in-biotite thermometer (Henry et al., 2005) for both samples to13-4 and to13-7.

Temperatures obtained with the garnet-biotite thermometer range between 490 and 532 ± 15 °C (Table 6). Temperature estimated from pairs of garnet-biotite rim analyses systematically show higher temperatures than the ones obtained with garnet-biotite core analyses. A similar trend of increasing temperature from core to rim is also obtained with Henry et al. (2005) thermometer (541–617 ± 20 °C for sample to13-4 and 550–610 ± 20 °C for sample to13-7, see Table 6). The slightly higher temperatures obtained with the Ti-in-biotite compared to...
garnet-biotite and Raman thermometer may be due to the fact that the absence of aluminous minerals as staurolite or sillimanite tends to concentrate the Ti in biotite (Henry et al., 2005).

7.3. Multi-equilibrium thermobarometry

Multi-equilibrium thermobarometry was used to model the P–T conditions of the high variance assemblages Chl + Ms + Qz following the procedure described in Lanari et al. (2012). This semi-empirical approach uses the internal consistent thermodynamic database of Berman (1988) with updates from Vidal et al. (2001, 2005, 2006), Parra et al. (2002) and Dubacq et al. (2010). The program CHLMICAEQUI (Lanari, 2012) was used to estimate the temperature for each chlorite analysis of samples lm09-221 and lm09-223 (e.g. Lanari et al., 2012, Scheffer et al., 2016). Pressure was fixed at 7 kbar and the activity of the water was set up to 1 since no carbonate phases were observed. Convergence between equilibria was achieved for a minimal XFe$^{3+}$ and a temperature difference less than 30 °C (Vidal et al., 2006). Qz-H$_2$O-Ms P–T equilibrium lines were calculated for muscovite of samples to13-4, to13-7, lm09-221 and lm09-223 using the technique of Dubacq et al. (2010). P–T conditions of the chlorite-muscovite assemblage were then estimated from the intersection of phengite lines at the T estimated for chlorite (Lanari et al., 2012).

The multi-equilibrium approach was not applicable to chlorite of metapelites to13-4 and to13-7 (convergence between the chlorite–quartz–water equilibria not achieved in the P–T space), suggesting...
a temperature for chlorite formation above 400 °C (Lanari, 2012). A fixed T of 400 °C was then used to investigate the relative differences in P conditions estimated for each generation of muscovite (Fig. 8). For sample to13-4 the P-conditions progressively decreases from 8 kbar (for mS4) to 2.5 kbar for mSc (Fig. 8a). This is also the case in sample to13-7 where P-conditions obtained for mSc yield at 6 ± 1 kbar, while the ones obtained for mS4 plot at 4 ± 1 kbar (Fig. 8b).

For samples lm09-221a and lm09-223 no differences in P–T conditions were observed among muscovite occupying different microstructural positions, in agreement with the chemical results. However, for a nominal T of 400 °C, mSc of sample lm09-221 is predicted at higher pressure (10 ± 2 kbar) than mSc of sample lm09-223 (5 ± 1 kbar) (Fig. 8c). The Chl + Qz + H2O multi-equilibrium method of Vidal et al. (2005, 2006) was applied to each pixel of chlorite of these samples. P–T equilibrium conditions yield at 7 ± 1 kbar, 365 ± 25 °C for sample lm09-221a and at 3.5 ± 1 kbar, 380 ± 20 °C for sample lm09-223 (Fig. 8c).

### 8. Discussion

#### 8.1. A multi-method approach: comparison between thermobarometric methods

Results from the multi-equilibrium approach of Dubacq et al. (2010) are in line with the data obtained by phase equilibria modelling (Fig. 9). For a given temperature, a relative uncertainty of ±2 kbar was estimated using Monte-Carlo simulations, following the technique described in Cantarero et al. (2014) for chlorite. Fig. 9 shows that the pressures predicted at temperature > 450 °C are slightly higher than those obtained with the phase diagrams. Dubacq et al. (2010) observed a similar increase of the absolute uncertainty with increasing temperature.

Temperatures estimated with empirical thermobarometers (biotite thermometer, garnet-biotite thermometer and RSCM) are in line with the peak temperatures from phase equilibria. The excellent agreement between empirical, semi-empirical thermometers and phase diagrams ensures that P–T conditions are known with a high level of reliability. Moreover it demonstrates that the bulk composition used for modelling can be considered as representative of the reactive bulk rock composition and that the fractionation hypothesis caused by porphyroblasts growth is valid.

Phase diagrams calculated with Berman (1988) and Holland and Powell (1998) thermodynamic datasets share similar features (Fig. S1-1 and S1-2). Garnet P–T conditions calculated with GRTMOD for metapelite to13-4 yield at slightly lower temperatures (530 ± 20 °C) than the ones predicted by Holland and Powell from the garnet isopleths (560 ± 20 °C). The proximity between the P–T conditions for garnet core and garnet rims obtained with GRTMOD is compatible with the slight chemical zoning observed in garnet. At ca. 550 °C, intragranular diffusion is limited to a few microns (e.g. Chapman et al., 2011) and has probably not affected the P–T estimates. It is interesting to note that the XMo of biotite is best predicted by the Holland and Powell dataset (Fig. S1-4), whereas both XMo and Si4+ in phengite are better predicted with the Berman dataset. As muscovite is the main focus of this study the Berman (1988) dataset was used to model the evolution of muscovite composition along the P–T path.
The two samples that preserve the most complete record of the successive P–T stages (to13-4 and to13-7) have been used to constrain a clockwise P–T path characterized by a pressure-peak at $11 \pm 2$ kbar, $530 \pm 20$ °C (insets in Fig. 10). Such P–T trajectory is in line with the one proposed by Worley and Wilson (1996) and Dirks et al. (1994) for the Xuelongbao area (internal Longmen Shan). However the pressure peak conditions are higher than the ones previously estimated (which rather correspond to P–T conditions of our T-peak).

The pressure peak is followed by the thermal peak, which occurs at lower pressure (ca. 6 kbar). The increasing $X_{sp}$ content from core to rims of garnet porphyroblast as well as the enrichment of Ti (pfu) in the rims of biotite suggest a crystallization of porphyroblasts during temperature increase up to ca. 580 °C (as also supported by the empirical thermometers). The $T_{max}$ is well constrained and supported by all the thermometers used in this study. Similar RSCM temperatures have been reported by Robert et al. (2010) for metapelites collected south-west of the Pengguan massif (external Longmen Shan). They are in fairly accord with thermometric estimates of Dirks et al. (1994) Worley et al. (1997) and Worley and Wilson (1996) performed in the Xuelongbao area. The thermal peak was then followed by a greenschist retrogression accompanied by a partial exhumation up to 4 kbar, 380–450 °C, in agreement with

### Table 6

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (± 15 °C)</th>
<th>P (kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>to13-4 core</td>
<td>509</td>
<td>11</td>
</tr>
<tr>
<td>to13-4 core</td>
<td>512</td>
<td>11</td>
</tr>
<tr>
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<td>515</td>
<td>11</td>
</tr>
<tr>
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</tr>
<tr>
<td>to13-7 bt core</td>
<td>610 (± 20 °C)</td>
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</tr>
</tbody>
</table>

#### 8.2. P–T path recorded by metapelites

The two samples that preserve the most complete record of the successive P–T stages (to13-4 and to13-7) have been used to constrain a clockwise P–T path characterized by a pressure-peak at $11 \pm 2$ kbar, $530 \pm 20$ °C (insets in Fig. 10). Such P–T trajectory is in line with the one proposed by Worley and Wilson (1996) and Dirks et al. (1994) for the Xuelongbao area (internal Longmen Shan). However the pressure peak conditions are higher than the ones previously estimated (which rather correspond to P–T conditions of our T-peak).

The pressure peak is followed by the thermal peak, which occurs at lower pressure (ca. 6 kbar). The increasing $X_{sp}$ content from core to rims of garnet porphyroblast as well as the enrichment of Ti (pfu) in the rims of biotite suggest a crystallization of porphyroblasts during temperature increase up to ca. 580 °C (as also supported by the empirical thermometers). The $T_{max}$ is well constrained and supported by all the thermometers used in this study. Similar RSCM temperatures have been reported by Robert et al. (2010) for metapelites collected south-west of the Pengguan massif (external Longmen Shan). They are in fairly accord with thermometric estimates of Dirks et al. (1994) Worley et al. (1997) and Worley and Wilson (1996) performed in the Xuelongbao area. The thermal peak was then followed by a greenschist retrogression accompanied by a partial exhumation up to 4 kbar, 380–450 °C, in agreement with

![Fig. 8. P–T lines calculated with the multi-equilibrium approach for the different generations of muscovite identified in samples to13-4, to13-7, lm09-221a and lm09-223. (a) P–T lines calculated for all muscovite generations of sample to13-4 (msA, msB, msC). (b) P–T lines calculated for the more preserved msB and msC generations of sample to13-7. (c) P–T lines calculated for muscovite in different structural position (in the early S1–S2 cleavage and in the late retrogressed microstructures) of samples lm09-221a and lm09-223. Black frames indicate estimated P–T conditions for the greenschist stable assemblage (from chl-ms multi-equilibria).](image1)

![Fig. 9. Comparison between P–T conditions calculated with the phase diagrams for the different generations of muscovite (circles) and the ones estimated with the multi-equilibrium approach of Dubacq et al. (2010) and Lanari et al. (2012) (triangles), for samples to13-4 and to13-7.](image2)
Dirks et al. (1994) estimates. Late porphyroblasts of muscovite (D3b) show a chemical composition similar to the one of msC observed in porphyroblasts P-shadows suggesting that they may have crystallized under similar P–T conditions.

Samples geographically close to lm09-221 and lm09-223 reached peak temperatures above 520 °C (see Section 7.1). This clearly indicates that these samples experienced amphibolite peak conditions similar to the ones reached by samples to13-4 and to13-7. They thus belonged to the same metamorphic unit at the time of the metamorphic peak and do not come from different structural levels. In these samples, however, the only late greenschist assemblage that characterizes the retrograde evolution is preserved. The fact that sample lm09-223 was collected in the footwall of a minor thrust parallel to the Wenchuan Shear Zone (Fig. 1), while sample lm09-221a comes from its hanging wall may explain the slightly higher P–T conditions obtained for greenschist assemblage.

In summary, the multi-method approach used in this study allows a precise reconstruction of the P–T path experienced by the studied metapelites despite the scarcity of index minerals. It demonstrates that a fairly precise P–T trajectory with relatively small uncertainties can be obtained by combining quantitative compositional mapping with several thermobarometric methods and thermodynamic datasets.

### 8.3. Microstructures vs chemical re-equilibration in muscovite

Thermobarometry, and in particular the predictions of the phase diagrams, show that muscovite msB (mainly observed in the S2) is stable close to the T-peak conditions. Microstructures show, on the contrary, that the development of the S2 cleavage precedes the T-peak conditions since HP msA are still preserved in the cores of the muscovite grains defining the S2 cleavage. Similarly, msA is predicted to be stable at the P-peak, while it should precede the development of S2 according to microstructure record. These mismatches suggest that a discrepancy exists between the microstructural and the chemical records in muscovite.

In order to further investigate the timing of muscovite re-equilibration, it is interesting to compare the observed Si^{4+} (pfu) and XMg contents of msA, msB and msC with the predictions of an equilibrium model along a synthetic P–T loop of 50 steps (Fig. 10, see Section 6.1).
The phyllosilicate-rich matrix was assumed to continuously re-equilibrate at each step of the P–T path while a fractionation model of the effective bulk composition was used for garnet. This last assumption does not significantly affect the composition of muscovite as demonstrated in Fig. 6a and b. The prograde portion of the P–T path was constructed by combining this study results with preliminary P–T estimations of Robert (2011). For the P–T loop, different starting conditions were tested but they do not significantly affect our results since muscovites in S1 and S2 cleavage completely re-equilibrated at the P-peak (see below). As a small fraction of cpx was predicted at low-T for sample to13-4, the evolution of muscovite composition was also modeled in a Ca-free system (colored dashed lines in Fig. 10b). The presence of cpx in this P–T interval does not significantly affect the modeled muscovite composition.

In Fig. 10b (sample to13-4), msA is predicted stable at the P-peak, msB is predicted stable close to the T-peak (marked by the appearance of biotite, Fig. 10a) and msC during the retrograde path. The same characteristics are observed for the metapelite to13-7 (Fig. 10c and d).

By comparing these results with the degrees of preservation of msA, msB and msC obtained from the micro-chemical study (Table 3) we propose that msA formed at the P-peak, overprinting any previous record. The muscovite grains of S1 and S2 cleavages were then partially replaced by msB, at different extents according to the sample considered (Table 3). The replacement of msB by msC is massive in S2 cleavage (particularly in sample to13-7) and occurred at the thermal peak as shown by Fig. 10. In samples to13-4 and to13-7 the record of the P-peak (in msA) is thus strongly overprinted by re-equilibration at the T-peak. In these samples the record of the T-peak survives the retrograde history, as suggested by the high degree of preservation of msC.

In sample lm09-223, where the greenschist retrogression is more pronounced, the replacement of msC in msC is almost complete, especially in the very fine-grained muscovite (Fig. 5f).

The presence of msA in both S1 and S2 cleavage however clearly show that both microstructures developed before or near the P-peak. This shows that P–T conditions deduced from different generations of muscovite do not directly correlated to P–T conditions at which the different deformation phases (D1, and the early D2) occurred. They rather indicate the conditions at which successive stages of re-equilibration took place, thus giving an upper limit to the relative age of each deformation phase. In the metamorphic conditions of our studied samples re-equilibration may indeed continue after the deformation ceased (Worley et al., 1997).

The observations reported in this study suggest that the original composition of muscovite occupying the S1 cleavage has been completely replaced by msA at the P-peak. Any record of the metamorphic history that precedes the P-peak is thus no longer preserved. The muscovite composition in the S1 cleavage (msA) is therefore related, in our case, to the early D2 deformation phase (development of S2 cleavage). This explains why a small amount of msC is still visible in the core of the grains defining the S2 cleavage (Table 3 and Fig. 11). msB re-equilibrated after D2 deformation phase. The studied samples re-equilibrated at different extent, despite the same number of deformation phases recorded in microstructures. Hence, re-equilibration processes do not affect the preservation of the microstructures.

None of our sample can then be related to the case of total chemical preservation presented in the introduction (Fig. 3a). Sample to13-4 is, on the contrary, an example of an intermediate scenario where muscovite only partially re-equilibrated during the whole metamorphic history (Fig. 11a). Contrastingly, samples lm09-221a and lm09-223 can be related to the case of total re-equilibration (Fig. 3b) since almost only retrograde muscovite is observed.

### 8.4. Processes of muscovite re-equilibration

The results of this study show that muscovite can partially re-equilibrate during metamorphism without affecting the microstructures. Different processes may be evoked for muscovite re-equilibration: (i) solid state intragranular diffusion, (ii) a coupled process involving fluid-controlled dissolution transport and precipitation in a new growth site, and (iii) fluid-controlled dissolution-reprecipitation through a

*Fig. 11. Partial re-equilibration of muscovite by pseudomorphic replacement in sample to13-4. (a) Schematic sketch showing the partial re-equilibration of muscovite in the matrix, an intermediate scenario between the two end-member of Fig. 3. Blue arrow represents biotite resorption. (b) SEM image showing the typical features of mineral replacement described in Putnis (2009) and Putnis and Timm (2010). (c) zoom of the SiX (pfu) map for muscovite in the S1 cleavage (sample to13-4). A sharp reaction front can be recognized between the parent (msA) and the product (msB).*
moving interface within a single crystal, leading to pseudomorphic replacement. These different processes are separately addressed below.

- In the studied samples, the T-peak occurred at temperatures below 550 °C, where intragranular diffusion in muscovite is extremely limited (Dempster, 1992), especially for Si4+ cations that move through the Tschermak substitution (Si4+(Mg,Fe2+)4+ ↔ Al4+(Al3+). It has been shown for instance that high pressure phengitic white mica can preserve its original composition during decompression at temperature up to 700 °C (Hermann, 2003). This conclusion is confirmed by the sharp change in composition observed between msA, msB, and msC (Fig. 11c), not characteristic of a solid-state intragranular diffusion profile. The muscovite re-equilibration textures observed in the studied samples cannot therefore be explained by solid-state intergranular diffusion.

- Fluid circulating through the rock may cause net dissolution of muscovite, transport of the dissolved material through the intergranular medium – caused by the chemical potential gradients generated by the garnet and biotite forming reactions – and precipitation of new muscovite crystals in a different growth site. This would result in the alteration of the previous microstructural record. However, in the studied samples, muscovite msA, msB and msC in S1 and S2 preserve the shape of the older grains (Fig. 11b and c). These observations suggest that the partial re-equilibration of the muscovite grains in S1 and S2 cannot be explained by dissolution-transport-prediction mechanisms. However, msC in the P-shadow (or as porphyroblasts in samples to13-4 and to13-7) shows characteristics features of neo-crystallization in a new nucleation site (the opening P-shadows). Hence, in this case, muscovite formed by dissolution-transport-precipitation processes.

- The last process involves fluid-assisted dissolution-reprecipitation through an interface moving within a single crystal. This process is known as “pseudomorphic replacement” and has been described in details by Putnis (2009) and Putnis and Timm (2010). The pseudomorphic replacement generally leads to the creation of porosity in the replaced phase to connect the fluid interface with the intergranular medium (e.g. Putnis, 2002). Moreover, if the replacement is partial, a reaction front is preserved between the parent and the product. In the sample to13-4, both BSE images and compositional maps show that the crystalline shape of muscovite grains in S1 and S2 is preserved (Fig. 11a). The sharp reaction front observed between the parent and the product (Fig. 11c) suggests that the process of pseudomorphic replacement plays a significant role in the formation of msA, msB, and msC, allowing the preservation of the previous microstructures and the creation of a porosity in the replaced phase (e.g. Putnis, 2002).

In summary we propose that muscovite partially re-equilibrates during the successive P–T–ε stages by pseudomorphic replacement (msB, msC and msC in S1 and S2) and dissolution-transport-prediction (msC in the pressure shadow). The major process taking place during the prograde stage is therefore the pseudomorphic replacement that has often been evoked as the most likely process that drives the successive re-equilibration stages at microscopic scale in both major and accessory minerals (e.g. Lanari and Engi, 2017; Putnis, 2002; Putnis and Timm, 2010; Putnis, 2009).

8.5. Factors controlling the extent of re-equilibration in metapelites

It is interesting to compare the different re-equilibration behaviors of the studied samples. As the bulk rock compositions are similar – for at least samples to13-4, to13-7 and lm09-221a – other factors such as the intensity of deformation and fluid availability during metamorphism must be invoked to explain the differences in the extent of re-equilibration (Table 3).

8.5.1. Intensity of deformation

Significant differences in the grade of deformation are observed among the analyzed samples. Sample to13-4 is classified at the 3rd stage of Bell and Rubenach (1983) scale (see Section 4.2). Sample to13-7 recorded a higher deformation grade and is classified at stage 4. In samples lm09-221a and lm09-223, D3 is much more pronounced. This increase of the degree of deformation is correlated with decreasing degree of preservation of msA (Table 3). An increase in the deformation intensity enhances fluid diffusion and therefore favored the redistribution of the components within mineral phases resulting in the homogenization of chemistry in muscovite of the most deformed samples.

8.5.2. Fluid availability during metamorphism

Fluid availability is another key factor controlling the extent of matrix re-equilibration. Fluids are known to trigger the metamorphic reactions, enhancing mineral replacement, (Austrheim, 1987; Pattison and Tinkham, 2009; Vernon et al., 2008; Waters and Lovegrove, 2002).

The partial preservation of msA, msB and msC in metapelites to13-4 and to13-7 and the thermodynamic models (Fig. 10a and c) suggest a variability of the fluid availability during the metamorphic history at the scale of the mineral assemblage, which may favor muscovite pseudomorphic replacement.

The fluid can be released indeed through continuous and discontinuous metamorphic reactions (e.g. Baxter and Caddick, 2013). The forward thermodynamic models were used to predict the amount of fluid (H2O) released by the breakdown of hydrous minerals along the P–T trajectory (Fig. 10a and c). During the prograde P–T path, H2O is continuously released with some discontinuous stages (pulses) marked by the growth of garnet and biotite rims. These stages are likely to produce a larger amount of fluid in the intergranular medium in a shorter time interval than the continuous release.

The first pulse of internally derived fluid release is predicted to occur near the pressure peak (i.e. sample to13-4, 515–530 °C, Fig. 10a), in response to the growth of garnet at the expense of chlorite (Fig. 10a, c). This major stage of dehydration can explain why the muscovite originally associated to the S1 (or D1) has been completely overprinted by msA during D2.

A second pulse of fluid release is predicted to occur near the thermal peak (Fig. 10a, c) in response to the growth of the biotite rim, favoring the re-equilibration of msA in a muscovite of msC chemical composition. The compositional maps show that msA is mainly replaced in the S2 cleavage (at 80–85%, see Table 3) suggesting that during this stage the fluid preferentially percolated along the main cleavage S2.

A third stage of fluid circulation took place during exhumation and cooling since neo-crystallized phyllosilicates resulting from fluid-bearing retrograde reactions (Yardley et al., 2000, Jamtveit et al., 2008) are observed in porphyroblast P-shadows. At this stage two mechanisms for internal fluid release may be proposed: (1) the partial resorption of biotite (Fig. 10a, c) and (2) the discharge of fluids released during the prograde metamorphic history that may have been stored in the porosity created by replacement reactions. However, there is no internally derived fluid release predicted by the model during the retrograde P–T path (Fig. 10a and c). Fig. 10a and c show indeed that the amount of fluid considered “in excess” decreases after the metamorphic peak. Hence, the participation of externally derived fluids in the retrograde reactions is likely to be significant at this stage of the P–T path.

The fluid availability thus plays a major role in the re-equilibration of muscovite. In particular, internally derived fluids seem to strongly control this process along the prograde path. This interpretation is also supported by the fact that in sample to13-7, where the amount of H2O released during the pressure peak was higher than in the sample to13-4 (Fig. 10b), msA is less preserved.

While the modelling approach indicates the existence of three successive stages of fluid release at the scale of the mineral assemblage, external fluids may also participate in the re-equilibration of muscovite. When external fluids are involved the permeability of the rock may
change the length of the fluid flow phase and the time necessary for the rock to reach a partial equilibrium (Sanchez et al., 2011). Hence, in this case, partial equilibrium may have been reached during a longer phase of fluid flow.

The additional effect of external fluids is particularly evident in the samples close to the faults, (e.g. lm09-223) where $m_{\text{sys}}$ and $m_{\text{fl}}$ have been totally replaced. Metamorphic veins associated to the D3 deformation phase are mainly observed at the outcrop scale in the sample with the higher replacement rates. This observation suggests that externally derived fluid circulation – favored by the presence of the fault – triggers the re-equilibration at the sample scale. Further field and chemical investigations are however required to confirm this interpretation. A complete retrogression of garnet-biotite bearing metapelites into greenschist facies conditions is not only observed close to minor faults but also at the scale of the whole central Longmen Shan, along the Whenchuan Shear Zone (Worley and Wilson, 1996). This suggests that the faults acting as favored fluid pathways facilitate the chemical re-equilibration of the adjacent rocks.

In summary our observations indicate a strong correlation between the amount of fluid (internal and external) circulating through the rock and the extent of muscovite re-equilibration. The samples in which externally derived fluids have circulated during the retrograde path have therefore less chance to preserve the record of the early P–T stages.

8.5.3. A general model for the re-equilibration of metapelites

In nature fluid availability and deformation can concur together: the fluid efficiently circulates when the metamorphic rock is highly permeable. Permeability is created, at its turn, at microscale by deformation through grain-scale dilatancy or hydraulic fracturing from fluid overpressure (Putnis and Timm, 2010) or, at macroscale, through tectonically-induced fracturing (Jamtveit and Yardley, 1997). In studied metapelites the (re)activation of the S2 cleavage during successive deformation phases (D2 and D3) probably provided, at the sample scale, a privileged path for fluid circulation.

8.6. Regional tectonic implications

Structural overprinting relations observed by Harrowfield and Wilson (2005) suggest that both D1 and D2 deformations phases occurred in the internal domains of the central Longmen Shan prior to the emplacement of ca. 180–190 Ma post-orogenic granites (Roger et al., 2004). Also in Danba area (South-Western Longmen Shan) migmatisation was reached between 200 and 180 Ma (Huang et al., 2003b, Weller et al., 2013). This could therefore mark a possible timing for the thermal metamorphic peak. Pressure peak conditions of ca. 11 kbar were consequently reached before 180–190 Ma. This implies that a pile of ca. 30 km of sediments (density for the crust equal to 2.7 kg m$^{-3}$) already covered the crust of eastern South China craton at Triassic-lower Jurassic time (Fig. 12a and Weller et al., 2013). A major episode of crustal thickening was therefore already ongoing in the eastern margin of the Tibetan plateau at that time. Although the erosion may have removed an important portion of the sedimentary pile since then, the contribution of the Mesozoic deformation to the ca. 60 km crustal thickness now observed below the Songpan-Garze block thus seems to be of great importance.

The pressure peak recorded in studied metapelites precedes the thermal peak along a clockwise metamorphic history, suggesting that sediments were buried fast enough during the first phases of crustal thickening to prevent a complete thermal relaxation of the system. Thermal relaxation was reached during the first stages of decompression down to ca. 6 kbar (Fig. 12a), in agreement with the interpretation of the P–T path recorded in the Danba sediments proposed by Huang et al. (2003a) and Weller et al. (2013).

The retrograde path that post-date the thermal peak is characterized by a low-P metamorphism, related to a top-to-the south D3 shearing and exhumation up to 4–5 kbar. During the D3 deformation phase the ancient faults were re-activated as suggested by the difference between retrograde pressure conditions of samples lm09-221a and lm09-223. The D3 deformation phase also involved the basement of the South China craton (Fig. 12b), as revealed by metamorphic and geochronological data obtained in the Pengguan massif (Airaghi et al., 2012).

Fig. 12. Schematic tectonic evolution of the Songpan-Ganze sedimentary units (white) through time and corresponding stages on the P–T path (left side) for a representative sample (red dot) belonging to these units. (a) During the prograde P–T path the Songpan-Ganze sedimentary pile was thickened and then partially exhumed while emplaced on the South China basement (gray) as an accretionary wedge. The original S1 cleavage, related to the compaction of sediments was folded by the S2 crenulation cleavage (S2). (b) The metamorphic overprint under greenschist facies conditions is related to the exhumation of the deep sedimentary units during the D3 deformation phase, associated with re-activation of ancient faults and a basement-involving deformation (Airaghi et al., 2012). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
9. Conclusion
Our petrological observations show that typical garnet-biotite metapelites, collected in the internal domains of the Longmen Shan thrust belt (Sichuan, China) record microstructural evidence of several deformation phases that can be related to different metamorphic assemblages. High-resolution X-ray compositional mapping and a multi-method thermobarometry approach based on the combination of empirical thermometers, phase equilibria and multi-equilibrium modelling successfully enable to reconstruct a P–T path despite the littleness of index minerals. This P–T path is characterized by a pressure peak at 11 ± 2 kbar, 530 ± 20 °C, related to the maximum burial, followed by a thermal peak at 6.5 ± 1 kbar, 575 ± 10 °C and by a greenschist low-P overprint during exhumation up to 4–5 kbar, 380–450 °C. However the chemical evolution of the muscovite-rich matrix along the P–T history reveals that the P–T conditions obtained from metamorphic muscovite preserved in different microstructures do not directly correlate with the metamorphic conditions at which the different phases of deformation occurred. Although pre-P peak microstructures are indeed preserved in the studied samples no chemical evidences of the burial history were observed. Moreover, muscovite re-equilibrated at each stage at different extents in metapelites. The main factors controlling re-equilibration are the degree of deformation and the amount of fluid available during the whole metamorphic history. In this sense P–T conditions obtained for the different metamorphic assemblage are more likely to reflect successive stages of re-equilibration and fluid circulation related to mineral resorption or larger scale fluid circulation. It is consequently crucial to perform a detailed petrological study to correctly retrieve P–T–ε paths and link microstructures to ages.

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Appendix A. Supplementary data
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