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**Nanoscale chemical zoning of chlorite and implications for low-temperature
thermometry: application to the Glarus Alps (Switzerland)**

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Abstract

A combination of adapted chlorite thermometry and high-spatial-resolution analytical techniques (TEM-EDX/FIB) shows that the low-grade metamorphic chlorites of the Glarus Alps, Central Alps (Switzerland), do not record the peak metamorphic conditions as commonly assumed in previous studies of this reference area for low-grade metamorphism. Chlorites have rather recorded several stages of the retrograde path, through an intracrystalline nanometric-scale compositional zoning. The consistency of the nanoscale zoning patterns observed both within sample and along the transect suggests that local equilibrium was achieved at this scale and maintained during growth or re-equilibration. Applying recent thermobarometers, we highlight that chlorites recorded a distinct behaviour between the northern and southern part of the studied transect: the south of the Glarus area displays a regular P - T exhumation path, from 3.0 ± 0.2 kbar and 310 ± 20 °C for maximum P - T (estimated with conventional thermometers), to ~ 0.8 kbar and ~ 220 °C according to chlorite crystal-core analysis, and to ~ 0.3 kbar and ~ 190 °C according to chlorite crystal-rim analysis. On the contrary, the north of the Glarus area shows an apparent break in the exhumation, with P estimates from chlorite crystal rims (~ 1.3 kbar) higher than from chlorite crystal cores (~ 0.8 kbar). Even if the absolute pressure values are fraught with large uncertainty, their contrasting core/rim pattern is not model dependent. We try to correlate these new thermobarometric results with independent data to refine the exhumation scenario of the North-Helvetic flyschs, confirming differential uplift along the transect. This reappraisal of Glarus chlorite thermometry demonstrates that an adapted thermometry/analysis protocol opens new prospects for investigating the evolution of low-grade metamorphic terranes.

Key words: chlorite, thermometry, Glarus, low-grade metamorphism

1. Introduction

Quantifying the thermal history of low-grade metamorphic rocks, *i.e.* in the temperature (T) range below 350 °C, is challenging because kinetics are much more sluggish than at higher metamorphic grade. For instance, the short diffusion lengths require the use of advanced *in situ* analytical approaches to obtain accurate crystallochemical information in chemically heterogeneous crystals down to the nanoscale. A first necessity is therefore to choose the appropriate thermometer for the targeted rocks among the multiple tools available, e.g. composition of phyllosilicates, oxygen isotope partitioning, structural and/or chemical evolution of carbonaceous material, or thermochronologic methods.

In this respect, since the 1980s, the compositional change of chlorite in low- T settings has been considered as a good proxy for the temperature of formation (e.g., Cathelineau and Nieva, 1985). As a consequence, many chlorite thermometers have been developed, first via empirical equations linking chlorite Al^{IV} content and temperature, with a correction based on the Fe/Mg ratio (Kranidiotis and McLean, 1987; Jowett, 1991; Zang and Fyfe, 1995; Xie et al., 1997) or without such (Cathelineau, 1988; Hillier and Velde, 1991). In the absence of constrained thermodynamic models – able to take into account all the substitutions occurring in chlorites – these empirical thermometers were widely used during the 1990s to estimate T conditions in diagenetic and low-grade metamorphic environments, like the Glarus Alps complex in Switzerland (e.g., Rahn et al., 1994, 1995). In reality, each of these empirical thermometers was calibrated for a particular context with specific applicability conditions (as reviewed by Bourdelle and Cathelineau, 2015), and their systematic application without due consideration of these conditions failed or led to erroneous geological interpretations in many instances, as shown by de Caritat et al. (1993) for instance.

Since the 2000s, chlorite thermometry is reappraised and several thermodynamic (Vidal et al., 2001, 2005, 2006; Lanari et al., 2014) or semi-empirical models (Inoue et al., 2009; Bourdelle et al., 2013a; Lanari et al., 2014) have been published, with the goal to improve the theoretical background beyond these methods and their reliability. These models

consider the chlorite + quartz equilibrium and are based on a combination of chlorite end-members. They take into account the Tschermak ($\text{Al}^{\text{IV}}\text{Al}^{\text{VI}} = \text{Si}[\text{Mg}, \text{Fe}^{2+}]$), the ferromagnesian ($\text{Fe}^{2+} = \text{Mg}$) and the di/trioctahedral ($3[\text{Mg}, \text{Fe}^{2+}] = \square + 2\text{Al}^{\text{VI}}$; where $\square$ represents an octahedral vacancy) substitutions occurring in chlorites. Each of these thermometers has its own formulation, assumptions (like Fe^{3+} consideration, non-ideality, compositional field, etc) and applicability field (low T and P , high T and P). When correctly applied, they have shown their efficiency in various geological contexts (see Inoue et al., 2010; Kameda et al., 2011, 2012; Ganne et al., 2012; Trincal et al., 2015; Scheffer et al., 2016; Mamane Mamadou et al., 2016; Chinchilla et al., 2016) as well as in experimental cases (e.g. Mosser-Ruck et al., 2016).

Another possible issue at low T is that diffusion is sluggish and therefore the composition of chlorites may be modified only over very short distances, *i.e.* at the nanoscale, during advanced diagenesis and/or metamorphic evolution. Fortunately, several high-spatial-resolution analytical techniques have become more accessible for petrology, such as Focused Ion Beam (FIB), Transmission Electron Microscopy (TEM) coupled with EDX probe (Energy Dispersive X-ray spectroscopy), or synchrotron (EXAFS or STXM-XANES, see for phyllosilicates, Bourdelle et al., 2013b; de Andrade et al., 2014). Recent thermometer formulations coupled with these nanometric-scale analytical techniques (Bourdelle et al., 2013c) allow one to obtain accurate temperature estimations, and open new prospects for the study of low-grade rocks (Vidal et al., 2016).

In this study, we use recent analytical developments coupling FIB and TEM-EDX to characterize the chemistry of chlorite down to the nanoscale. We have targeted the Glarus Alps (Switzerland) which are one of the reference zones for low-grade metamorphism and where chlorite occurs all along the metamorphic profile. Eighteen FIB foils (9 samples, 2 FIB foils per sample) were cut in chlorite–illite assemblages to preserve the textural relationships and were analysed with a calibrated TEM-EDX. On this analytical basis, we apply recent chlorite thermometry (Bourdelle et al., 2013a) and compare our results with previous chlorite

thermometric studies. We then discuss the results in terms of methodology for the assessment of thermal history in low-grade metamorphism and we highlight some implications for the exhumation history of the Glarus Alps.

2. Materials and methods

2.1. Geological setting and sampling

2.1.1. Geological setting

The mountainous region of Glarus is located in the Central Alps south of the Walensee lake (eastern Switzerland) and is cut by two main valleys along the Linth (west) and Sernft rivers (east). This part of the Central Alps exhibits a remarkable yet rather complex geological structure resulting from at least two orogenic cycles (Hercynian and Alpine) (e.g. Pfiffner, 1993; Schmid et al., 1996). During the Alpine phase, the whole region has been deformed and structured resulting in a spectacular thrust (Glarus thrust) separating the Helvetic nappes in the hanging wall from the Infrahelvetetic complex in the footwall (Fig. 1). The Helvetic nappes are composed by Permian conglomerates (Verrucano), Jurassic and Triassic carbonates and Tertiary flyschs (e.g. Rahn et al., 1995; Merriman and Frey, 1999), while the Infrahelvetetic complex is made by the crystalline basement of the Aar massif and its parautochthonous cover including Cretaceous and Cenozoic sediments (flyschs). The activity of the Glarus thrust from Eocene to mid-Miocene resulted in burial of the Infrahelvetetic units and metamorphism up to greenschist-facies conditions (e.g. Frey and Ferreiro Mählmann, 1999).

As shown below, considering the extensive work that has been done there, the Glarus area is like a showcase of low-grade metamorphism in sediments (Merriman and Frey, 1999). Further details on the local geology are given by Milnes and Pfiffner (1977), Pfiffner (1986), and Pfiffner et al. (1990).

2.1.2. Metamorphic conditions in the Glarus Alps: a historical case study

Hunziker et al. (1986) and Rahn et al. (1995) performed a thorough mineralogical study of the Glarus area and observed the following southward succession of index minerals: kaolinite close to Glarus, pyrophyllite and glauconite in the surroundings of Schwanden, stilpnomelane and pumpellyite between Linthal and Panix Pass, biotite and chloritoid to the south (Panix Pass). These authors also documented a transition from illite to muscovite using chemical and structural analyses, and an illite crystallinity index (IC) decreasing from the north ($IC > 0.42 \text{ }^{\circ}2\theta$) to the south ($IC < 0.25 \text{ }^{\circ}2\theta$) of the area (see also Frey, 1988; Wang et al., 1996). In addition, calcite–dolomite thermometry data (Ebert et al., 2007) combined with phase-relation data show a gradient in metamorphism from NW to SE, *i.e.* from advanced diagenesis in the surroundings of Walensee lake and Glarus up to greenschist-facies conditions around Panix Pass, reflecting southward increasing thermal overprint due to increasing burial. This gradient was also observed by Mullis (1979), Frey (1986) and Tarantola et al. (2007) by investigating fluid inclusions. To the west of Walensee lake, a hydrocarbon-rich zone was identified (HHC: higher hydrocarbons), whereas methane (CH_4 zone, anchizone indicator) was found by going south to Linthal (Linth valley) and Engi (Sernft valley). These two locations mark the limit between the CH_4 zone and a H_2O zone, to the south of which the fluid inclusions consist mostly of H_2O . Vitrinite reflectance (Rahn et al., 1994, 1995; Merriman and Frey, 1999; Tarantola et al., 2007; Mullis et al., 2017) also records a thermal variation from Walensee to Panix Pass. Whereas vitrinite reflectance data show a very low-rank coal to the north, with $R_{\text{max}} = 0.77 \%$ (indicator of 100–120 $^{\circ}\text{C}$), they refer to anthracite around Panix Pass, with $R_{\text{max}} > 8 \%$ (indicator of $T > 270 \text{ }^{\circ}\text{C}$). This is confirmed by the evolution of the Raman spectrum of carbonaceous material which is characteristic of very disordered graphitic carbon, with a marked southward increase of structural ordering (Lahfid et al., 2010). All these independent proxies (noted “independent conventional thermometers”) give information on peak metamorphism (noted “maximum temperature” below); they concur to the picture of a NW-SE thermal gradient (Fig. 1) which

can be approximated by a linear regression linking maximum temperature and structural distance through the Glarus Alps (Ebert et al., 2007).

Constraints on pressure are poor, and only based on the b_0 crystallographic parameter (Sassi and Scolar, 1974) of micas in the North-Helvetic flyschs (2.0-2.5 kbar, Frey, 1988), and on fluid inclusion data around Elm (2.0-2.4 kbar; Bowers and Helgeson, 1983; Potter and Brown, 1977; Tarantola et al., 2007; Caumon et al., 2014). By extrapolation, considering these works and the barometric gradient (lithostatic pressure assumed; Frey, 1988), we can approximately estimate pressures of 1.3-1.5 kbar close to Walensee Lake, 1.5-2.0 kbar in the surroundings of Glarus, 2.0-2.4 kbar around Elm, and 2.4-3.0 kbar at Panix Pass.

2.1.3. Sampling

Samples come from the Cenozoic North-Helvetic flyschs (Infrahelvetic complex; Table 1; Fig. 1) in the footwall of the Glarus thrust, which have undergone only one metamorphic cycle, *i.e.* the Alpine orogeny. Eleven samples were collected along a N-S profile around Elm (along the Sernft valley, following the regional thermal gradient), and nine were selected (two samples were analysed but finally discarded because FIB foils were not correctly cut through chlorite–illite contacts, see below). As the chlorite thermometer used here is based on chlorite + quartz equilibrium (see section 2.2), all the samples were selected based on the presence of quartz (even samples with calcschist lithology; Table 1). From the data compilation of Ebert et al. (2007), a metamorphic peak temperature can be assigned by interpolation to each of our samples (Table 1), from 245 °C north of Elm to 330 °C south of Panix pass.

2.2. Chlorite thermometers and barometer

Investigating the relationship between chlorite composition and crystallization temperature in geothermal fields of Salton Sea and Los Azufres, Cathelineau (1988) showed

that chlorite Al^{IV} content increases with temperature, and established the following linear regression:

$$T^{\circ}\text{C} = -61.92 + 321.98 (\text{Al}^{\text{IV}} \text{ apfu}) \quad (1)$$

where Al^{IV} is expressed in atoms per 18 oxygen formula unit. This pioneer equation became the most used chlorite thermometer (including studies of Glarus metamorphism) and is the base of several other empirical thermometers (Kranidiotis and McLean, 1987; Cathelineau, 1988; Hillier and Velde, 1991; Jowett, 1991). However, empirical equations have shown their limits: Bourdelle and Cathelineau (2015) demonstrate that these equations are all specific cases of the Si₋₁□₋₁R₂²⁺ exchange vector (combining Tschermak and di/trioctahedral substitutions), linked to the geological setting in which they were calibrated, and are consequently limited to restricted chlorite compositional ranges and geological contexts. It is therefore irrelevant to apply one empirical equation rather than another in a different geological setting; Eq. 1 is applied here only to test and compare empirical thermometry to literature and semi-empirical approaches.

To circumvent limitations of empirical calibrations, semi-empirical and thermodynamic chlorite thermometers were later proposed. Semi-empirical thermometers are ideal models based on a ratio of end-member activities and directly link the temperature to a *K* equilibrium constant (for a chlorite + quartz equilibrium, calculated from chlorite end-members, H₂O and SiO₂ activities) as:

$$\log K = \frac{-\Delta G_r^0}{2.303(R.T)} = \frac{A}{T} + B \quad (2)$$

where *A* and *B* are constants, Δ*G*_{*r*}⁰ the Gibbs free energy of reaction, and *R* the gas constant. With this approach, effects of pressure are neglected; this assumption is especially justified in low-*T*/low-*P* contexts such as the Glarus Alps.

Here, the model of Bourdelle et al. (2013a) was used because (i) it is specially calibrated for low- P - T chlorites, *i.e.* $T < 350$ °C and $P < 3$ -4 kbar, and (ii) it does not require a prior quantification of the Fe^{3+} content, considering that all iron is divalent. The latter assumption does not compromise reliable temperature estimation, as shown by Bourdelle and Cathelineau (2015) and Chinchilla et al. (2016). The formulation of Bourdelle et al. (2013a) considers magnesian end-members and an ordered cationic site repartition model following the recommendations of Bailey (1988) and Vidal et al. (2001) for di-trioctahedral chlorites, an approach reinforced by several crystal-chemical studies (*e.g.* Welch et al., 1995; Inoue and Kogure, 2016). The calibrated thermometric equation is:

$$T(^{\circ}\text{C}) = \frac{9400}{23.40 - \log K} - 273.15 \quad (3)$$

where K is the equilibrium constant of the chlorite + quartz reaction as:

This formalism considers only the magnesian system, but that does not affect temperature estimates because the ferromagnesian substitution is not sensitive to temperature in low- T contexts (for more details, see Bourdelle and Cathelineau, 2015).

Based on the same assumptions as Bourdelle et al. (2013a), but considering the pressure effect and a different set of end-members, Lanari et al. (2014) proposed a semi-empirical thermometer as:

$$T(^{\circ}\text{C}) = \frac{203093 + 4996.99P(\text{kbar})}{-R \ln K + 455.782} - 273.15 \quad (5)$$

based on the reaction:

240

241 $2 \text{ Clinocllore} + 3 \text{ Sudoite} = 4 \text{ Amesite} + 7 \text{ Quartz} + 4 \text{ H}_2\text{O}$ (6).

242

243 It is important to note that this model – as the thermodynamic model of Vidal et al. (2005,
244 2006) – excludes Si-rich chlorites ($\text{Si} > 3 \text{ apfu}$); it was used here to try to estimate pressure,
245 using as input the temperature obtained with equation (3).

246 Semi-empirical thermometers were calibrated assuming H_2O and SiO_2 activities as
247 $a_{\text{H}_2\text{O}} = a_{\text{SiO}_2} = 1$. In the Glarus context, chlorites were sampled in the H_2O -dominated zone,
248 except for sample GL07 13 from the CH_4 zone (Figure 1). Tarantola et al. (2007, 2009)
249 showed that fluid inclusions in the H_2O zone along the Sernft valley are CO_2 -free or contain
250 less than 1 mol% of CO_2 and are composed by > 99 mol% of H_2O . Consequently, the H_2O
251 activity could be considered as close to 1. Although it can be assumed that H_2O -dominated
252 fluid inclusions are formed at peak metamorphism (Tarantola et al., 2007), it is not possible to
253 determine whether the H_2O activity in the system varied during exhumation. However, the
254 assumption that $a_{\text{H}_2\text{O}} = 1$ is usually reasonable under diagenetic to low-grade metamorphic
255 conditions (Inoue et al., 2009; Lanari et al., 2014). Besides, $a_{\text{SiO}_2} = 1$ is justified in the case
256 of quartz-bearing rocks.

257

258 2.3. Analytical techniques

259 Detailed petrologic investigations of petrographic thin sections from the Glarus
260 samples were carried out using optical microscopy and Scanning Electron Microscopy (SEM)
261 to describe the texture of chlorites and precisely distinguish authigenic from detrital chlorites
262 before FIB milling. The SEM used was a Hitachi S-2500 instrument operating at 15 kV with a
263 1.5 nA current intensity (ENS Paris).

264 The FIB foils were cut using the FIB 200 FEI of CP2M (University of Aix-Marseille)
265 with a voltage of 30 kV and a gallium beam. The cutting intensity varied from 5000 to 50 pA,
266 following the protocol for FIB thin foil preparation given by Heaney et al. (2001) and Wirth

(2004). Eighteen FIB foils were cut from nine samples (two FIB foils by sample) across illite–chlorite contacts near one end of the interface, where re-equilibration is the most likely. The thin foils were cut out with a size of approximately 15 µm by 5 µm and a thickness between 50 and 300 nm. To check the preservation of the mineral crystalline structure after FIB-milling, lattice-fringe imaging was systematically carried out with the TEM.

Samples were analysed with a TEM-EDX/FIB coupled method and quantitative analyses were deduced and corrected thanks to the *t-O-protocol* (Van Cappellen and Doukhan, 1994; Bourdelle et al., 2012). The TEM-EDX used was a JEOL 2100-F at the Physics and Microanalysis Department of IFPEN Lyon-Solaize, using a 200 kV voltage, a counting time of 60 s and a dead time lower than 15%. The current density was maintained at 1.3 pA/cm². The sample tilt angle was 7°. In these conditions, the spot size was around 1 nm and defocused to 50 nm. The TEM-EDX *K* factors (Cliff and Lorimer, 1975) were calibrated on paragonite (Na, Al), pyrophyllite (Al), talc (Mg), muscovite (Fe, Al, K), chlorite (Fe, Al), clintonite (Mg, Ca, Al) and phengite (Mg, Fe, K, Al) and the standardizations were checked against electron microprobe analysis of reference clays (SMB-18; Kohler et al., 2009).

Given the high spatial resolution, the analysis points on FIB foils were targeted to reveal within-grain compositional variations. The structural formulae of chlorite were calculated on the anhydrous basis of 14 oxygens. Analyses containing K₂O + Na₂O + CaO > 1 wt% (of the 100 wt% total of TEM-EDX analyses) were discarded.

3. Results

3.1. Petrology of Infrahelvetetic nappe samples

The selected samples are schists ranging from calcschists to quartz-schists. SEM and optical microscopy observations reveal that the main minerals are quartz, carbonates, phyllosilicates and feldspars (albite and K-feldspars). Quartz grains are commonly angular, associated with prismatic altered feldspars. Phyllosilicates refer to micas (commonly muscovite/illite, occasionally detrital biotite in the CH₄ zone) and chlorite, either detrital or

authigenic. Several clusters of pyrite can be identified, with a framboidal or cubic habit.

Generally, a calcareous matrix surrounds other minerals.

Detrital micas and chlorites are mainly observed in GL07 13 sample, *i.e.* in the CH₄ zone (Table 1; Fig. 1), while phyllosilicates are mostly neo-formed in other samples – in the H₂O zone. Under the polarizing microscope, detrital chlorites have a dark green colour with a strong pleochroism. These chlorites are well-preserved and oriented sub-parallel to the nascent schistosity of the rock. Authigenic chlorites are light green and form intergrowths with authigenic muscovite/illite sheets, along the entire profile (Fig. 2). These chlorites generally show slight deformation features. According to these microtextural observations, the intergrowths of muscovite/illite and chlorite are quite similar to those observed and considered as authigenic by Tarantola et al. (2009). The FIB foils were cut across authigenic illite–chlorite intergrowths; detrital chlorites were discarded on the basis of the microtextural criteria described above.

3.2. Nanoscale chemical zoning in chlorites

All analyses considered, the targeted Glarus chlorites display a Si content between 2.65 and 3.08 apfu and a R²⁺ content (*i.e.* Fe²⁺ + Mg²⁺) between 4.46 and 3.71 apfu, referring to di-tri-octahedral compositions with $\square < 0.4$ apfu.

However, given the high spatial resolution of TEM-EDX and considering that FIB milling allows to preserve the crystal integrity, we can separate analyses into two categories: (i) crystal rim analyses, performed ~50 nm away from illite–chlorite contacts (this distance allows one to avoid contamination through the FIB foil thickness due to adjacent minerals, see Bourdelle et al., 2012), and (ii) crystal core analyses (see Bourdelle et al., 2013c). The comparison of core and rim analyses reveals a systematic trend: for each sample, crystal rims are enriched in Si and depleted in divalent cations compared to crystal cores (Table 2). As an example, compositional data obtained on one of GL07-19 FIB foils reveal a chemical variation of chlorite over a few tens of nanometers, with divalent cation content lower than

4.0 apfu in the crystal rim, but always higher than 4.1 apfu in the crystal core (Fig. 3). All the analysed grains show such a compositional variation and, for any given sample, the two analysed grains show the same trend (see section 4.2). This systematic difference between crystal core and rim compositions clearly suggests a chemical zoning at the nanoscale (Bourdelle et al., 2008).

3.3. Selection of chlorite analyses and chlorite thermometry

As a reference and like most previous studies, we applied the empirical thermometer of Cathelineau (1988) to all chlorite analyses. To simulate EMP data, crystal rim and core analyses were interpreted together. The obtained temperatures vary between 255 and 365 °C (Table 2) for all the samples (from north to south), in fair agreement with Rahn et al. (1995) and Ebert et al. (2007) from independent thermometers.

However, owing to the spatially resolved techniques employed here, which revealed the chemical zoning of Glarus chlorites, one is now able to consider separately crystal rim and core analyses. In addition, to clearly identify the re-equilibration or growth steps, only the “extreme” compositions should be considered (see Bourdelle et al., 2013c). Indeed, because of the difficulty to locate precisely the rim areas that recorded the last re-equilibration or the core areas that recorded the earliest re-equilibration or growth, we have considered only the three or four rim analyses and the three or four core analyses (noted “extreme” rim and “extreme” core compositions respectively) per sample (*i.e.* combining the two FIB foils of each sample) that represent the compositions closest to equilibrium. Equilibrium is here assessed by the extremum $\log K$ (Eq. 3), calculated from the analyses and considering the direction of the relevant reaction. The retained “extreme” rim compositions actually ignore some analyses having $\text{Si} > 3$ apfu (because they cannot be used further for pressure evaluation with Lanari et al. (2014) model). Therefore, the “extreme” rim results will represent a conservative estimate of (*i.e.* an upper bound to) the lowest (re)equilibration/growth temperatures.

The chlorite thermometer of Bourdelle et al. (2013a) applied on the “extreme” crystal rim and core compositions yields the following results (Table 2, Fig. 4):

- (1) Temperatures (from rim and core analyses) are systematically lower than maximum temperatures obtained with other independent thermometers along the sampling profile (difference in the range of ca. 50-100 °C, depending on rim and core analyses).
- (2) Temperatures from rim compositions are always lower than temperatures from core compositions, for any given sample. The difference ranges from 10 to 60 °C.
- (3) Temperatures from rim compositions are constant along the N-S profile (always around 190 ± 20 °C, except GL07 13 sample) whereas the maximum temperatures from other independent thermometers display a regular increase (from 245 to 330 °C).

3.4. Tentative reconstruction of the exhumation P - T path

To estimate the formation pressure from chlorite core and rim compositions, we used the thermobarometer of Lanari et al. (2014), *i.e.* the semi-empirical equation (5) linking T , P and $\log K$ of the chlorite + quartz equilibrium, in which the T estimates obtained with the Bourdelle et al. (2013a) model are used as input data (along with relevant K values). Figure 5 presents the results of P calculation, linking for each sample maximum P - T (estimated from literature, see section 2.1.2), chlorite-core and chlorite-rim thermobarometry. All chlorite core analyses give a pressure around 0.8 kbar (± 0.2 kbar, except for GL07 21), while pressures estimated from chlorite rim analyses are around 0.3 kbar (± 0.2 kbar) for samples from the south of the Glarus area (from GL07 19 sample to Elm) and around 1.3 kbar (± 0.3 kbar) for samples from the north (from Elm to GL01 13 sample). Therefore, the south of the area displays a regular P - T exhumation path (except GL07 20 sample), from 3.0 ± 0.2 kbar and 310 ± 20 °C for maximum P - T , to ~ 0.8 kbar and ~ 220 °C for chlorite cores, and to ~ 0.3 kbar and 190 °C for chlorite rims. On the contrary, the north of the area shows an apparent break in the exhumation, with P estimates higher for chlorite rims (~ 1.3 kbar) than chlorite cores (~ 0.8 kbar). All these pressure data may be too low, if one considers the geothermal gradients

implied; they should indeed *not* be taken at face value, considering that the reported uncertainties are just the standard deviation; they do not include propagation of analytical error nor the unknown but likely poor accuracy of the barometer (due to the low pressure dependence of chlorite composition in low-*P-T* contexts, Bourdelle et al., 2013a). However, regardless of absolute values, the differential of core and rim data and its regional pattern are solid, model-independent results. As will be shown below, the consistency of the results, both in rim/core temperature evolutions and in the areal distribution of the rim/core pressure difference, supports the equilibrium-thermodynamics approach and suggests two different exhumation histories for the northern and the southern part of the Glarus Alps.

4. Discussion

4.1. Micro- vs. nano-scale analysis

Our results show the necessity of using high-resolution spatially resolved techniques to analyse properly chlorites (as well as micas) in a low-grade metamorphic setting like the Glarus Alps. Indeed, the results using a recent chlorite thermometer and considering the nanoscale chlorite zoning are significantly different from those obtained on the same chlorite via conventional thermometers and empirical chlorite thermometers coupled with microscale analysis like EMPA.

Previous studies on Glarus chlorites used EMPA, which has a sampling volume of several μm^3 that does not allow identifying any compositional variation in submicrometric crystals. Glarus chlorites were therefore considered to have a homogeneous composition (Rahn et al., 1994). However, several chlorite compositions may coexist in the same rock sample or even in the same crystal, such as detrital, authigenic and/or metamorphic compositions (e.g. Bourdelle et al., 2013c). Only specific low-*T* cases, such as homogeneous chlorites directly precipitated from fluids make it possible to avoid a nanometric analytical protocol and yet to obtain compositions suitable for thermometry (Mamane Mamadou et al., 2016). Moreover, contaminations of chlorite analyses by quartz – which can strongly impact

thermometric calculation, especially with empirical thermometers – are undetectable in EMPA (see Schmidt et al., 1999 on chlorites from Taveyanne greywacke, Switzerland). Thanks to the excellent microtextural control offered by imaging modes down to the nanoscale, such contaminations are avoidable using TEM; contamination of chlorite analysis by a few smectite or illite layers is still possible, but (i) is limited by exclusion of analyses containing $K_2O + Na_2O + CaO > 1$ wt% and (ii) does not influence thermometric calculation (Bourdelle et al., 2015).

4.2. Significance of chlorite compositional variations, local equilibrium vs. kinetics

The EMP analyses of detrital chlorites (not presented here) show Si contents significantly lower (< 2.6 apfu) than the crystal-core analyses obtained by TEM on authigenic chlorites. As a consequence, crystal core compositions must be considered as the result of growth or re-equilibration of (prograde?) authigenic chlorite and not as a detrital relic.

A key issue is then the significance of compositional variations revealed by this study. The formation of chlorite takes place during metamorphic reactions which are transient disequilibrium states governed by local chemical potential gradients and kinetic processes. Its re-equilibration may proceed through diffusion or, more likely, dissolution-reprecipitation (*cf.* Putnis and Putnis, 2007; Putnis, 2009). Is then the observed compositional variability of chlorite the compositional record of reaction kinetics, or the record that local, grain-boundary equilibrium was achieved and maintained during growth or re-equilibration of a given metamorphic stage? Only in the latter case can the equilibrium-thermodynamic approach inherent to the applied thermometers be justified. The question must be addressed before any thermobarometric or geological consequence can be envisaged.

One way to address the equilibrium issue is through the consistency or heterogeneity of the compositional variations. In case kinetics and local-scale factors prevailed, one would expect different zoning in each grain depending on the local environment. If grain-boundary equilibrium prevailed, a local and larger-scale consistency is to be expected in the zoning

patterns. In other words, can the assumption of local equilibrium, which has been shown to offer a valid conceptual framework at the micro- to millimetre scale in higher-grade metamorphic terranes, also be valid in low-grade environments, then of course at nanoscale? This issue, which is of general bearing, is tested below on the basis of two case studies for which nanoscale data are available, the Glarus Alps (this study) and the advanced diagenesis of Gulf Coast sandstones, Texas (Bourdelle et al., 2013c).

The Glarus samples provide a first test of within-sample consistency. As explained in section 2.3, for each sample, compositional data were obtained from two FIB sections extracted from two different chlorite grains, and merged. They were merged, indeed, because the zoning patterns recorded were consistently the same in the two crystals of each pair of FIB foils. This is illustrated in Figure 6 for the representative sample GL07 17, about halfway in the Glarus transect. This figure depicts the Si and R^{2+} contents for rim and core of two different grains named B1 and A2. For clarity, we have considered only the four rim analyses and the four core analyses per grains (*i.e.* for B1 and A2) that give the extremum $\log K$ (Eq. 3; see section 3.3). It appears that crystal rims display a similar composition (Si content between 2.72 and 2.83 apfu, R^{2+} content between 4.16 and 4.24 apfu). Likewise the crystal cores of B1 and A2 grains show a similar “extreme” composition. Furthermore, the compositional trend from core to rim is not only the same within sample, but it is consistently observed along the whole transect, in all samples, with calculated rim temperatures consistently lower than core temperatures, whatever they mean. Last, a second type of inter-sample regional-scale consistency exists, with the northern samples showing higher or marginally higher calculated rim pressures than core pressures, whatever they mean, and the southern samples showing the reverse (Fig. 5). It seems unlikely that such within-sample and regional consistencies could be achieved if kinetics and local factors were controlling chlorite composition.

A similar conclusion was reached from the study of Gulf Coast chlorites (Bourdelle et al., 2013c). In chlorites sampled at different depths and various locations of the Gulf Coast area, TEM and FIB techniques highlight consistent within-grain patterns of major-elements

variations (see also Fig. 11 in Vidal et al. 2016). There, the zoning of chlorite at a nanoscale is due to various crystallization stages during burial, with a core composition corresponding to detrital chlorite and a rim composition of neo-formed chlorite. Moreover, the chlorite rim compositions display a T dependence with depth and location that is consistent with the diagenetic history described at a regional scale (see Bourdelle et al., 2013c). This T dependence of chlorite rim compositions, independently of chlorite core, clearly supports the idea that the zoning of low-grade chlorites is not controlled by a kinetic effect but rather by local equilibrium, in this case-study too. These observations lend credence to the thermometric approach used here, the results of which are further discussed below.

4.3. Thermometric implications of the compositional zoning of Glarus chlorite

The identification of chemical zoning in the Glarus chlorites has major thermometric implications. The fact that T estimates from EMP analysis of Glarus chlorites using an empirical thermometer are similar to maximum temperatures (Table 2) from other independent thermometers is a coincidence, resulting from the use of a low-spatial-resolution analytical protocol and of an empirical equation not calibrated for this geological context (see Bourdelle and Cathelineau (2015) for more explanations on the applicability of empirical thermometers). This erroneously led earlier authors to conclude that authigenic chlorites formed during the maximum burial step of the Glarus rocks and were not re-equilibrated during exhumation. In fact, along the sampling profile, temperatures from independent conventional thermometers are clearly higher than results of chlorite semi-empirical thermometry (Bourdelle et al., 2013a) applied to crystal core and rim compositions (Table 2), indicating different temperatures for different re-equilibration steps.

The chemical zoning identified in the Glarus chlorites is approximated through two sets of compositional data (from rims and cores) generating two sets of estimated temperatures, to be compared with the temperatures from independent conventional thermometers (maximum T). Considering that independent thermometers give the peak

metamorphic temperature (Ebert et al., 2007), that crystal-core compositions are not detrital, and that $T(\text{core}) > T(\text{rim})$, the three arrays of T estimates (in black, red and blue on Fig. 4) are assumed to correspond to two snapshots along the retrograde path recorded by chlorites. The first one is the re-equilibration of prograde chlorites that may happen due to fluid-rock interactions during the early exhumation and/or by chloritization of residual detrital biotites. The latter case may be valid when T estimate from core is close to maximum T , considering that biotite chloritization may be assigned to peak metamorphism with a fluid-controlled mineralogical isograd (Tarantola et al., 2009). The second one is the re-equilibration of the chlorite rims during the late stages of the exhumation.

4.4. Geological interpretations

Compositional variations within a chlorite crystal are not easy to detect. Even using the latest developments of the TEM-EDX/FIB coupling, it is difficult to understand whether the zoning observed represents a progressive zoning from core to rim (continuous evolution from core to rim) or is due to the juxtaposition of different compositions (*i.e.*, several juxtaposed and independent zones in a same chlorite, each with a specific composition). Therefore, we distinguish only two populations of chlorite compositions: core versus rim. Assuming that tens of analyses on two FIB foils for each of nine samples are representative (see Bourdelle et al., 2013c) and that targeted crystal rims refer to the late stages of the retrograde path, we can study the exhumation via the difference between the maximum temperature undergone by rocks (from independent conventional thermometers) and the temperature of the last recorded step of equilibration (our data retrieved from crystal rims). Figure 7 shows this difference (noted ΔT) along the sampling profile. We observe that ΔT noticeably increases from Schwanden-Elm to Panix Pass. This evolution of ΔT would indicate a difference in exhumation rate between North and South with the southern part of the Glarus area going up faster, if we consider that rims of all chlorites of the area crystallized simultaneously. The latter hypothesis, *i.e.* synchronous crystallization of chlorite rims, is

supported by the fact that (i) all chlorite rim compositions give similar temperatures ($190 \pm 20^\circ\text{C}$) and (ii) all chlorites are affected by a similar slight deformation, implying a formation preceding or contemporaneous to one or several tectonic deformations.

Rahn and Grasemann (1999), using fission-track data and numerical thermal modelling, proposed a scenario for exhumation including variations of the exhumation rate from the North to the South. The scenario starts 10 Ma ago and takes into account (i) a rotation of the southern area during the retrograde step (with a rotation point assumed at the north of the Alpine border in the south of the Molasse basin), (ii) erosion and (iii) the present topographic relief. The variations of the exhumation rate (i.e. from North to South) proposed by the authors and those of the ΔT parameter presented here converge. Therefore, based on the temperatures estimated in the present study and the isotherms calculated by Rahn and Grasemann (1999), the chlorite rims would have crystallized around or a little more than 10 Ma ago. To reconcile the rotation scenario (between 10 Ma and present), the maximum temperatures (which increase from North to South), and the variation of ΔT , we can envisage (i) an exhumation that would have begun much earlier than in the scenario proposed by Rahn and Grasemann (1999), with northern units initially less buried than the southern ones (crystallisation of chlorite cores), followed by (ii) a step at 10-12 Ma where northern and southern units are approximately at the same depth and during which the chlorite rims (re)crystallized, and finally by (iii) an exhumation to the surface, with the southern part exhumed structurally above the northern one. This scenario is summarized in Figure 8.

The chemical zoning of Glarus chlorite also gives valuable pressure information. Therefore, chlorite core and chlorite rim thermobarometry allowed us to outline the P - T retrograde path, and to identify a difference in exhumation history between the northern and southern parts of the studied area. These two retrograde paths could be linked to the exhumation scenario proposed above, completed by either (i) a slight compression step for the north of the area around 10-12 Ma, explaining the estimated P increase, or (ii) a differential exhumation rate between the north and the south, or a combination of both scenarios.

Scenario (i) would imply a thrust fault somewhere to accommodate the compression but there is no direct trace or evidence for a blind fault within the studied unit. Scenario (ii) implies that the southern rocks would be exhumed fast enough so that temperature would not reequilibrate during decompression, whereas the northern rocks would be exhumed at a slower rate. This latter scenario is in agreement with the discussion above and observations from Rahn and Grasemann (1999), although we note that their conclusions deal with the shallowest part of exhumation, as the apatite closure temperature is estimated at ca. 110-130 °C.

5. Conclusion

Over the last years, chlorite thermometry has made important progress and, combined with high-spatial-resolution analytical techniques, it allows one to obtain accurate temperature estimates, even in advanced diagenesis or very low-grade metamorphic contexts. Therein, selecting a thermometer should carefully consider all assumptions and the applicability field for this thermometer with regard to the case study. In addition, the analytical protocol should be chosen according to the targeted chlorites: EMP for homogeneous – large grain sizes – chlorites, TEM-EDX/FIB for heterogeneous – small grain sizes – chlorites. Studying the Glarus Alps metasediments, we show that low-*T* chlorites can record the retrograde rock history, and that earlier interpretations made on the basis of chlorite empirical thermometry must take this into account. In Glarus, past interpretations imply a crystallization of chlorites during the maximum burial step without re-equilibration during exhumation. These chlorites are actually heterogeneous and record a succession of re-equilibrations, giving new keys to understand the *P-T* history of this part of the Central Alps.

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Tables

Table 1: Sample description with name, geographical position (WGS 84 coordinates), area of sampling, lithology and temperature of peak metamorphism estimated by Rahn et al. (1995) and Ebert et al. (2007).

Structural unit	Sample	Longitude E	Latitude N	Zone	Lithology	Max T °C
Infrahelvetic nappe	GL07 13	9.1581	46.9854	East-Schwanden	Calc-schist	245
	GL07 15	9.1692	46.9441	Elm	Calc-schist	280
	GL07 16	9.1689	46.9319	Elm	Quartz-schist	285
	GL07 17	9.1793	46.9214	Elm	Schist	295
	GL07 19	9.1039	46.8514	Panix Pass	Schist	330
	GL07 20	9.1108	46.8572	Panix Pass	Quartz-schist	325
	GL07 21	9.1208	46.8736	Panix Pass	Quartz-schist	320
	GL07 23	9.1297	46.8797	Panix Pass	Schist	310
	GL07 24	9.1272	46.8872	Panix Pass	Schist	310

Table 2: Selection of TEM-EDX analyses of Glarus chlorite. For each sample, a crystal core and crystal rim analysis are given. Max T °C refers to maximum temperature (peak metamorphism) obtained from independent conventional thermometers (Ebert et al., 2007). Cathelineau T °C: temperatures estimated with the Cathelineau (1988) thermometer (Eq. 1). Bourdelle T °C: temperatures estimated with the Bourdelle et al. (2013a) thermometer (Eq. 3).

Sampling profile	N		ELM												S	
Sample	GL07 13		GL07 15		GL07 16		GL07 17		GL07 23/24		GL07 21		GL07 20		GL07 19	
rim/core analysis	rim	core	Rim	core	rim	core	rim	core	rim	core	Rim	core	rim	core	rim	core
analysis code	A2chl1	A1chl8	B3chl4	B2chl7	A5chl30	A5chl8	B1chl21	B1chl18	C3chl1	B2chl21	B1chl2	B1chl6	A2chl10	A4chl8	A2chl7	A3chl20
TEM-EDX analyses																
SiO ₂	33.57	30.15	31.72	29.21	31.88	31.52	31.27	30.19	30.10	30.15	30.28	29.28	31.38	30.44	29.94	28.96
TiO ₂	0.06	0.00	0.00	0.08	0.13	0.00	0.00	0.00	0.00	0.00	0.05	0.08	0.09	0.01	0.01	0.00
Al ₂ O ₃	26.38	27.50	26.40	29.02	26.71	24.69	26.63	27.57	27.55	26.42	28.45	27.98	25.02	25.61	26.32	26.17
FeO	26.52	29.54	23.70	28.34	22.70	26.68	24.85	25.51	29.53	28.84	28.68	30.46	29.80	26.36	30.47	31.31
MnO	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
MgO	13.27	12.63	18.07	12.57	17.98	16.19	16.77	16.70	12.64	14.56	12.54	12.20	13.26	17.42	13.04	13.51
CaO	0.11	0.16	0.00	0.26	0.55	0.67	0.03	0.02	0.03	0.00	0.00	0.00	0.00	0.05	0.00	0.06
Na ₂ O	0.00	0.00	0.00	0.20	0.00	0.25	0.08	0.00	0.03	0.00	0.00	0.00	0.04	0.00	0.00	0.00
K ₂ O	0.10	0.02	0.10	0.33	0.04	0.00	0.36	0.00	0.06	0.04	0.00	0.00	0.40	0.11	0.22	0.00
Struct. form. (apfu)																
Si	3.01	2.77	2.83	2.67	2.83	2.86	2.81	2.72	2.76	2.76	2.76	2.70	2.89	2.76	2.77	2.69
Ti	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00
Al(IV)	0.99	1.23	1.17	1.33	1.17	1.14	1.19	1.28	1.24	1.24	1.24	1.30	1.11	1.24	1.23	1.31
Al(VI)	1.80	1.74	1.61	1.80	1.63	1.51	1.63	1.65	1.74	1.61	1.82	1.74	1.60	1.50	1.63	1.56
Fe ²⁺	1.99	2.27	1.77	2.17	1.69	2.03	1.87	1.92	2.27	2.21	2.19	2.35	2.29	2.00	2.35	2.43
Mn	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
Mg	1.78	1.73	2.40	1.72	2.38	2.19	2.25	2.24	1.73	1.99	1.70	1.68	1.82	2.36	1.80	1.87
Ca	0.01	0.02	0.00	0.03	0.05	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Na	0.00	0.00	0.00	0.03	0.00	0.04	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
K	0.01	0.00	0.01	0.04	0.00	0.00	0.04	0.00	0.01	0.00	0.00	0.00	0.05	0.01	0.03	0.00
T°C estimates																
max T°C	245	245	280	280	285	285	295	295	310	310	320	320	325	325	330	330
Cathelineau T°C	255	336	315	363	311	304	321	350	336	337	336	355	294	337	335	359
Bourdelle T°C	120	183	186	202	176	197	189	217	183	209	172	201	168	245	203	261

Fig. 1: Simplified geological map of the Glarus Alps (Central Switzerland). Sample location and sampling N-S profile are reported. The diagenetic zone/anchizone and the anchizone/epizone boundaries are depicted as red dashed lines; HHC/CH₄ and CH₄/H₂O limits based on fluid inclusion data are shown as green dashed lines (Rahn et al., 1995; Merriman and Frey, 1999; Ebert et al., 2007; Tarantola et al., 2007).

Fig. 2: Back-Scattered Electron SEM images of several petrographic thin sections showing authigenic chlorites, and illite–chlorite intergrowth structures. On these images, chlorite appears in pale grey whereas illite is in darker grey.

Fig. 3: Analysis of an illite–chlorite assemblage (GL07 19 sample). (a) SEM image of the petrographic thin section showing the emplacement of the FIB foil to be cut across the illite–chlorite interface. (b) Bright-field TEM image of the FIB foil extracted from the section, with the platinum strap on top of it. (c) Enlargement of part b showing the R^{2+} (Fe $^{2+}$ + Mg $^{2+}$) contents of chlorite (apfu) and their variation from crystal core to crystal rim.

Fig. 4: Comparison of thermal profiles obtained between East-Schwanden and Panix Pass from literature by a compilation of methods (in black), with Bourdelle et al. (2013a) thermometer on chlorite crystal cores (in red), and with Bourdelle et al. (2013a) thermometer on chlorite crystal rims (in blue). Chlorite core and rim thermometry: for each sample, representation of the average of T estimates from selected “extreme” chlorite compositions (analysis of two FIB foils for each sample; for more details, see text). Error bars refer to uncertainty given by Ebert et al. (2007) (black points) and to standard deviation (red and blue points).

Fig. 5: Exhumation path drawn in a P - T diagram by linking maximum P - T , chlorite-core and chlorite-rim thermobarometry results for each sample. P - T data from independent conventional thermometers (in black), from combining Bourdelle et al. (2013a)/Lanari et al. (2014) thermometers on chlorite crystal cores (in red), and combining Bourdelle et al. (2013a)/Lanari et al. (2014) thermometers on chlorite crystal rims (in blue). Error bars on T refer to uncertainty given by Ebert et al. (2007) (black points) and to standard deviation (red and blue points). Error bars on P refer to an assumed uncertainty of $\pm 10\%$ (black points) and to standard deviation (red and blue points). The N-S sampling profile is schematically indicated at the top, on the basis of maximum T and P .

Fig. 6: Comparison of analyzed rim and core compositions of two chlorite grains (noted B1 and A2) from one sample (GL07 17). Compositions are represented by Si and R²⁺ contents (in apfu). For clarity, we have considered only the four rim analyses and the four core analyses per grain (*i.e.* for B1 and A2) that give the “extreme” $\log K$ (Eq. 3; see section 3.3).

Fig. 7: Evolution of ΔT along the sampling profile (between East-Schwanden and Panix Pass). For each sample, ΔT was calculated as the difference between maximum T from the literature and the average T from chlorite rim thermometry (based on “extreme” compositions, see text; Bourdelle et al. (2013a) thermometer). Error bars refer to the maximum of standard deviations. Dark line: linear regression. Grey area: linear regression ± 15 °C.

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839 Fig. 8: Schematic exhumation scenario for the North-Helvetich flyschs along the studied
 840 North-South profile, established from Rahn and Grasemann (1999; from fission track data and
 841 numerical modelling) and the new thermobarometric data obtained from Glarus chlorites
 842 (present study). Black, red and blue lines represent the relative rock burial at each exhumation
 843 step, according to T .