Applied Clay Science 134 (2016) 175–185

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Reliability of very low-grade metamorphic methods to decipher basin evolution: Case study from the Markstein basin (Southern Vosges, NE France)

Sébastien Potel [a,*], Tatiana Maison [a], Marine Maillet [a], Anta-Clarisse Sarr [a], Michael Patrick Doublier [b,c], Ghislain Trullenque [a], Rafael Ferreiro Mählmann [d]

[a] *B2R, Institut Polytechnique LaSalle Beauvais, Geosciences Department, 19 Rue Pierre Waguet, F-60026 Beauvais, France*
[b] *Geoscience Australia, Resources Division, Cnr Jerrabomberra Avenue and Hindmarsh Drive, Symonston 2609, ACT, Australia*
[c] *Centre for Exploration Targeting, School of Earth and Environment, University of Western Australia, 35 Stirling Highway, Crawley 6009, WA, Australia*
[d] *Technische Universität Darmstadt, Institut für Angewandte Geowissenschaften, Schnittspahnstraße 9, D-64287 Darmstadt, Germany*

ARTICLE INFO

Article history:
Received 31 March 2016
Received in revised form 29 September 2016
Accepted 2 October 2016
Available online 18 October 2016

Keywords:
Clay minerals
Very low-grade metamorphic petrology
Chlorite geothermometry
Kübler Index
Basin evolution
Vosges

ABSTRACT

Low- and very low-grade metamorphic studies investigating the alteration and reaction progress of clay minerals are powerful tools to decipher the thermal evolution of sedimentary and inverted meta-sedimentary basins. Sheet silicates such as illite and chlorite are very common in sedimentary basin sequences. They can be used to determine the grade of diagenesis and low-temperature metamorphism as measured through the XRD: illite Kübler-Index (KI; illite "crystallinity" in older literature) and the chlorite Árkai-Index (ÁI; chlorite "crystallinity" in older literature), respectively. Although the ÁI method is considered to be slightly less sensitive than the KI method, a reliable correlation between both methods is often observed in metamorphic domains with a uniform heat-flow history and minor tectono-structural complexity. Complementary to these methods, the K-white mica *b* cell dimension provides a robust estimate of pressure facies reached in very low- to low-grade temperature domains.

Here, we present a case-study from the Markstein basin located in the Southern Vosges. The lithostratigraphic units in the basin are characterized by deep marine flysch sequences of Upper Devonian to Upper Visean age and volcano-clastic sediments, respectively. The Markstein basin is surrounded by granitoids with intrusion ages between 340 and 326 Ma. A previous study showed orogenic deformation characterized by regional folding, and a contact metamorphism found in an outer halo of the granitoids up to 1500 m away from the contact (delineated by the occurrence of biotite). Here we present a multi-disciplinary study combining mineral assemblages, illite and chlorite "crystallinity indices", and K-white mica *b* cell dimension. Our approach allows to (i) map in (great) detail the areal extent of both regional/burial metamorphic and contact metamorphic domains; (ii) reveal the metamorphic zonation within both domains; and (iii) better constrain regional/burial and contact metamorphic history. The contact metamorphic domain is characterized by the occurrence of biotite and/or actinolite and low K-white mica *b* cell dimensions, whereas the zone of incipient orogenic metamorphism yields KI and ÁI values of the high-grade diagenesis and anchizone with intermediate K-white *b* cell dimensions.

1. Introduction

The metamorphic grade of rocks which underwent "very low- and low-grade metamorphism" (as follows the term will include also grade of diagenesis) is difficult to assess. The classical methods applied are the so-called illite "crystallinity" and the vitrinite reflectance. The methods are dependent on several factors: while the dominant factor is duration of thermal metamorphism, they also depend on pressure and the kinetics in mineral and organic matter reaction progress, respectively. In metamorphic studies, contrary to the diagenesis research, the very low temperature range has been little considered due to few mineral-reaction isograds established (zeolites and phyllosilicates) and to diverse disequilibrium states in the rocks to be studied (Ferreiro Mählmann et al., 2012). For these reasons, most publications regarding the determination of grade of metamorphism deal with conditions above 300 °C and the first occurrence of neoformed metamorphic minerals with well-defined reaction-isograds such as biotite, chloritoid, and actinolite (Turner, 1968; Winkler, 1979; Bucher and Frey, 1994). Basic methods developed in low-temperature petrology

---

* Corresponding author.
E-mail address: sebastien.potel@lasalle-beauvais.fr (S. Potel).

http://dx.doi.org/10.1016/j.clay.2016.10.003

of sedimentary rocks applied in very low-grade studies use clay mineral indices. In this field, changes in the shape and sharpness ratio of the XRD 10 Å illite peak are characteristic for changes in grade of incipient metamorphism. It is recognized that a steady increase in the height-to-width ration of the 10 Å peak occurs with increasing diagenetic/incipient metamorphic grade (Weaver, 1961). Since Kübler (1967), illite "crystallinity" (IC) is used as a parameter, empirically related with the aggradation of illite (Ferreiro Mählmann et al., 2012). Temperature is believed to be the most important parameter affecting the IC (Kübler, 1967, 1968). As a rule, the IC value decreases (i.e., "crystallinity" increases) with increasing temperature (i.e. during sedimentary burial or tectonic overburden). The change in the IC value is attributed to: 1) a decrease of the proportion of swelling mixed-layers (especially at low-temperature diagenetic conditions); 2) an increase of the mean thickness of crystallites, often caused by a decrease in the amount of defects affecting the coherency of layer-to-layer bonding; 3) a decrease of lattice strain of crystallites (Merriman and Peacor, 1999; Árkai et al., 2002). This is best illustrated in contact metamorphic aureoles and is also supported by a small number of hydrothermal experiments (Krumm, 1984). In addition, some crystal-chemical clay parameters, like the measurement of the K-white mica *b* cell dimension (Sassi, 1972; Sassi and Scolari, 1974) can be used to decipher the metamorphic evolution of the rocks. This method is used as an estimate of pressure facies reached in low-grade meta-pelitic rocks (Frey and Robinson, 1999). Recently, Potel et al. (2006) have shown that this method is less prone to resetting than KI and the K-white mica *b* cell dimension. In New Calediona it preserved early K-white mica neoformation conditions after a pluri-facies metamorphic evolution.

In summary, it is recommendable to use a multi-method clay-mineral approach for deciphering orogenic histories and in general geodynamic scenarios and -if possible- a combined investigation of mineralogical and organo-petrological methods (Ferreiro Mählmann et al., 2012). The aim of the present paper is to test the reliability of the different methods generally used to study metamorphic series implying clay minerals in a pluri-facies metamorphic evolution (burial and contact metamorphisms).

2. Geological setting

In the Vosges, two of the central European Variscan Zones can be distinguished (Kossmat, 1927): the Saxothuringian zone in the north and the Moldanubian zone in the central and southern part (Fig. 1), both separated by a major SW-NE trending steep dipping fault, the shear zone of Lalaye Lubine (LLSZ) (Edel and Fluck, 1989). The northern area represents the Saxothuringian part of the Vosges Mountains and consists of sedimentary and volcanic sequences of Precambrian (schists of Villé), Silurian (schists of Steige) and Devonian to Early Carboniferous age (Bruche valley and Bande-médiane occurrences), and a series of dioritic to granitic plutons of early Carboniferous age. The central and southern, Moldanubian parts consist of very low- to high-grade metamorphic sequences that were intruded by numerous granitoid plutons (intrusion ages between 340 ± 2 and 345 ± 2 Ma, Schaltegger et al., 1996). The variscan basement (peak metamorphism at 337 to 334 Ma, Schaltegger et al., 1999) is divided into an upper, high-grade unit (granulites with garnet peridotites, leptynites, kinzingites and amphibolite facies paragneiss) and an underlying medium grade unit with migmatic paragneiss and anatectic orthogneiss with granite neosomes (Kalt et al., 1994; Kalt and Altherr, 1996). The southernmost part of the area is occupied by two main sedimentary basin, the Visean volcano sedimentary Markstein basin in the north and the Permian Giromagny basin in its south (Fig. 1).

In the Markstein basin, three sedimentary units can be distinguished (Jung, 1928): a northern allochtonous Markstein unit, and the southern autochtonous Oderen and Thann units. The Markstein unit is separated from the southern units by a thrust containing ophiolitic nappe fragments - the Klippen Belt (Jung, 1928) - which represents discontinuous exposures of serpentinized harzburgite, ophicalcite, gabbro, gneiss and conglomerate (Fig. 2). The Klippen Belt is interpreted as exhumed relicts from deep parts of small, marginal back-arc basins developed during closure of a Palaeozoic subduction (Skrzypek et al., 2012). The Markstein unit is formed by an Early Carboniferous siliciclastic turbidite sequence of flysch-like rocks (up to 3500 m thick) consisting of inter-bedded pelites and greywackes (Gagny, 1962; Krecher, 2005; Krecher et al., 2007). The volcano-sedimentary rocks of the autochtonous units are of Lower to Upper Visean age. The base of the Oderen unit is characterized by a succession of carbonates (probably of Frasnian age) overlain by Fammenian sediments and Early Carboniferous pelites and greywackes (Skrzypek et al., 2012). The Lower to Middle Visean sediments are composed of inter-bedded pelites and distal fine grained turbidites together with an associated volcanism documented by spilites (Maas, 1988; Schneider, 1990; Hammel, 1996).

The Markstein unit is framed to the west, north and east by granitic plutons, and is also intruded by syn-genetic microgranitic dikes (Gagny, 1968; Schaltegger et al., 1996) related to the "granite des Crêtes" (Gagny, 1968). The Metzeral granite intrusion, bordering the northern part of the Markstein basin, is dated at 341 ± 1 Ma (Schaltegger et al., 1996). The contact between sediments and granitoids is either a tectonic one formed by brittle faults and/or contact metamorphism as characterized by a secondary growth of biotites and hornblendes (Petrini and Burg, 1998). According to these authors, the contact metamorphism can be recognized in an outer halo up to 1500 m away from the intrusion contacts (based on the occurrence of microscopic and mesoscopic determined biotite and cordierite at the contact).

The whole Markstein formation is affected by intense folding causing the formation of tight structures with fold axis striking N130 to N140 (Fig. 2). This fold axis orientation is in agreement with results by Petrini and Burg (1998). The folding produces in places an intense cleavage best developed in the more competent layers, as already noticed by these last authors. According to Petrini and Burg (1998), regional deformation should have occurred about 340 Ma ago, i.e. shortly after deposition.

3. Materials and methods

3.1. X-ray diffraction

In pelitic rocks diagnostic minerals and mineral assemblages of the very low-grade metamorphic zone are scarce and only found in rocks with a very specific geochemical composition. In these rocks, the transitions from non-metamorphic to low-grade (referring to the term greenschist facies of Winkler, 1979) and from the very low-grade (chlorite zone of Tilley, 1925) to low-grade metamorphic zone (biotite zone of Barrow, 1893) take place through the diagenetic zone, the anchizone and the epizone (according to Kisch, 1987), each zone being characterized by specific values of the illite Kübler Index (Kisch, 1987; Árkai et al., 2003, 2007). The illite "crystallinity" (IC) or Kübler-Index (referring to the pioneer study of Kübler, 1964) is defined as the full width at half maximum (FWHM) of the first illite basal reflection in XRD patterns and expressed in $\Delta°2\theta$ (Frey, 1987; Guggenheim et al., 2002). Guggenheim et al. (2002) recommended that the use of the term "crystallinity index" should be avoided, although it may be placed within quotation marks when referring to previously referenced work. They also recommended to refer the values to an index by citing the author describing the procedures to generate the index value. The proposed way of citing is much more important because the IC method is not calibrated uniformly (Kisch et al., 2004). Therefore, we will refer for 10 Å FWHM values to the illite "crystallinity" for raw data and to KI after calibration against Kübler's scale (Table 2).

IC is considered to be a function of crystallite thickness, the number of lattice defects (Merriman et al., 1990) and the peak interference with discrete smectite or illite-smectite mixed layer composition (Ferreiro Mählmann et al., 2012). Temperature is thought to be the main factor