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Preface: clay mineral diagenesis and very low-grade metamorphic processes. Proceedings of the 2011 Frey–Kübler symposium

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1 Introduction

In 2002, after the death of Prof. Bernard Kübler (Univ. Neuchâtel) and Prof. Martin Frey (Univ. Basel), Schmidt and Ferreiro Mählmann published a special issue on "Diagenesis and Low-Grade Metamorphism" in the Swiss Bulletin of Mineralogy and Petrology. Most contributions had been presented during the Symposium on "Diagenesis and Low-Grade Metamorphism" at the EUG meeting 2001 in Strasbourg, France, and had been dedicated to the two most important researchers in that field. The underlying philosophy of the "Diagenesis and Low-Grade Metamorphism" issue, was to provide a compilation of the state of the art in very low-grade metamorphic (VLGM) and low temperature petrologic research to:

(i) Geologists who wanted to use low-grade metamorphic petrologic, geochemical, clay mineralogical, isotopic and coal petrographic methods for their specific studies (e.g. in sedimentary geology, basin analysis, hydrocarbon geology, and regional metamorphic geology),
(ii) Research scientists interested in methodical and process aspects of diagenesis and low-grade metamorphism, and
(iii) Structural geologists with specialization in orogenic research.

Ten years later, it was planned to hold a 10th anniversary symposium but the VLGM family was strongly dispersed and changes in the EUG organisation and the management of the Copernicus Company made it difficult to continue with the traditional (1989–2003) meetings. With the death of Martin Frey the main organizer was also missing.

At the Mid European Clay Conference 2010 in Budapest (Hungary) contributions dealing with VLGM subjects were dispersed over several sessions and partly also included in the IMA conference part. Jan Środoń, Peter Árkai and the first author initiated "Crystallite" a special session focussed on "Clay mineral diagenesis and VLGM processes" at the EUROCLAY 2011 conference in Antalya, Turkey. The Turkish National Committee on Clay Science kindly supported this delayed 10th anniversary Frey–Kübler Symposium.

The present Swiss Journal of Geosciences issue dedicated to "Clay mineral diagenesis and very low-grade metamorphic processes" emphasizes that clay mineral reaction processes, chemical reaction progress and structural reorganisation and ordering play important roles in sedimentary and igneous rocks prior to the transformation into metamorphic rocks. Both Bernard Kübler and Martin

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Frey had strong interest in and have strongly influenced those specific fields. For this reason, two topics were selected for the Frey–Kübler Symposium:

1. Elucidating geothermal evolutions of basins and orogenic wedges using clay mineral indices (regional case studies, tectono-metamorphic studies and metamorphic mapping), and
2. New advances in palaeo-geothermometry: comparing clay mineral indices with other methods (theoretical approaches, new methods and improvements in methodology and calibration methods to determine grade of diagenesis and metamorphism).

It is a pleasure to realize that nearly all contributors to the Frey–Kübler symposium at EUROCLAY in Antalya 2011 have submitted their presentation for publication in this issue.

2 Content of the issue

The issue starts with a review study by the four chairman of the symposium together with B. Šegvić and R. Le Bayon (Ferreiro Mählmann et al.), which gives a historical view of the pioneer work of Martin Frey and Bernard Kübler and the evolution of very low-grade studies in the last five decades. This review covers their research in the Alps, stressing the Kübler-Index (KI) versus vitrinite reflectance (VR) and bituminite reflectance (BR) correlation. We discuss also the progress in understanding the physical meaning of the KI since the studies of Merriman et al. (1990); Środoń et al. (1992); Nieto and Sanchez-Navas (1994) and Árkai et al. (1996).

In comparison with KI, VR and BR data give different regressions and slope trends depending on the geodynamic conditions. Finally a critical discussion of the geo-thermometric use of KI and VR data (including Raman studies) is presented. For comparison of VR and BR with KI data, a unified and homogeneous data set of values is necessary. The study refers to nearly 5,000 values compiled and correlated with the help of an inter-laboratory calibration study (Ferreiro Mählmann and Frey). At the same time the study is a late result of the data compilation for the metamorphic maps of the Alps under the leadership of Frey et al. (1999) and Oberhänsli et al. (2004). Problems to include all published data from the Alps are due to different preparation and measurement techniques. It is shown in the review that standardisation and calibration of methods used to determine grade of diagenesis to incipient metamorphism are a fundamental pre-condition to successfully draw VLGM maps (Frey and Ferreiro Mählmann 1999) and to reconstruct paleo-geothermal conditions and geodynamic settings.

The following contributions are arranged according to the two topics of the Frey–Kübler symposium starting with two studies showing the methodical progress to determine grade of diagenesis to low-grade metamorphism and methods to calibrate the clay indices (Ferreiro Mählmann and Frey; Le Bayon). The first study emphasizes that KI should only be used if a standardisation was done with Kübler-Frey-Kisch standards, substantiating the previous conclusions by Brime (1999) and Kisch et al. (2004). CIS standards produce CIS values, which should not be mixed with KI values in the traditional KI subdivision of diagenetic zones, anchizone and epizone according to Kübler (1967, 1968). The second study describes an experimental kinetic maturity model using VR, which shows that the heat up effect has a tremendous influence on the T-P–t relationship and calculated regressions. The most important result, corroborating previous studies (Le Bayon et al. 2011; Le Bayon et al. 2012a; Le Bayon et al. 2012b), is the recognition of the varying pressure dependence with increasing maturity (Le Bayon et al. 2011). This experimental study emphasizes that pressure has a significant effect on VR at low temperature. The conclusion of the study must be considered for KI and other clay mineral indices calibrated with VR determinations when applying numerical temperature modelling packages in very low-grade studies (see Ferreiro Mählmann et al.).

The following studies deal with prograde and retrograde orogenic evolution and late geodynamic consolidation of an orogenic event. It is shown how crystal-chemical studies of clays (KI, white K-mica *b* cell dimension and polytype) can contribute to decipher between burial and previous sedimentary influences inherited through clay minerals re-deposited in sedimentary basins, in contrast to later orogenic thermal re-crystallisation and reaction progress (Bozkaya et al.). Even in very low-grade metasedimentary rocks burial information is recorded (see also Merriman and Frey 1999; Bozkaya et al. 2002). The importance of low-grade studies in deciphering the regional evolution of sedimentary terranes is also illustrated (Bozkaya et al.).

The comparison of KI with coal petrological data (Ferreiro Mählmann and Giger) and clay mineral data, fluid inclusion studies and fission track ages (Potel and Trullenque) are applied to determine diagenetic to incipient metamorphic conditions. In the first study it is demonstrated that a strong increase of data using a smaller sampling grid can strongly influence the interpretation of the data. From both studies it is evident that non-calibrated illite-"crystallinity" data (Ferreiro Mählmann and Giger) or the use of different standard sets (KI-values or CIS-values) (Potel and Trullenque) can obscure a compilation and/or give very different metamorphic grade.

It is also shown that, in agreement with Merriman and Peacor (1999), a short thermal climax produces different results using clay minerals or coal petrology due to different reaction kinetics. However, at steady state conditions during long time metamorphism the relationships are similar and equilibrated as previously shown by Ferreiro Mählmann (2001) and Potel et al. (2006).

Wang et al. focuses on a deep (7,000 meter) well in China, determining paleo-geothermal conditions, grade of metamorphism and applying the recently developed chlorite thermodynamic geo-thermometer (Inoue et al. 2009). The studied foreland basin shows a complete evolution from diagenetic to greenschist facies conditions, up to 350 °C. Studies to determine grade of diagenesis and metamorphism to establish P–T conditions imply multimethodical approaches (Frey 1987) as evidenced again by Wang et al.

A next group of papers deals with transformations mediated by fluids after the metamorphic-diagenetic peak. The post-orogenic metamorphic retrogression is often underestimated in very low-grade studies (Abad et al. 2003). Árkai et al. present conditions of hydrothermal-alteration processes which affected an epizonal slate series in Szendrő Mountains (Hungary), where progressively colder pulses produced Na–K white micas and muscovite-chlorite mixed-layers, halloysite and kaolinite, smectites and goethite. Abad et al. describe a very low-grade process, which reaches anchizone conditions, caused by transpressional deformation coeval with the movement of a major strike-slip fault in the Canadian Appalachians. No correlation was found between metamorphic grade, which increases towards the fault, and stratigraphic depth or strain values obtained by phyllosilicates orientation analyses. Changes in the illite XRD 10Å-peak sharpness can be the unique indicative method to detect a fluid-driven low-grade metamorphism along faults (Abad et al.). In a late stage of a hydrothermal process, the cooling of the circulating fluids favours the formation of clay minerals changing the original metamorphic pattern. Final stages of a hydrothermal activity and/or an influence of a younger near-surface weathering have also to be considered (Árkai et al.).

Fluid and phyllosilicate studies are also of importance to understand fault evolution and displacement mechanisms as shown by Leclère et al. and Buatier et al. Leclère et al. study the role of phyllosilicates in highly buried fault zones. By using thermometers based on the chemical composition of chlorite, they determine a temperature of 200 ± 20 °C, which corresponds to burial conditions between 6.5 and 8 km. They show that under deep burial conditions the fault petrophysic properties are mostly controlled by precipitation of synkinematic phyllosilicates.

The role of phyllosilicates in fault reactivation is also deciphered in the last article by Buatier et al. They combine high-resolution TEM and SEM studies with classical low-grade P–T characterisation based on K-white *b* cell dimension and phyllosilicate evolution. In agreement with Leclère et al., they show that the abundance of phyllosilicates allowed thrust fault reactivation.

3 Personality and research

Comparing Bernard Kübler (Fig. 1) and Martin Frey (Fig. 2) is not possible. Both had a very different personality and research character. Even so, it is evident from their literature lists that they were very different. Bernard Kübler used to be innovative and curious to try new things (either applying KI and the smectite-illite reaction progress in different fields). Martin Frey was more systematic with a focus on orogenic belts and restricted areas and applying different methods. During excursions, Bernard tended to deep and long, stimulating discussions retarding the approach to the next outcrop; Martin was enthusiastic on facts and memorising incredible details and he was just on time at the next outcrop. Nevertheless, the collaboration of the Neuchâtel and Basel groups are the reason why Switzerland was a leading country in very low-grade studies during two decades.

Fig. 1 Bernard Kübler in 1991 (with yellow cap) visiting a piemontite-schist quarry on the South Island of New Zealand during the IGCP project 294 excursion. Photograph by Rafael Ferreiro Mählmann

Fig. 2 Martin Frey in 1991 on the Pilatus with "his" Helvetic Alps in the background. Photograph by Anja Frey

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