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Standardisation, calibration and correlation of the Kübler-index and the vitrinite/bituminite reflectance: an inter-laboratory and field related study

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Abstract A multiple inter-laboratory calibration with illite Kübler–Frey–Kisch "crystallinity" index and related standards is presented and compared with CIS standards used in the last two decades in very low-grade metamorphic studies. Comparing CIS values with KI standards the CIS values show a higher full width at half-high maximum peak intensity. In all cases due to broadening effects on the Kübler-index, zone-limits, specifically the diagenetic zone/anchizone boundary, a shift is produced in geographical dimensions in a metamorphic map-view. Combining standardised Kübler-index and vitrinite–bituminite reflectance measurements a coherent data set for compilation studies can be generated from the data of different research groups. This attempt to establish a unified database of independent measures to determine diagenetic/metamorphic zones with different analytical instrumental methods are indispensable to present metamorphic maps at very low-grade conditions. Given that the Kübler–Frey–Kisch standards are difficult to preserve for the future and presumably they will be replaced with ongoing time by the CIS standards, a rescue of the laboratory settings from Frey, Kübler and others is done. After having compiled the Kübler-index—vitrinite reflectance zones in the Alps for the "New Metamorphic Map of the Alps", the presented calibration and inter-laboratory correlation gives a chance to save the KI values obtained by very different preparation procedures applied. This is an important step for further studies in an area like the Central Alps with a very high data grid. This correlation study will also make it possible that nearly 90 % of Kübler-index data from Switzerland can be compared in future work. Using the same calibration and preparation technique no fundamental problem in data comparison is achieved for the vitrinite/bituminite reflectance data operation. The main problem arises when rock maturity is compared with CIS calibrated Kübler-index values. Kübler-index values obtained by the so-called CIS calibration are not compatible with Kübler–Frey–Kisch (Árkai, Aprahamian, Brime, Ferreiro Mählmann, H. Krumm, Leoni, Petschick) calibrated Kübler-Indices. Applying both standardisation approaches for field studies, partially different results are obtained.

Keywords Illite "crystallinity" · Kübler-index · Vitrinite–bituminite reflectance · Standardisation · Calibration · Correlation

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1 Preface

In diagenesis and low temperature metamorphic petrological studies a wide range of organic and inorganic indices have been routinely used to determine zones of diagenesis and incipient metamorphism in the temperature interval between 50 and 400 °C. The most frequent methods used in sedimentary basin, tectono-metamorphic, hydrocarbon generation, geothermal and hydrothermal studies are

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restricted to a limited routinely used number, as vitrinite (VR)–bituminite (BR) reflectance (used as organic matter reflectance (OMR) in the combined form), conodont colour alteration index (CAI), Kübler-index (KI), smectite–illite reaction progress (SIR) and fluid inclusion micro-thermo-barometry. Other methods to quantify the finite thermal grade of sedimentary and meta-sedimentary rocks, as graphitisation (structural ordering), organic combustion, clay mineral dehydration, chlorite "crystallinity" Árkai-index (Guggenheim et al. 2002), smectite–corrensite–chlorite reaction progress and C–O isotope studies are less known or of minor potential. All these are very useful complementary methods, which may help the researchers to avoid pitfalls that often occur when they use only one (KI) or two (KI and VR) methods (Ferreiro Mählmann 1994, 2001; Árkai et al. 2004, 2008). Application is often limited along a small temperature interval in diagenesis, very low-(anchizone) or low-grade temperature (epizone, low greenschist to blueschist facies) metamorphism (Ferreiro Mählmann et al. 2012). Through a Georef research the reader will find more than 500 ISI publications referred to one of these methods, but "only" 185 based on a comparative methodology and including some 50 with a systematic methodical background frequently cited in literature.

Most of the more than 500 studies deal with a limited number of samples (commonly used for a routine control of other methods) or are restricted to a correlation between indices of similar nature [e.g. KI vs. SIR, IC vs. apparent mean crystallite thickness and lattice strain, coalification (VR, OMR, CAI, BR) versus graphitisation (Raman spectroscopy, XRD peak sharpness ratios), VR versus BR or CAI or graptolite reflectance]. If the parameters used are controlled by the same factors as temperature, pressure, host rock chemistry, structural ordering process, strain, crystallisation process and or fluid-rock chemistry, an accurate temperature determination assuming steady-state conditions (specifically heat flux) is mostly close to maximum temperature. In most rocks different stages of equilibrium between two parameters are frequently found and probably one or both indices did not equilibrate at the maximum thermal level and at finite temperature (Ferreiro Mählmann et al. 2012). Therefore, in the last decade more interest was given to study internally independent indices, e.g. the comparison of organic and inorganic geo-thermometers with strongly different kinetics. If two indices selected from both methodological fields (clay mineralogy and coal petrography) do determine the same thermal level, it is thought that temperatures at peak-conditions are well approached (Frey 1987; Frey and Robinson 1999) and thus are the basis for a precise geo-thermometry (Ferreiro Mählmann 2001). Given the reason for a comparative standardisation and correlation of KI/VR (OMR) data, the present research will focus on Alpine studies as field of reference.

2 Introduction

With the compilation of the data set for the New Metamorphic Map of the Alps (Frey et al. 1999) it was planned to include all very-low grade metamorphic data. The central part of the map was the most complicated task including some 5,000 samples of very different provenance. Part of a new revision and inclusion of these data have been published in this special issue by Ferreiro Mählmann et al. (2012) and Ferreiro Mählmann and Giger (2012). From the Morcles (Bernese Alps) to the Arosa zone (Grison Alps) close to 10,000 samples are available. For a uniform data presentation and drawing of iso-lines of KI and iso-maturity levels (iso-lines of OMR) it was necessary to prove the comparability of data, laboratory preparation procedure, measurement devise settings, standardisation used and data comparison in the map-view studied by different research groups. The largest number of very-low grade data in the Alps is presented using the KI and as next follows VR and fluid inclusion (FI) micro-thermometry. The last method is nearly exclusively limited to the Helvetic nappe pile and the foreland basin of the Swiss Molasse. Thus, it was decided to attempt first a uniform data presentation of KI and VR (Frey et al. 1999; Frey and Ferreiro Mählmann 1999). The intra-laboratory study started much earlier when the Hans Krumm group of Frankfurt am Main (Germany) directed very-low grade studies (Krumm 1984; Kralik et al. 1987; Krumm et al. 1988; Petschick 1989) from the Northern Calcareous Alps (Germany, Austria) to the Swiss-Austrian boundary (Ferreiro Mählmann 1994). In that area a large number of older studies were present (for a review see Ferreiro Mählmann and Giger 2012). When presenting the first draft on the IGCP project 294 "Low Temperature Metamorphism" (1987–1993) meeting in Auckland (Krumm et al. 1991; see also the first available map of Ferreiro Mählmann and Petschick 1996) iso-lines of KI of different groups have caused sub-parallel iso-lines with some erroneous low-angle intersections (including maturity data more complex intersecting KI and VR iso-line patterns resulted).

Some recommendations from these calibration and correlation research will be given corroborating prior suggestions (Kisch 1987, 1991; Kisch and Frey 1987). The correlation of the KI measurements carried out in the various Swiss and German laboratories is presented, including the still debated problem of the differences found between the original ("orthodox") Kübler–Frey–Kisch calibration of the KI-based metamorphic zones and that of the so called CIS calibration introduced and suggested by Warr and Rice (1994). This question was already discussed and the discrepancies explained by Kisch et al. (2004). However, the present study would give valuable contributions to this question, which still causes problems within the society of researchers dealing with very low-grade metamorphism (see also Leoni 2001).

3 Sampling and selection of standards

3.1 Kübler-index standards

To compare calibrations and KI values published, two ways are possible to recognise the accuracy and analytical sensitivity to determine zones of diagenesis and metamorphism: (a) From a field based KI correlation in comparison with VR (BR) data, and (b) from an inter-laboratory calibration of KI and VR (BR) standards.

A. During recent field studies 2,000 KI-VR measurements of samples from a complex lithology from Switzerland (excluding the Swiss Molasse) were recovered. Samples include pelite, clayey-siltstone, marls, marly-limestones and their meta-equivalents to incipient metamorphic conditions with the first occurrence of metamorphic facies-indicative phases.

Some strata are problematic to be used for KI metamorphic studies: (1) The Alpine Verrucano, Taveyanne formation and Flysch formations of the Helvetic nappes, (2) the North Penninic flysch rocks, (3) the flysch formations of the South Penninic nappes, (4) the Mesozoic detrital basis of the nappe and of the Austroalpine nappe stack, and (5) the Saluver group (Jurassic) and the Raibl formation (Triassic) of the Austroalpine Mesozoic cover (some of these formations are well suited for VR studies). All these were excluded from the following interpretation. All these stratigraphic units contain a high amount of detrital minerals or detrital graphite. The phyllosilicate detritus is often difficult to distinguish from newly formed clay minerals. Using the rest of the samples a field comparison is carried out using the results of different research groups based on their calibration and measurement procedure.

B. In the laboratory approach, several standards were used:

1. Mica schist rock chip (greenschist facies) and powder sample standards (low epizone to high anchizone) were kindly provided by Bernard Kübler (Petschick 1989, not shown in Table 1).
2. Mica schist rock chip (greenschist facies) of Martin Frey to detect the lower limit of the measuring device control. Alternatively, a single pegmatitic muscovite crystal can be used.
3. Powder sample standards of the Bern group (series available in Basel University) and used mostly in studies in Bern and Basel until 1988 (also at ETH Zürich, Switzerland by A. Stahel; and Frey 1988, not shown in Table 1).
4. Powder sample standard series available at Basel University and used since 1988. Unfortunately the original material was lost in Basel after the death of Martin Frey (first series in Table 1, M. Frey samples).
5. Powder sample standards of the Basel group compared and used later by the Krumm group in Frankfurt (Germany), kindly provided by R. Petschick (Frankfurt University), and now used at the Technische Universität Darmstadt (third series in Table 1, Ferreiro samples). These specimens were newly prepared from the powder material of the series (4) by Ferreiro Mählmann (1994).
6. Phyllite rock chip (M 6/2) and powder sample standards, now used at the Technische Universität Darmstadt (fourth series in Table 1, Ferreiro samples). Samples contain illite, chlorite and some quartz. Sample Be 5/III shows 12 % of discrete smectite (the smectite determination was done on ethylene-glycolated samples).
7. CIS standards kindly provided by L. Warr (second series in Table 1, SW samples—Heidelberg, Warr and Rice 1994).

Standards selected for the first, third and fourth series were taken from the large sample collections in Basel and Frankfurt (Table 1). The samples used have a high KI value precision after repeated XRD-runs (measurement device control) also using different specimens or changing the specimen holder x–y plane position (sample variation control) with a very low standard deviation (Ferreiro Mählmann 1994). Standards used in a pre-selection were run 6 times (Frey 1988; also Kübler and Stahel pers. communication) to 20 times (Ferreiro Mählmann 1994; also Krumm and Petschick pers. communication). Using newer generators and with available current stabilised X-ray tubes there is less scattering of XRD peak shapes observed. Later, initiating the daily XRD-run the standard measure was repeated for two times (at run start and run end). With this procedure an additional control of the X-ray tube stability was possible and the final run-out (crash) predictable. During the final alteration process of the Cu$K\alpha$ radiation-tube (1 week, but mostly several month to 3 years) until break, alteration corrections in intensity (counts per second, cps) and KI values were necessary.

For standards, only samples with no discrete smectite content (13–15 Å in air dried, 17 Å in ethylene glycol treatments) were used (<5 %, below the detection limit). The standards chosen did not exhibit asymmetries in the peak shape (Brindley and Brown 1980). The use of smectite-rich samples was avoided and thus no significant smectite influence on air-dry sample KI measure should happen. Re-measuring some smectite bearing samples

Table 1 Illite data of standards measured in the inter-laboratory project are presented from the University of Frankfurt, the University of Basel and the Technische Universität Darmstadt (TUD)

Laboratory	Frankfurt	Frankfurt	Frankfurt	Basel	Basel	TUD	TUD		All
Standard	Illie (001)	Illite (001)	Illite (001)	D. 500	D. 5000	Phillips	D. 5000	CIS	Illite
Sample number	10 Å	10 Å	10 Å	10 Å	10 Å	10 Å	10 Å	10 Å	FWHM
	Intensity	Area	FWHM	FWHM	FWHM	FWHM	FWHM	FWHM	s2
Series 1									
ALL73-113 M. Frey	1,307	53,796	0.704	0.75	0.71				
MF 993–M. Frey	2,275	36,739	0.241	0.21	0.21				
MF 996–M. Frey	2,804	44,320	0.247	0.20	0.19				
MF 1,030–M. Frey	2,786	56,814	0.326	0.33	0.31				
MF 1,031–M. Frey	2,632	63,933	0.386	0.35	0.37				
G 33–M. Frey	1,952	46,277	0.382	0.40	0.39				
G 34–M. Frey	2,370	57,396	0.373	0.43	0.42				
G 36-6–M. Frey	2,178	68,754	0.525	0.52	0.55				
G 36-21–M. Frey	1,621	45,003	0.448	0.44	0.47				
G 36-35–M. Frey	3,566	106,666	0.486	0.58	0.62				
G 37-1–M. Frey	1,201	25,930	0.320	0.33	0.35				
G 37-7–M. Frey	1,566	54,038	0.565	0.69	0.70				
Series 2									
SW-1/a–Heidelberg	2,297	77,344	0.528	0.55				0.63	
SW-1/b–Heidelberg	2,602	83,809	0.533	0.59				0.63	
SW-1/c–Heidelberg	2,010	64,182	0.519	0.54				0.63	
SW-1/e–Heidelberg	1,734	54,906	0.520	0.57				0.63	
SW-1/d–Heidelberg	2,188	70,259	0.522	0.58				0.63	
SW-2/a–Heidelberg	2,132	51,533	0.377	0.40				0.47	
SW-2/b–Heidelberg	2,152	52,011	0.375	0.43				0.47	
SW-2/c–Heidelberg	1,766	43,392	0.376	0.39				0.47	
SW-2/d–Heidelberg	2,103	51,917	0.374	0.40				0.47	
SW-4/1–Heidelberg	2,258	46,598	0.314	0.33				0.38	
SW-4/1–Heidelberg	1,931	41,676	0.325	0.35				0.38	
SW-4/2–Heidelberg	2,214	44,837	0.295	0.31				0.38	
SW-4/3–Heidelberg	2,155	44,005	0.304	0.31				0.38	
SW-4/7–Heidelberg	2,041	42,349	0.312	0.33				0.38	
SW-4/5–Heidelberg	1,907	40,806	0.320	0.34				0.38	
SW-6/a–Heidelberg	4,560	63,565	0.220	0.23				0.25	
SW-6/2–Heidelberg	5,065	69,545	0.215	0.22				0.25	
SW-6/6–Heidelberg	5,379	72,507	0.212	0.21				0.25	
Series 3									
ALL73-113–Ferreiro	1,079	43,996	0.729			0.81	0.78		0.05
MF 993–Ferreiro	2,252	39,579	0.265			0.21	0.21		0.00
MF 996–Ferreiro	2,424	42,762	0.256			0.21	0.22		0.01
MF 1,030–Ferreiro	2,306	50,153	0.344			0.32	0.33		0.03
MF 1,031–Ferreiro	2,734	66,693	0.393			0.37	0.39		0.02
G 33–Ferreiro	2,190	53,986	0.388			0.34	0.34		0.02
G 34–Ferreiro	2,607	62,707	0.379			0.35	0.37		0.04
G 36-6–Ferreiro	1,541	51,315	0.547			0.53	0.53		0.02
G 36-21–Ferreiro	1,866	52,632	0.456			0.42	0.45		0.04
G 36-35–Ferreiro	4,132	130,498	0.511			0.52	0.54		0.02
G 37-1–Ferreiro	1,133	23,618	0.321			0.26	0.25		0.01
G 37-7–Ferreiro	1,835	65,325	0.595			0.61	0.72		0.06

Table 1 continued

Laboratory	Frankfurt	Frankfurt	Frankfurt	Basel	Basel	TUD	TUD	All
Series 4								
M 6/2–Ferreiro	10,614	159,702	0.230	0.20	0.19	0.21	0.21	0.01
K 5/2–Ferreiro	1,151	37,613	0.531	0.55	0.54	0.51	0.54	0.04
J 32/III–Ferreiro	868	33,660	0.665	0.56	0.59	0.57	0.57	0.02
AS 3/1–Ferreiro	1,316	41,201	0.487	0.46	0.46	0.43	0.45	0.02
Pa 14/3–Ferreiro	2,764	49,109	0.263	0.22	0.21	0.21	0.21	0.01
Pa 19/1–Ferreiro	2,440	52,374	0.319	0.27	0.28	0.25	0.28	0.03
KR 71/I–Ferreiro	774	21,594	0.408	0.34	0.34	0.33	0.33	0.01
KR 72/III–Ferreiro	2,624	80,501	0.509	0.50	0.49	0.50	0.48	0.03
J 37/bII–Ferreiro	918	28,273	0.483	0.37	0.37	0.39	0.39	0.03
KM 33/2–Ferreiro	899	37,890	0.742	0.69	0.74	0.69	0.70	0.05
Be 5/III–Ferreiro	907	51,195	1.137	1.00	0.92	0.97	0.99	0.07
Re 8/II–Ferreiro	833	40,245	0.919	0.80	0.81	0.81	0.83	0.02

The first sample series is from Martin Frey (Basel), the second series was also measured at the University of Heidelberg and is from the CIS series provided by Warr and Rice (1994), the third is a newly prepared series from the rock standard collection of Martin Frey and used at the TUD, the forth standard series is prepared from own samples to have sufficient reference material for future studies

(All 73–113 of M. Frey, SW 4 of Warr and Rice and Be 5/III of Ferreiro Mählmann) and using the Cu$K\alpha$ radiation-tube control described, it was found that the sharpness of the 10 Å-illite peaks changed and lower cps intensities occurred during a time span of 10 years. At the same time the variances of 3–6 re-measurements increased drastically (10 % and more). Presumably the smectite expandability was changed under laboratory storage conditions. In other laboratories no smectite layers were detected in sample SW-4 after ethylene–glycol checking (pers. communication F. Nieto and R. Petschick).

Some samples also showed piling scratches and bulging from the slide, provoking that the samples were no more utilisable because the x–y plane is disturbed and thus the illite aggregates are no more oriented in the lattice plane (a–b). According to the Scherrer equation (Scherrer 1918) FWHM is a variable and reversibly dependent of the domain size. Using the Debye–Scherrer geometry diffraction KI is referred to the number of lattice basal planes in a textured sample (diffraction domain). Peak position, maximum intensity, peak shape and asymmetry are dependent according the Bragg′s law. Thus, if the x–y plane is disturbed the samples are no more utilisable.

The Frey standard (e.g. All 73–113) from the low-grade diagenesis showed piling phenomena and, because of this, it is now lost at the laboratory in Darmstadt. Also, some of the Frey standards got disappeared (lost in Basel) or altered and with time, it is to expect, will also in the international KI community. The new availability of the CIS standards of Warr and Rice (1994) is of course in this respect a principal advantage.

3.2 Vitrinite–bituminite reflectance standards

Standards used for the VR, BR and OMR calibration were:

1. Yttrium–aluminium–garnet, with a reflectance $R =$ 0.880 %,
2. Gadolinium–gallium–garnet ($R = 1.719$ %),
3. Cubic-zirconia ($R = 3.114$ %),
4. Diamond ($R = 5.237$ %).

Also some standards from USGS standards of coals were used and measured at different laboratories (RWTH Aachen, University Basel, TU Darmstadt). The preparation of standard vitrinite mounts consisted of plucking numerous vitrinite particles from the recovered samples, embedding them in epoxy resin and then polishing the mounts at room temperature using 3.0, 1.0 and 0.5 µm diamond powder and felted wool for the last polish to avoid scratches that cause relief and shadows that could change reflectance.

To detect the lowest VR the xylite sample for the experimental studies of Dalla Torre et al. (1997) and Ernst and Ferreiro Mählmann (2004) was used as standard. This material is a lignite, gymnosperm wood (huminite), originated from seam Frimmersdorf in the mining area of the Lower Rhine Basin, open cut Hambach (Germany) and has yielded a vitrinite reflectance value of 0.197 ± 0.008 %R_r. The reflectance of ulminite B and densinite components of the seam is 0.30 %R_r. The texture of the bi-maceral microlithotype clarite is characterized by well-preserved ulminite (huminite) with liptinite (resinite) as cell infillings and shows only slight effects by the process of compaction and altering by peatification, humification, and gelification of huminite. For the petrographic and organic-geochemical description of the micro-lithotype and the seam see Dehmer (1988). Standard calibration was done by 1,000 measurements and the standard variation on all standards was smaller than 1 %. Thus for the KI/VR correlation the starting reflectance of 0.20 %R_r will be used. For this value only a theoretical KI value as computed on extrapolated regression lines can be calculated, but is not reasonable, thus in the graphs only the high grade diagenetic zone to epizone is shown.

3.3 Kübler-index method

For the rock-slab specimens (mica schist chips from Kübler and Frey, and phyllite chip M6/2) a thick section was cut parallel to the bedding or cleavage (to get the best phyllosilicate orientation perpendicular to the c-axis) and then polished at room temperature using 3.0, 1.0 and 0.5 µm diamond powder and felted wool for the last polish.

For the powder specimens (all other samples from Table 1) a 200 g clay or meta-pelite rock-slab was crashed to 1 cm particles and grinded in a mortar-mill, as used in Frankfurt and Darmstadt for maximum 2 min (in disc-mill for less than 40 s, as used in Basel). After 20–300 s grinding, important influences were detected (Wang et al. 1995). Also using the mortar-mill (Darmstadt) a decrease of coarser mica fractions was observed and a increase of the <2 µm fraction (controlled using Atterberg fraction separation), resulted in smaller KI values. This is explained by the destruction of detritic coarser micas and the particle size reduction of well-ordered material, which was included in the authigenic clay fraction after grinding.

If possible, clay samples were only treated to be disintegrated in an ultrasonic bath. Later the sample was de-carbonated with 100 ml 20 normal formic acid (other low oxidising acids can be also used). Formic acid has the advantage that salt-products precipitated in the solution during a 3-day treatment (with continuous control to keep the pH below 7.0 by adding acid) do not interfere with illite peaks. Also frequently used, 10 normal hydrochloric acid (e.g. by the Frey group) has no influence on illite but it can alter discrete smectite, other Fe-rich smectites, mixed layer phases and in a large extend vermiculite (causing decrease in cps and broadening of the sharpness ratio). Later, the method was changed to remove carbonate by treating with 5 % acetic acid and by washing with de-ionized water. In a comparative study, higher acid concentrations (normalities) have caused different intensity and peak-shape changes, thus have an influence on the KI values. This effect is more prominent in low-grade diagenesis samples but less recognised in epizone samples.

To solve formicates the samples can be washed with de-ionized water after removing the solution during Atterberg sedimentation. The fraction <2 µm (clay fraction) was extracted by Atterberg technique. In Frankfurt and Darmstadt the slight acidic solution was then neutralised with NH_3 and in Basel and Zürich untreated. In Basel and Neuchâtel the clay fraction was Ca-saturated with 2 N $CaCl_2$ and, as in Zürich, a suspension is sedimented on a glass slide settled on tubes and a Millipore filters with 0.1 µm pore size (Schmidt et al. 1997).

Preferred orientated clay specimens enhances their (00*l*) reflections by arranging basal surfaces parallel to the specimen surface. Oriented slides were prepared by pipetting suspension onto glass slides ($\sim$5 mg cm^{-2}) and allowing to air dry (as done in Basel and many other laboratories). Others (e.g. Árkai) used 3 mg cm^{-2}, but in such circumstances (5–3 mg cm^{-2}) a differential settling within the suspension column pipetted onto the glass slide can be observed. In addition, the surface often will not be smooth. It is thought that 2 mg cm^{-2} of clay material is the optimum amount.

In Frankfurt the suspension of 5 (later 2 mg clay material) was sedimented in a copper cylinder on a glass slide and 23 °C air-dried (mostly during 3 days). Comparing the technique from Basel and Frankfurt a better orientation (no *hkl*) was evident using the copper cylinder textured slides (a precise description is given by Petschick 1989). This technique is now obsolete in Frankfurt since 1994, because of the problem of much different sinking times of the clay material having different suspension amounts (Ferreiro Mählmann 1994). In the last decades R. Petschick used exact weighed ultrasonic re-suspended dried clay samples for all texturated preparations. The preferred orientation of the clay minerals was noted to be slightly better on glass slides than on ceramic tiles as documented also by Dohrmann et al. (2009).

Compared to illite, smectites are very fine grained with flexible morphology, which is believed to be the reason for their tendency to exhibit poor orientation, but mixtures of phyllosilicates homogenises preferential ordering (Dohrmann et al. 2009). Due to the smectite alteration, the standards All 73–113 of M. Frey, SW 4 of Warr and Rice, and Be 5/III of Ferreiro Mählmann showed high variations in KI values from the very beginning of the study (Table 1). Probably a lower orientation or variance in orientation is another reason for the standard deviations found in Basel and Darmstadt. An amount of 1 mg, later 5 mg cm^{-2} of textured material is attempted for most samples (Krumm et al. 1988). For more details see the recommendations of Frey (1987) and Kisch (1991). Values from 5 mg cm^{-2} mounts have a more homogeneous KI spectrum than thinner glass-slide specimens, but show slightly broaden KI values at low-grade conditions.

Nevertheless, as demonstrated from Table 1 the values from the different laboratories are compatible. Below 1 mg cm^{-2} the variance increases. In very thin slides (<1 mg cm^2), in quartz and feldspar rich rocks the *hkl*-lines increase in cps and the KI equivalent value differs strongly. Non-platy minerals cause a disorder in preferred orientation.

Drying at laboratory air conditions is preferred to drying in an oven at <40 to 50 °C (specially for diagenesis standards). Temperature drying has shown some important differences in regard to air-dried samples. After finishing preparation the texture specimen is ready for the XRD run. Run conditions have been the same in all laboratories, but using different generators (Table 1):

- CuKα radiation, 40 (42) kV, 30 mA;
- Automatic primary slit (V20) and secondary (V20) divergence slits (Siemens D 5000)
- Ni filter, slits 1°, 2.0 mm, 1° (Philips PW 1320)
- Secondary graphite monochromator (proportional counter, Philips PW 1965/50)
- Goniometer settings for air-dried preparates: 2–21°2θ with a step increment of 0.02°2θ per minute and a time constant of 30 s.
- For the other generators (e.g. Siemens D 500) the setting was chosen to be similar.

With increasing grade of diagenesis and metamorphism a steady sharpening of the 10 Å-illite peak is characteristic (Kübler 1964; Frey 1969). Due to that trend it is possible to characterise a diagnostic and continuous sensitive parameter to determine grade of metamorphism over a wide range, using the full width at half-high maximum peak intensity (FWHM) systematically elaborated by Kübler (1967, 1968, 1990) and Dunoyer de Segonzac et al. (1968). In that early days Frey (1969) was one of the first scientist who has proved the illite "crystallinity" in a regional work to study very low-grade metamorphism in the Helvetic Alps (Ferreiro Mählmann et al. 2012).

The results of the standard measurements at the different laboratories are given in Table 1. Using the original standards of Kübler (Fig. 1) and including in the graph of Petschick (1989) Kübler's mica schist rock chip (0.125Δ°2θ) and the M6/2 standard, the anchizone is defined with the limiting KI values as follows: diagenetic zone (zone of diagenesis) $\geq$0.42 Δ°2θ, anchizone 0.42–0.25 Δ°2θ, and epizone $\leq$0.25 Δ°2θ (Kisch 1987). The KI values and the KI equivalent values correlate 1:1 ($r = 0.982$). Thus, the limiting values can be transferred to the standard series of the different laboratories shown in Table 1. The anchizone limits, using the illite fraction <2 µm (Kübler 1967), are recommended by the International Union of Geological Sciences Subcommission on the Systematics of Metamorphic Rocks (Árkai et al. 1990, 2007).

The KI mica schist rock chip (Frey-standard) to detect the lower limit of the measuring device control gave 0.125 Δ°2θ (Philips PW 1320, Frankfurt and Siemens D 500, Basel), 0.13 Δ°2θ (Philips PW 1320, TU Darmstadt) and 0.122 Δ°2θ (Siemens D 5000, Basel). By use of the Frankfurt equipment the same limit was observed on a single muscovite crystal. The D 5000 in Basel was in general (regarding peak intensities and sharpness ratios) the most sensitive equipment used in the calibration project. In the correlation KI/VR graphs the limit of the XRD measurement device control is indicated.

3.4 Vitrinite–bituminite reflectance method

Vitrinite reflectance was measured according to standard procedures (Stach et al. 1982). The 546 nm wavelength monochromatic-light reflected from the vitrinite mount surface is measured using a photomultiplier coupled to a Leitz 319 Orthoplan-photometer microscope (Basel, Darmstadt) and calibrated with a single standard. The microscope is equipped with a 125× oil-immersion objective coupled with a 10× ocular. A non-drying immersion oil with a refraction index $n_e = 1.518$ (at 23 °C and for 546 nm wavelength monochromatic-light) was used for reflectance measurements. The VR measurement equipment was placed on a sturdy workbench to avoid vibration during measurement.

In addition, measurements were operated in dim light at about 23 °C. Calibration was done according to standard procedures detailed by Taylor et al. (1998). The quality of calibration was checked every 20–30 min during measurements. Measured VR is the mean random vitrinite

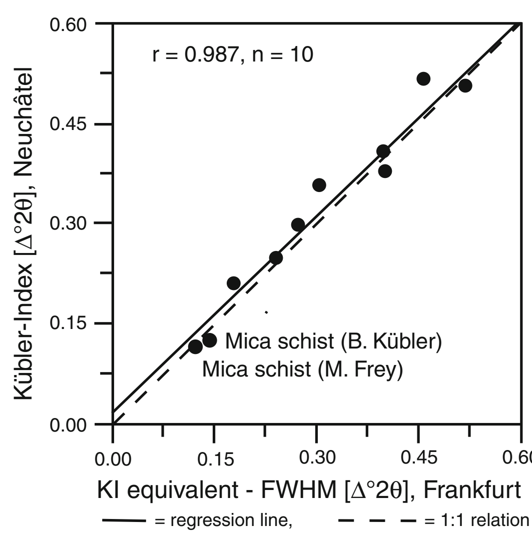

Fig. 1 Correlation between standards used by B. Kübler and re-measured in Frankfurt by R. Petschick (Petschick 1989). The same standards were used in Basel for the present study and the correlation was nearly 1:1, $n = 10$, $r = 0.982$ (not shown)

reflectance (%R_r) below 1.3 %. VR measurements were only carried out on telinite. At higher rank, maximum reflectance was measured under polarised light (Taylor et al. 1998). In this case VR is written as %R_{max} (mean maximum reflectance).

4 Results

4.1 Inter-laboratory vitrinite–bituminite reflectance comparison

The same instrumental procedure than shown for VR was used for BR measurements. Because BR measurements are not very frequently correlated with KI, but of importance in VR-OMR studies in coal petrology, it is shortly reported how to select useful secondary macerals of bituminite: Maximum and minimum reflectance was measured for large and anisotropic cata-bituminite. Bituminite gives qualitative information about metamorphism in rocks without vitrinite phytoclasts, which is very frequent in many rocks of the Alps (most Austroalpine Triassic rocks, Helvetic Permo-Triassic cover, Middle Penninic formations and most North Penninic Flysch units). In the Triassic of the above-mentioned tectonic mega-units solid-bituminite is the most abundant dispersed organic matter. In the zone of diagenesis it is often associated with alginite (proto-bituminite). In some limestone formations of the Austroalpine nappes vitrinite is even completely missing. This paper contains only few values of proto-bituminite, because most areas used for this calibration have surpassed the low-grade diagenesis. Nevertheless the few data included in the study show that the reflectance values according to Bertrand (1993) are only a semi-quantitative indicator of maturation. The proto-bituminite population shows mostly a high standard deviation for single samples.

Bi-reflecting bituminite with homogeneous extinction is preserved in the studied units until VR = 8.0 %R_{max} (see also Bertrand 1993; Koch 1997). Between 1.5 and 4.5 %, when oxidised, the slightly brownish –grey colour changes to bronze and reflectance increases in relation to the less influenced vitrinite (more resistant to oxidation). In low-grade diagenesis the rims are mostly darker than the unaltered isotropic core and associated with undulatory extinction, as also cracks with alteration rims. Bituminite is a good marker for oxidation stages, like later when at higher alteration pyrite is altered to limonite. In pelites (clay to claystone) the irregular isotropic bituminite patches have sometimes a darker grey dendritic vein-like texture. Within the formation of a slaty cleavage the bituminite interfingers in the lepidoblastic framework and between the sheets of illite/mica–chlorite and frequently shows a large mass of degassing pores (cata-impsonite of Jacob 1967).

Resin mounted sections were prepared from the KI standards. No oxidation on bituminite was found. In few samples, pyrite was detected with a high metallic glance. Thus, the standard material is regarded to be very fresh without weathering features. The smectite content determined by XRD is of diagenetic to low anchizonal authigenic origin. This control was performed for the M. Frey and Ferreiro samples (Table 1). From the SW standards only powdered material was available.

Homogeneous isotropic bituminite occurs as broken particles very similar to vitrinite. The rounded habitus and the low relief are distinctly different from vitrinite. Also the soft material is fingering into the pores. These bitumens probably are solid residues of oil (Robert 1988) and can be easily misinterpreted as vitrinite (see also Koch 1997). The bituminite reflectance of the homogeneous anisotropic and isotropic bituminite shows a significant correlation (Fig. 2) with VR and (if autochthonous) can be used as a rank-indicator for the grade of diagenesis and metamorphism. Migrated bituminite can reflect a stage posterior to peak thermal conditions of burial, e.g. by penetrating from lower grade tectonic units overthrusted.

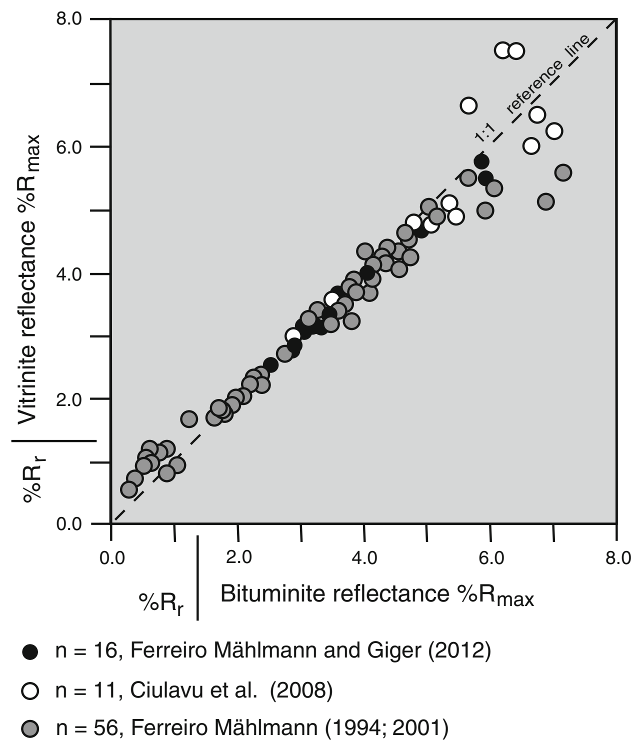

Fig. 2 Plot of vitrinite reflectance and bituminite reflectance values from samples where both macerals were measured. In all areas referred, the same preparation and measurement technique was applied and may give the reason of the low variance along the 1:1 reference line between 1.5 and 4.5. Solid bituminite can be used for determining very low-grade metamorphism. The scattering above 5.5 is due to different trends related to strain increase and contact metamorphism in the studied tectonic settings

A second group, an anisotropic bituminite with a high bi-reflectance and undulatory extinction and bituminite with a small bi-reflectance (0.0–1.0 %), shows a mean reflection with a high standard deviation (>10 to 30) and strongly varying mean values (±2.0 %). The bituminite was generated mostly from alginite (lam-alginite) and probably also from other liptinite and should not be used for calibration and correlation studies.

A third group, bituminite at higher grade than anchizone shows a reflectance around 4.0 % and a feature similar to pre-graphitization. This bituminite appears as rounded, forming nearly sub-microscopic spheres with poorly developed or no Brewster cross and helicitic extinction in cross-polarized light (probably the initial stage of forming 'graphitoid spheroliths', Stach et al. 1982; Robert 1985; Bertrand 1993). It is, however, very difficult to measure reflectance when areas are so small, causing a decrease of reflectivity. Also in these rocks, vitrinite has an abnormal bi-reflectance and a high VR of 6.0–7.0 $\%R_{max}$. In some samples, bituminite has some characteristics of natural coke. These bituminite show sometimes hexagonal joints perpendicular to the rim and contain many fine fissures, pores and vesicles. The natural coke (pyro-bituminite) occurrence would be important for reconstructing the thermal history, but it is not useful for calibration purposes.

Comparing the calibrated samples interchanged between RWTH Aachen, University Basel and TU Darmstadt the results gave same values with an error lower than 2 %.

4.2 Correlation of vitrinite reflectance and bituminite reflectance

Bituminite reflectance is equivalent to VR between 2.5 and 4.5 % (Fig. 2). Below 1.5 $\%R_r$ the regression is similar to that of Jacob (1989):

VR $\%R_r = 0.618 \times$ BR $\%R_r + 0.4$ (BR $\%R_r = \%R_o$-solid, Jacob 1967).

The difference is ±0.1 to 0.2 %. At even lower rank, below 0.5 $\%R_r$ the bituminite (migra-bituminite) shows an irregular darker grey (Jacob and Hiltmann 1988). In the range of 1.5–3.0 $\%R_{max}$, the regression is close to that found by Landis and Castaño (1995):

VR $\%R_r =$ (BR $\%R_r + 0.41)/1.09$.

Also it is relevant the correlation over all the VR range from 0.20 to 8.0 $\%R_r/R_{max}$. Excluding the samples of the high temperature–low pressure facies in the Danubian window of Romania (Ciulavu et al. 2008) the equation fits to the regression given by Ferreiro Mählmann (1994):

BR $\%R_{max} = -0.519 + 1.341$ (VR $\%R_{max}) - 0.0977$ (VR $\%R_{max})^2 + 0.0151$(VR $\%R_{max})^3$ ($n = 83$, $r = 0.989$).

At higher maturity, the BR values increases more rapidly than VR values. This was also observed in the Oberhalbstein (Ferreiro Mählmann 1994, 1995, 2001) and Romania (Ciulavu et al. 2008) and could be explained by a clear strain effect. These samples are mostly close to, or located in, prominent shear zones (Ferreiro Mählmann and Giger 2012). Nevertheless, it is not clearly evidenced from an orogenic setting, if the effect is mainly strain related (Árkai et al. 2002) or caused by frictional heating (Suchý et al. 1997; Schönherr et al. 2004). From the mentioned areas in the Alps a frictional cause of that effect can be ruled out (Ferreiro Mählmann et al. 2012). Yet, the general equation of Jacob (1989) and Landis and Castaño (1995) is not applicable for the complete range of 0.20–8.0 VR ($\%R_r$, $\%R_{max}$). The difference may be explained by the differences in deformation history between a sedimentary basin with lack of strain (linear regressions) and an orogenic setting with high-strain rates (cubic regression). To exclude strain influences, for further calibration only the rank range of 2.0–5.0 $\%R_{max}$ will be used.

Furthermore it is to remember that a cata-impsonite does not have the same optical properties as a pyro-bituminite (Robert 1985; Ferreiro Mählmann 1994, 2001; Landis and Castaño 1995). We have therefore used only solid bituminite reflectance on homogeneous bi-reflecting particles (anisotropy not exceeding 3.0 %) without pre-graphitic or sphaerolitic-granular or undulating structures (Ferreiro Mählmann 2001; Ferreiro Mählmann et al. 2002). Linear regressions as used in sedimentary basins (Schönherr et al. 2007) probably cannot be applied to meta-sedimentary units in nappe tectonic areas. With increasing maturity and pressure, as indicated by Le Bayon et al. (2011) for VR data, a kinetic relationship may best explain the differences found (Ferreiro Mählmann et al. 2012) and these have to be similar for the increase of VR and BR values. Calibrated with the kinetically independent VR–BR method from KI, the use of different KI standard series and their impact on the correlation will be shown in the field study.

4.3 Calibration of the illite 10 Å-reflection measurements

Between the illite standard studies from Neuchâtel (Kübler) and Frankfurt (Krumm) a nearly 1:1 correlation was found (Fig. 1, Petschick 1989). The same was reported by Frey (1988) for the correlation between KI (Neuchâtel) and KI (Basel), but is less well established between KI (Basel) and KI (Frankfurt) published by Erdelbrock (1994). Inter-laboratory calibrations were established among B. Kübler, M. Frey, H. Krumm, R. Petschick and R. Ferreiro Mählmann using different equipments (Philips PW 1320, Siemens D500, Siemens D5000 and Bruker-AXS D-5000, see Table 1). A good re-production of measured values and a significant correlation is found between KI Basel (D 500) and KI equivalent FWHM Frankfurt (PW 1320) using the samples of series 1 ($n = 12$) and 4 ($n = 12$), including the mica schist rock chip of M. Frey:

KI Basel = 0.0545 + (0.8572 × FWHM Frankfurt), $r = 0.965$, $n = 25$ (Fig. 3).

The data were kindly provided by R. Petschick (Frankfurt). A later correlation used by Ferreiro Mählmann (2001) with the D 5000 (Basel) and also the AXS D 5000 (Darmstadt) gave no significant difference. With a lower range of error the same is valid for the correlation:

FWHM Darmstadt = −0.0278 + (1.0857 × KI Basel), $r > 0.99$, $n = 12$ (series 4, see Fig. 4).

Also including the measurements in mm (used in first very low-grade studies on analogues plots/measurements) with the correlation of Fig. 5 (see also Frey 1986) the values e.g. from older publications, e.g. of Kübler et al. (1979) and Frey et al. (1980) can be re-calculated as KI values and fit perfectly with data from samples from the same localities:

KI-FWHM ($\Delta°2\theta$), Basel = (KI-FWHM (mm, Bern)−0.57)/12.53, $r = 0.97$, $n = 69$ (see Fig. 5).

Regarding older studies (e.g. Dietrich 1969; Thum and Nabholz 1972), M. Frey calculated in Basel in comparison to Bern and Zürich anchizone limits of 7.5 and 4.0 mm and 7.7 and 4.2 mm respectively (aproximatively until 1975), later 7.8 and 4.6 mm due to an aging of the XRD measurement device control. In older studies from Frankfurt, 8.6 and 4.8 mm was given for the anchizone limits (for more details see Petschick 1989; Ferreiro Mählmann 1994). With the correlation shown in Fig. 5 the old IC/KI values can be adapted to the Basel data and thus expressed as KI values for a uniform data set presentation.

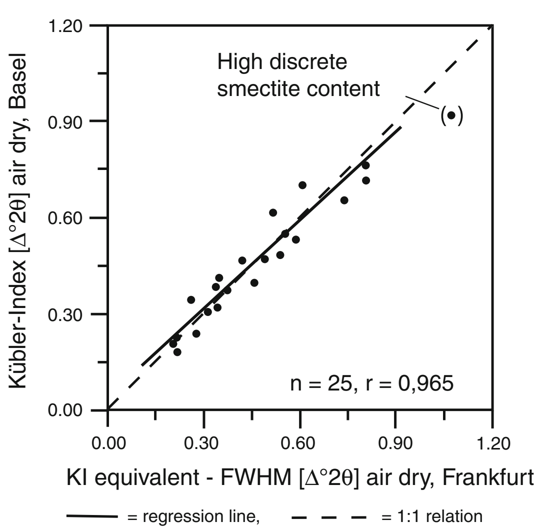

Fig. 3 Correlation between standards used by Martin Frey and re-measured in Frankfurt by R. Petschick (Petschick 1989). The same standards were used in Darmstadt for the present study and the correlation was nearly 1:1 ($n = 25$, $r = 0.965$). See text for regression equation

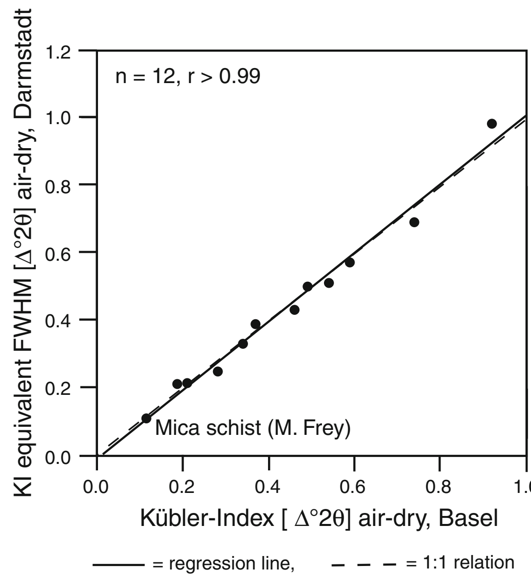

Fig. 4 Correlation between standards of Martin Frey and standards used by the technical petrology group at the TU Darmstadt (Table 1) to adapt the standard FWHM-values in $\Delta°2\theta$ to Kübler-Index data measured in Basel ($n = 12$, $r > 0.99$). See text for regression equation

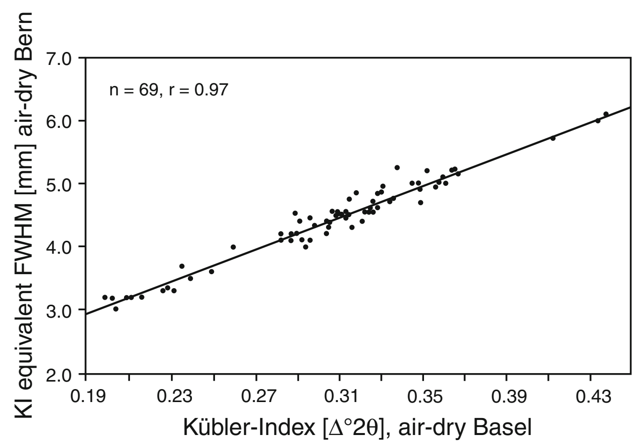

Fig. 5 Correlation between standards used by Martin Frey in Bern and in Basel to re-calculate the mm-values to KI $\Delta°2\theta$. The plot was re-drawn from an ink-painted graph by Martin Frey ($n = 69$, $r = 0.97$). See text for regression equation

It was a chance to get samples from the excellently organised rock collections of the ETH Zürich and the former Mineralogical and Petrological Institute of Basel. Therefore, it was possible to include samples for correlation purposes (series 1 and 3, Table 1) from F. Allemann (samples ALL), M. Frey (samples MF) and U. Gruner (samples G). Samples from P. Lüdin, M. Schweizer-Brüggemann, I. Thum and W. Winkler (Ferreiro Mählmann 1994, Table 1) were re-named according to the nomenclature of the reference rock-collection of the first author. These standard samples were included in the new series

(series 4, samples Ferreiro, Table 1). Unfortunately, after the retirement or death of the researchers, the rock collections, but also stored rock standards are more and more neglected at Swiss and German Universities, due to financial and space reasons. The excellence status of a university should be visible also in the potential to further re-investigate and use of published data (excellently demonstrated at the ETH Zürich). Refusing this responsibility will complicate research in many geo-science fields.

Samples of ALL, MF and G are now used for the recent correlation studies and calibration in Darmstadt (Table 1, series 3). Series 3 is identical to series 1, but a new specimen was prepared from the rock powder. Thus the present study is also a chance to save the documentation pre-dating the year 2000.

Data analysed at other universities during the interchange with working groups dedicated to the Swiss Alps, e.g. from Tübingen (Ring 1989) and Bochum (Henrichs 1993; Kürmann 1993) are not used for the presented comparison (Fig. 8) because calibration of this illite "crystallinity" (IC) data is missing or difficult (thus they cannot be referred as KI). All three authors have worked using IC data in the same Arosa zone shown on Fig. 8. But also having sampled the same localities, an acceptable correlation in the range of KI zones with the data from Henrichs (1993) and Kürmann (1993) has not been possible. The correlation with their IC data does not reach the level of a significant data re-calculation of KI-single values regarding the sensitivity of the method (Table 2b) using KI mm Basel (second column), KI Δ° 2θ Frankfurt (third column) and comparing with KI Δ° 2θ data of the Kübler standards (forth column).

The Bochum group (D. K. Richter) applied the Weber-Index (Hb_{rel}; Table 2b) and measured glycolated specimens, therefore not following the recommendations of Kisch (1987, 1991) to use air-dried samples. Nevertheless, a zone comparison in metamorphic grade is possible and fits with the trends observed, but the determined grade is in general slightly lower (see Ferreiro Mählmann 1994). In Table 2, the IC/KI data were calibrated referring to VR for the specific research area. The reader should note that, based on new studies, for kinetic reasons, a KI/VR correlation is only valid for specific tectonic units with the same thermal history (see Le Bayon et al. 2011; Ferreiro Mählmann et al. 2012).

Concerning the data of Ring (1989), no correlation with other laboratories was found. The resulting values are irregularly high and scattered ($r = 0.62$, see also Ferreiro Mählmann 1994). This may be one of the reasons why the author (also in later publications) refers the Arosa zone (Fig. 8) to have been metamorphosed mainly at low-epizone conditions, in contrast with low- to high-anchizone grade determined by Ferreiro Mählmann (1995) and Ferreiro Mählmann and Giger (2012). An inter-laboratory calibration is missing and using the raw-data from the laboratory in Tübingen, neither a proper sample preparation in respect to KI is indicated (Daniel Biehler, pers. communication), nor KI-standards were applied (Bernard Kübler and Martin Frey, pers. communications). Former IC values cannot be automatically transformed to equal KI values and need to be re-calibrated. During the compilation of "The New Metamorphic Map of the Alps" (Frey et al. 1999) it was decided to use none of these values. Except these data groups, all other IC and KI values were also used for drawing of the very low-grade areas in the "Metamorphic structure of the Alps, 1:1'000'000", Oberhänsli et al. (2004).

This paper is a late result of these data compilations, using also the wealth of data of Martin Frey. In recent years it is observed that IC (KI) is again "routinely" used without using standards or standards not calibrated with the Kübler–Frey–Kisch samples (or with crystallinity index standards; CIS). This will again increase the uncertainties and these values should not be used as KI data in comparative studies and correlations. Such IC values will depict the illite ordering and illite particle size evolution for a metamorphic field gradient or geotherm, but not in the range of order of KI zones of Kübler (1967, 1968), see Kisch (1987) using KI data calibrated by KI standards (Kübler–Frey–Kisch standards). Unfortunately, due to the

Table 2 Vitrinite reflectance and illite "crystallinity"-indices measured at different laboratories

(a) Vitrinite reflectance		(b) Illite crystallinity				
VR_o Bochum	VR_{max} Aachen-Darmstadt	IC Hb_{rel} Bochum	KI mm Basel	KI Δ° 2θ Frankfurt	KI Δ° 2θ Kübler standards	Zone transitions
2.7	2.6	222 ± 20	5.8	0.43 ± 0.04	0.42	Diagenesis/Anchizone
4.1	3.9	175 ± 15	4.7	0.36 ± 0.02	0.33	Low/High Anchizone
5.5	5.3	125 ± 10	3.7	0.24 ± 0.01	0.25	Anchizone/Epizone

The IC and KI values are correlated with the Kübler standards

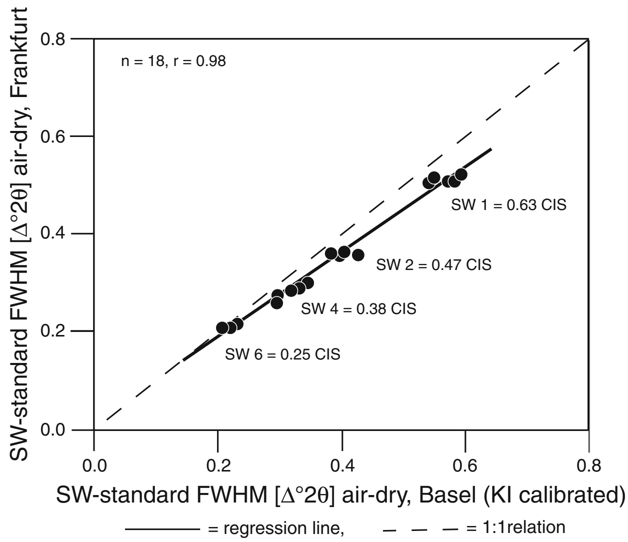

Fig. 6 Correlation between CIS standards used by L. Warr in Heidelberg (Table 2) to adapt the SW standard FWHM-values in $\Delta°2\theta$ to Kübler-Index data measured in Basel. The plot was re-drawn from a plot of D. Schmidt. Due to the scattering and the broader FWHM values the traditional Kübler – Frey standards were used (Schmidt et al. 1997). Three to seven specimens were prepared from each SW standard. ($n = 18$, $r = 0.98$)

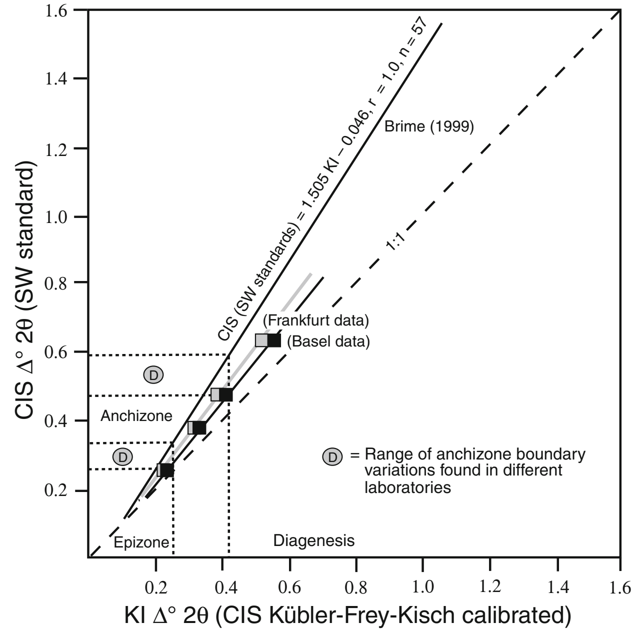

Fig. 7 Comparison of the SW values given by Warr and Rice (1994) with values obtained for SW samples measured on a Kisch-Frey-Kübler calibrated XRD devise at the laboratories of Basel and Frankfurt. The CIS anchizone shows larger IC values than the KI anchizone. See discussion in the text

death of M. Frey and B. Kübler in 2000 the inter-laboratory calibration was not finished, specifically not with the French groups (e.g. J. Aprahamian) in the Western Alps (part of the work was published in Kisch et al. 2004).

A systematic study on the crystallinity index standards (CIS) was conducted in Basel, Frankfurt and Darmstadt. According to Guggenheim et al. (2002), the CIS can be used as Kübler-index values. The material quality was tested using different specimens prepared from sample powder.

Using the preparation technique of Warr and Rice (1994), following the suggestions of the IGCP 294 IC working group (Krumm 1984 and Kisch 1991) and see the chapter about the Kübler-index method, results are not compatible with the data from most researches compiled in this paper. This is evident from Fig. 6 and was also observed by Kisch et al. (2004).

Brime (1999) correlated for a large KI range of 0.2–1.0 $\Delta°\ 2\theta$ KI with CIS giving a correlation:

CIS (SW standards) $= 1.505$ KI-0.046, $r^2 = 1.0$, $n = 57$ (Fig. 7).

Because Warr and Rice (1994) refer that the CIS standards are calibrated with KI standards (Guggenheim et al. 2002) the anchizone defined with CIS values would produce the limits of 0.59 and 0.33 $\Delta°\ 2\theta$. The correlation with KI equivalent values (Frankfurt, see Table 1; Fig. 7) would give similar larger values of 0.51 and 0.30 $\Delta°\ 2\theta$ and regarding the Kübler standards from Basel the limits would shift to 0.48 and 0.29 $\Delta°\ 2\theta$. This study confirms, in part, the results obtained by Brime (1999) and Leoni (2001). This comparison also shows that the KI values obtained by Kisch et al. (2004) for the anchizone limits (0.49–0.30) are well compatible with the original KI values. The results from Brime (1999), Leoni (2001) and Kisch et al. (2004) are not identical, the latter are closer to those obtained in Frankfurt and Basel.

First of all the shift of the anchizone limits toward higher values is explained by an erroneous correlation between the scales of Kisch and the scales of Warr and Rice (Brime 1999 and shown in this study). One reason may be the use of polished sections as standards and not sedimented oriented specimens (see also Kisch et al. 2004). A re-calibration would increase the KI error if adapted to the SW standards. Therefore for the calibration of the zones in the New Metamorphic Map of the Alps the standardisation from M. Frey and B. Kübler, using Tables 1 and 2 and the respective correlations (Figs. 1, 3, 4, 5), was applied and all data could be expressed as Kübler-index values as shown by Frey and Ferreiro Mählmann (1999) and Ferreiro Mählmann et al. (2012). This is an important step for further studies in an area like the Central Alps with a very high data density. This correlation study will also make it possible that nearly the 90 % of illite-FWHM data from Switzerland can be compared in future work.

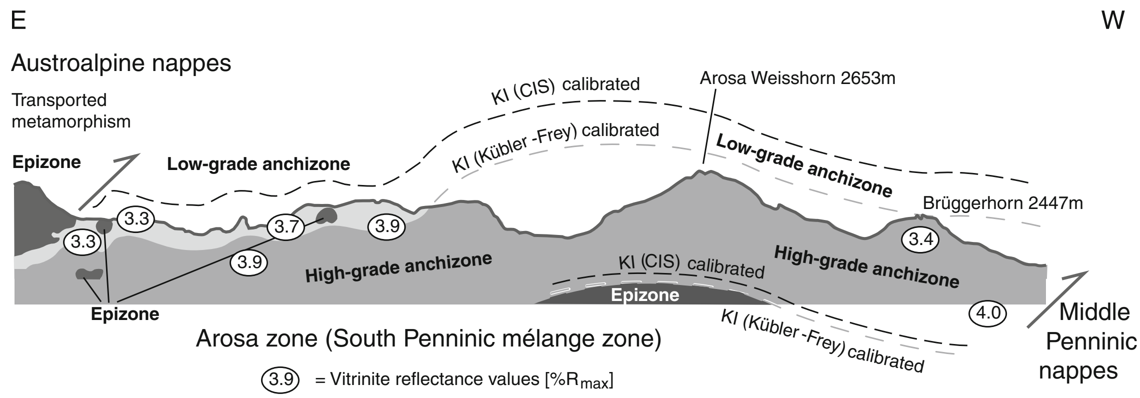

Fig. 8 Simplified cross section of the Arosa zone near Arosa (Grisons, Switzerland). KI-VR values are combined to draw metamorphic zones (low-grade and high-grade anchizone and epizone). At three localities, spots of the epizone are related to occurrences with a Jurassic hydrothermal oceanic metamorphism. Using the CIS standards according to the Basel calibration (see Fig. 7), the low anchizone would shift out of the tectonic limits and all the Arosa zone would be of high anchizone. The shift represents an altitudinal difference of 200 m compared to the Küber-Frey standard calibration (compare Ferreiro Mählmann and Giger 2012)

4.4 Two case studies from the Alps showing differences in the metamorphic pattern comparing Kübler–Frey–Kisch and CIS calibrations

Two examples how a different calibrations can result in a different anchizone presentation on a metamorphic map (profile) will be given from our studies: When KI data are summarised to KI zones—may be increased due to scale problems or low data grids—the broader FWHM of CIS based values, like published by Potel and Trullenque (2012) from the Western Alps, has compared to KI values calibrated with Kübler–Frey–Kisch standards (Aprahamian 1974, 1988) a strong effect on the anchizone iso-line. The anchizone gets a broader area in the map-view (similar to the increase of the anchizone range using CIS, shown in Fig. 7).

In the field area of the Arosa zone (Ferreiro Mählmann and Giger 2012) a CIS-KI re-calculation would let disappear the higher limit of the low-grade anchizone in the Arosa section. CIS calibration was carried out in the same laboratories where original KI data were obtained, using the same preparation methods. The effect can be neglected at the anchizone–epizone limit because that iso-line is not affected by the correlation in the same proportion (Fig. 8). This may be also one reason why in the Dauphinois units studied by Potel and Trullenque (2012) only anchizone conditions are recovered and not a diagenesis—anchizone trend as in the postulate of Aprahamian (1974, 1988)—the iso-reflectance line is no more in between the nappe boundaries shown on the tectonic map. The boundary between zone of diagenesis and anchizone shifts to the NW-tectonic limit in the Dauphinois units (Potel and Trullenque 2012) and to the E in the Arosa zone (Ferreiro Mählmann and Giger 2012). The epizone and zone of diagenesis limit disappears by broaden of the KI zone between the limiting faults. In the Arosa zone this would be evident due to same reasons (Fig. 8). Differences, like recovered, may be typical compiling data calibrated with the different standard series. Leoni (2001) showed that “IC from CIS calibration indicate in relation to petrogenesis higher metamorphic grade than KI (Kübler calibrated). KI in general exhibit good overall agreement with the thermal conditions”. In the Tuscan nappes, “depending on whether the CIS or the Kübler’s scale is applied, the metamorphic grade estimated points to middle anchizone or to upper anchizonal conditions” (Carosi et al. 2003).

Nevertheless, it seems that the difference found is a mere visualising problem. It is widely accepted that KI is not a geo-thermometer (Frey 1987) and if not calibrated with other independent methods to determine temperatures (as VR maturity modelling), a shift like that should have no important metamorphic P–T consequences. Compared to the VR (OMR) iso-reflectance line of 3.7 $\%R_{max}$ (not well established, Fig. 8) different KI iso-lines would correlate using KI or CIS standards. Therefore a modelled temperature (iso-therm) would correlate with a different KI, but without an important metamorphic peak difference. This is a logic consequence, because the KI or CIS value is modelled with the algorithm of the maturity model. For more details to these case studies see Potel and Trullenque (2012) and Ferreiro Mählmann and Giger (2012) included in the present issue.

4.5 Comparison of vitrinite reflectance data and calibrated Kübler-index data

The relatively high $R_m\%$ (mean) values of Henrichs (1993) and Kürmann (1993) in respect to the $R_{max}\%$ values used (Table 2) have two reasons: for their studies a 50× oil immersion objective was used and mean reflectance was calculated from the formulism of Ting and Lo (1978). Both methods are the reason for higher VR values. We apply a 125× oil immersion objective to prevent a bulk measurement of vitrinite particles and also grain boundary and relief influences (Le Bayon et al. 2012). In comparison with the 50× oil immersion objective, mostly VR measure is lower. In addition, the Ting and Lo (1978) calculation (formalism) is strongly dependent from the bi-reflectance. Bi-reflectance changes are strongly dependent from strain rates (Teichmüller et al. 1979). In deformed rocks, as studied in Mittelbünden by Henrichs (1993) and Kürmann (1993), this method causes a higher reflectance values. Unfortunately the VR–BR method presented is much more time consuming and the lab workload is much higher. Nevertheless the work done merits that effort, demonstrated by the sensitive results obtained in comparison (Ferreiro Mählmann 1995, 2001; Ferreiro Mählmann et al. 2012; Ferreiro Mählmann and Giger 2012).

Uniform calibrated KI and VR data sets are correlated in the comparative study presented by Ferreiro Mählmann et al. (2012) from different tectonic settings. The trend from diagenesis to epizone shown and correlated by KI and VR values have a paleo-geothermal background and thus a geodynamic consequence (Fig. 9). A shift of the anchizone limit caused by the difference between KI and CIS values (see Fig. 9, shown is the maximum difference found by Brime 1999) would cause an important difference in the metamorphic and tectonic interpretation of the data set (in other laboratories the difference is smaller). In the case of the Arosa zone instead of a low orogenic geothermal gradient as discussed by Ferreiro Mählmann and Giger (2012) a moderate to high geothermal gradient would result from CIS data plotted in the KI/VR diagram calibrated with Kübler–Frey–Kisch standards. Such a hyper-thermal scenario results from the CIS values and is completely different from an accretionary (moderate geotherm) and subduction related (low geotherm) tectonic setting as found in the study area.

5 Conclusion

Having expressed some concerns about the Kübler–Frey–Kisch standards versus CIS standards, it is absolutely necessary to calibrate illite FWHM data with standards for determining grade of diagenesis and metamorphism. A steady control of the XRD measurement devise and a control of the CuKα radiation tube is a pre-condition for routine KI studies together with a standardised specimen preparation on sedimented well oriented slides.

The use of different standard techniques (e.g. Kübler–Frey–Kisch standards vs. CIS) can cause differences in the map-view depending on the proportions of sub-divisions of KI zones and thus will cause differences in the interpretation and confirms the earlier results of Brime (1999). Using Kisch's original rock slab standards, and Kübler's rock slab standards Brime (1999) and Kisch et al. (2004) stated that the boundary values based on the CIS calibration are shifted towards higher Δ° 2θ, causing confusion and misinterpretation in petrogenesis (Leoni 2001; Carosi et al. 2003). From Fig. 1 of Kisch et al. (2004) the differences are just the same as in our (Swiss-German) laboratories. Using CIS determined values in a KI study, a serious change in the geodynamic interpretation could

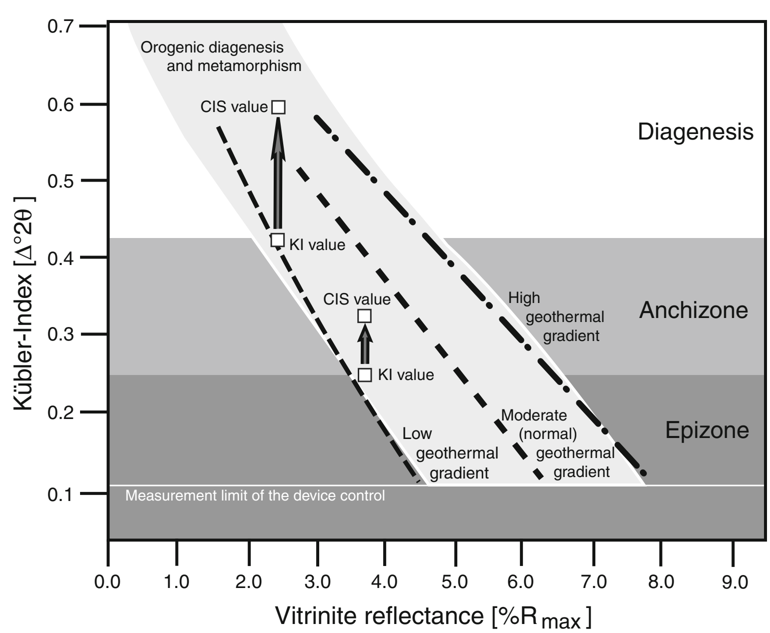

Fig. 9 Summarized relation between vitrinite and the illite maturation paths from high diagenesis to the epizone, divided by low, moderate, and high geothermal trends (Ferreiro Mählmann et al. 2012). Note the shift of CIS to KI values at the Kübler limits of the anchizone from low to high orogenic geothermal gradient. The maximum difference on the CIS values (published by Brime 1999) has been chosen to show the largest possible discrepancy on the correlation variance

result. Thus, this kind of mixing KI with CIS data should be avoided. In areas with a high data grid gathered by KI a re-consideration with CIS calibrations is not recommended.

The CIS calibration with Kübler–Frey–Kisch standards evidences that CIS generated values which, in contradiction to Guggenheim et al. (2002), cannot be used as KI values *senso stricto* (Brime 1999). As this is a nomenclature question and it is important to respect the international recommendation of committees in order to avoid confusion, the recommendation could be always specifying CIS-KI in order to advice that the type of calibration has been different.

Nevertheless, the Kübler–Frey–Kisch or CIS calibration technique will have no pressure–temperature consequences or cause paleo-geothermal changes in heat-flux determinations if the KI vales are calibrated with other independent methods (e.g. VR maturity modelling). It is to state that KI data show the grade of reaction progress of illite-aggradations but this cannot be used as an absolute geo-thermometer. Thus, because KI values cannot be translated to temperature, KI standards have to obey the rules to represent equivalently KI values to characterise a diagenesis–anchizone–epizone metamorphic evolution as defined by Kübler (1967).

The calibration and inter-laboratory correlation gives a chance to continue representing KI–VR data in the Central Alps based on a homogenised data set. Very low-grade studies can be continued in a uniform way.

Due to the fact that rock collections disappeared and with time the availability of Kübler–Frey–Kisch standards will get more and more complicated, for the moment it is pre-requested, only for new very low-grade studies and in areas without available KI calibrated data, to use CIS standards. It would be an important task for clay mineral societies to take responsibility to save standards and reference materials because universities will not do it.

From field observations it is demonstrated that the standards chosen from samples of the Helvetic tectonic realm (Kübler–Frey standards) and the Austroalpine nappe stack (standards of Petschick–Ferreiro Mählmann) have originated KI values under similar geodynamic P–T–t conditions (Ferreiro Mählmann et al. 2012), which is not evident for the CIS standards. It is to conclude, that standards still available over a long period are needed. At the moment it is possible to continue using the standard material from Kübler, Frey, Kisch and Ferreiro Mählmann (Table 1), excluding the samples with smectite—mixed layer content, probably including also the CIS standards. It is not sure that, after retirement of the first author or Warr (for CIS standards) at the universities of the TU Darmstadt or Greifswald the standard material is still available. As experienced by the first author, it is difficult to get standard material from the universities in Neufchâtel (Kübler-standards) and Basel (Frey-standards).

Based on the KI–VR zone compilations in the Central Alps and other orogenic areas (Ferreiro Mählmann et al. 2012) a scenario with a verified steady state thermal regime would be an excellent reference area for new standard samples. Standards being highly repeatable, very precise and having high intra-sample homogeneity (most standards discussed in the present paper have this characteristics) should be available for a far future.

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