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Recommendations for Kübler Index standardization

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ABSTRACT: Following a round table discussion at the Mid European Clay Conference in Dresden 2014, new recommendations for illite “crystallinity” Kübler index standardization have been agreed upon. The use of Crystallinity Index standards in the form of rock fragment samples will be continued, along with the same numerical scale of measurement presented by Warr & Rice (1994). However, in order to be compatible with the original working definition of the Küblers’ (1967) anchizone, the upper and lower boundary limits of the Crystallinity Index Standard (CIS) scale are appropriately adjusted from $0.25^\circ 2\theta$ and $0.42^\circ 2\theta$ to $0.32^\circ 2\theta$ and $0.52^\circ 2\theta$, accordingly. This adjustment is based on an inter-laboratory correlation between the laboratories of Basel, Neuchâtel and the CIS scale. The details of this correction are presented in this first note, as discussed at the round table meeting, and will be further substantiated by a correlation program between CIS and former Kübler – Frey – Kisch standards.

Keywords: Kübler index, Crystallinity Index Standard, Kübler – Frey – Kisch standards, Very-low grade metamorphism, anchizone

This note reports on the results of a Kübler Index (illite “crystallinity”) round table discussion that took place at the Mid European Clay Conference (MECC 2014) in Dresden, Germany, on the 17. September 2014. The objective of the meeting was to discuss current problems concerning the standardization of illite Kübler Index (KI) values used for very-low grade metamorphic study and determination of the anchizone. In the past, considerable variation in KI values have occurred between laboratories that arise due to differences in both X-ray diffraction (XRD) instrumental settings (Blenkinsop, 1988; Kisch, 1990) and sample preparation differences (Kisch, 1991; Krumm & Buggisch, 1991). Subsequently, Warr & Rice (1994) presented a calibration approach known as the Crystallinity Index Standard (CIS), which uses a widely available set of standards in the form of rock fragments that requires full preparation by the user. This method has now become the common method of Kübler Index (Kübler 1967, 1968, 1984) or Árkai Index (Árkai, 1991) standardization. Such profile broadening XRD standards contrast to available National (NIST) mica standards that are used for line positioning only (<https://www-s.nist.gov/srmors/viewTableV.cfm?tableid=149>).

However, despite the success of the CIS approach in standardizing numerical data between laboratories, the study did not successfully reproduce Küblers' (1967) original scale of measurement that was used to define the anchizone (Kisch et al., 2004; Ferreiro Mählmann & Frey, 2012; see also the review paper of Ferreiro Mählmann et al., 2012). Therefore the prime aim of the workshop was to discuss a solution to this problem (Ferreiro Mählmann & Nguyen-Thanh, 2014; Warr, 2014).

A first point of agreement could be reached in terms of the type of standards that should be used for inter-laboratory correlation and calibration purposes. Only standards that require full preparation (rock fragments) are considered suitable so that all sources of inter-laboratory variation are included in the calibration procedure. The use of polished rock slabs for this purpose should be avoided as significant variations due to sample preparation differences do occur between many laboratories, which has led to significant errors in past calibrations (Warr, 2014).

The current and future availability of standards was discussed. The original sets of CIS standards first used by Warr & Rice (1994) are now approaching depletion. These are currently being replaced by a new set of samples, partly collected from the same localities. A total of 9 samples will shortly be available for calibration purposes, which can be requested free of charge to academic institutions over the <http://claylab.de> website. The $Mf1_c$ muscovite crystal used for measuring instrumental broadening can no longer be provided. Whereas enough material has been collected to serve the community for another 20 years, some concern was expressed as the long-term availability of standards, particularly when circulated by individual researchers.

Due to the increasing tendency of many universities not to continue the maintenance of science collections, the preservation of standard rock sets do not have a secure future and continuous availability is not guaranteed (Ferreiro Mählmann & Frey, 2012). Consequently, because most of the original Kübler – Frey – Kisch (KFK) standards are now lost, some scientific loss of information has occurred. Some KF standards are, however, still available but also approaching depletion. Therefore key inter-laboratory correlations are required to help facilitate the use of past published KI data recorded by KFK standardization, and to aid comparison between CIS and KFK standardized KI values in study areas where both methods have been adopted. As Kisch's standards are polished rock slabs that are no longer recommended for calibration purposes, in the next section we refer only to CIS and Kübler-Frey (KF) standards that are available in the form of rock fragments.

One solution to the problem of maintaining availability would be to provide the standards through a community provider, such as the Clay Minerals Source Clays

(<http://www.clays.org/>), or through a nationalized institution such as the Swiss National Museum in Bern. Whereas both of these suggestions present possibilities to secure the distribution of standards into the long term, it was pointed out that such a distribution of materials would involve costs, and the standards would no longer be distributed free of charge for academic institutions. Another possibility is that in future more standard sets could be made available and supplied by various laboratories or institutions. Generally speaking, the more standards used for calibration purposes the better. Such standards should be: i) Suitable for calibration purposes. ii) Available in large quantities. iii) Effectively homogenized prior to distribution, iv) Sufficiently measured to produce precise and representative Kübler Index values and v) new CIS or KF values based on reliable correlations with currently available standard sets. In future, building up a catalogue of available standards and distribution sources would probably be the best method to secure the long-term future of an effective calibration procedure.

The main concern of the round table was the need to maintain the original working definition of the anchizone as defined by Kübler (1967), which was not successfully reproduced by the CIS scale that attempted to reproduce the same scale using polished rock chips standards (Warr & Rice, 1994). After much discussion prior to and during the round table, the common consensus was that laboratories using Kübler index measurements on the CIS scale should adjust the definition of the anchizone to values that are consistent with Küblers' original usage of the anchizone. This is particularly important in regional studies when different very-low grade metamorphic study groups have used both calibration techniques. This approach has the advantage that the numerous laboratories that now adopt this method of standardization do not require any recalibration of their numerical results. Appropriate adjustments can be made by adopting the revised anchizone limits according to the CIS scale in past and ongoing studies to maintain consistence with its primary usage by Neuchâtel (working group of B. Kübler) and Basel (working group of M. Frey and W.B. Stern).

Following a discussion of available data sets that have been made available by use of the CIS rock fragment standards in both the Neuchâtel and Basel laboratories, correlations have been made that allow the original working definition of the anchizone to be reconstructed (Table 1, Figure 1). Four data points are available for Küblers' original Philips 1010 diffractometer on which the first historical anchizone boundary limits were defined. As only one textured slide was measured per sample (i.e. no repeat analyses) were made, this data set is not considered reliable enough to construct a usable correlation curve. However, the Kübler scale used in Basel (M. Frey and W.B. Stern) calibrated its KI measurements with standards run on Küblers' original instrument and therefore is considered to be equivalent

(Frey, 1988). The results provided by M. Frey and W.B. Stern allow an accurate linear correlation curve to be reconstructed. This data set is based on three repeat analyses of both the SW and ILC sample sets (Warr & Rice, 1994; Krumm et al. 1996), which gives 10 sample points used for regression analysis. The correlation coefficient (R^2) of this data set when plotted against the CIS scale is notably good at 0.986. Importantly, a good correspondence between the results of Neuchâtel and Basel data sets exist, except for the SW1 diagenetic sample measured on Küblers' original instrument, which deviates from best line of correlation.

After evaluating the available data sets in the round table discussion, it was agreed that using the Basel correlation presents the most appropriate method to reconstruct Küblers' anchizone boundaries set at 0.25 and $0.42^\circ 2\theta$, for the upper and lower limits. Using the linear regression presented (Kübler Index "CIS" = $1.1523 \times$ Kübler index "Basel lab" + 0.036), the equivalent working boundary limits of the anchizone measured using the CIS scale is 0.32 and $0.52^\circ 2\theta$, respectively (Figure 1). The boundary between the low and high-grade anchizone placed at $0.335^\circ 2\theta$ on the KF scale is equivalent to $KI = 0.42^\circ 2\theta$ when CIS calibrated. These revised limits are therefore here recommended for use in future studies in conjunction with half-peak-width calibration procedures. This recommendation is a first note of progress made during the round table discussion and will be further substantiated by a more a detailed correlation program for currently available CIS and KF standards (Warr & Rice, 1994; Ferreiro Mählmann & Frey, 2012) and following the preparation recommendations proposed by Kisch (1991).

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References

- Árkai, P. (1991). Chlorite crystallinity: an empirical approach and correlation with illite crystallinity, coal rank and mineral facies as exemplified by Palaeozoic and Mesozoic rocks of northeast Hungary. *Journal of Metamorphic Geology*, 9 (6), 723-734.
- Blenkinsop, T.G. (1988). Definition of low-grade metamorphic zones using illite crystallinity. *Journal of Metamorphic Geology*, 6 (5), 623–636.
- Krumm, S. Buggisch, W. (1991). Sample preparation effects on illite crystallinity measurement: grain-size gradation and particle orientation. *Journal of Metamorphic Geology*, 9 (6), 671–677.
- Ferreiro Máhlmann, R. & Frey, M. (2012). Standardisation, calibration and correlation of the Kübler-index and the vitrinite/bituminite reflectance: an interlaboratory and field related study. *Swiss Journal of Geosciences*, 105, (2), 153-170
- Ferreiro Máhlmann, R. & Nguyen-Thanh, L. (2014). Standardisation, calibration and correlation of the Kübler-Index. MECC 2014 conference abstract, Dresden, Germany. Presentation available at http://www.geo.tu-darmstadt.de/fg/petrol/rfm_about_us
- Ferreiro Máhlmann, R., Bozkaya, Ö., Potel, S., Le Bayon, R., Šegvić, B. & Nieto, F. (2012). The pioneer work of Bernard Kübler and Martin Frey in very low-grade metamorphic terranes: paleo-geothermal potential of variation in Kübler-Index/organic matter reflectance correlations. A review. *Swiss Journal of Geosciences*, 105, (2), 121-152.
- Frey, M. (1988). Discontinuous inverse metamorphic zonation, Glarus Alps, Switzerland: evidence from illite "crystallinity" data. *Schweizerische Mineralogische und Petrographische Mitteilungen*, 68, (1), 171-183.
- Kübler B. (1967). La cristallinité de l'illite et les zones tout a fait superieures du métamorphisme. In: *Étages tectoniques, Colloque de Neuchâtel 1966*, A La Baconniere, Neuchâtel 105-121.
- Kübler B. (1968). Evaluation quantitative du métamorphisme par la cristallinité d'illite. *Bull. Centre Rech. Pau -- S.N.P.A.* 2, 385-397.
- Kübler B. (1984). Les indicateurs des transformations physiques et chimiques dans la diagenèse, température et calorimétrie. in: "Thermobarométrie et barométrie géologiques", M. Lagache ed., Soc. Franc. Minéral. Cristallogr., Paris, 489-596.
- Kisch, H.J. (1990). Calibration of the anchizone: a critical comparison of illite 'crystallinity' scales used for definition. *Journal of Metamorphic Geology*, 9, (6), 665–670.
- Kisch, H.J. (1991). Illite crystallinity: recommendations on sample preparation, X-ray diffraction settings, and interlaboratory samples. *Journal of Metamorphic Geology*, 9, (6), 665–670.

Kisch, H.J., Arkai, P. & Brime, C. (2004). On the calibration of the illite Kübler index (illite „crystallinity“). Schweizerische Mineralogische und Petrographische Mitteilungen, 84, 323-331.

Krumm, S., Kisch, H.J. & Warr, L.N. (1996). Interlaboratory study of the effects of sample preparation on illite crystallinity: a progress report. XIIIth Conference on Clay Mineralogy and Petrology, Praha (1994). Acta Universitatis Carolinae Geologica, 38, 263-270.

Warr, L.N. & Rice, A.H.N. (1994). Interlaboratory standardization and calibration of clay mineral crystallinity and crystallite size data. Journal of Metamorphic Geology, 12, (2) 141-152.

Warr, L.N. (2014). 20 years of the Crystallinity Index Standard – a progress report. MECC 2014 conference abstract, Dresden, Germany. Presentation available at https://www.researchgate.net/profile/Laurence_Warr/contributions

Standard	MF1c	SW1	SW2	SW4	SW6	ILC1	ILC2	ILC3	ILC4	ILC5
KI-CIS	0.11	0.630	0.470	0.380	0.250	0.424	0.282	0.533	0.293	0.453
KI-Basel	0.06	0.518	0.353	0.283	0.178	0.327	0.234	0.430	0.244	0.380
KI-Neuchâtel	-	0.410	0.350	0.310	0.160	-	-	-	-	-

Table 1. Kübler index (KI) values of Crystallinity Index Standards (CIS) prepared using air-dried textured preparation of the <2 µm fractions. KI-CIS values are after Warr & Rice (1994). KI-Basel values were provided by M. Frey and W.B. Stern, and represent results from their D5000 Bruker/Siemens diffractometer using a Cu-anode, 40 kV and 30 mA, step increment of 0.05°, count time of 30 s per step, primary slits of 3°- 3°, receiving slits of 1° - 0.05°- 0.15° and no antiscatter slit. The narrowest FWHM value measured on a muscovite standard was 0.05° and the sharpest reflection measured on a sedimented slide was 0.15°. The textured XRD slides were prepared by sedimentation of the separated Ca-saturated <2µm fraction with a concentration of 4mg/cm². The KI-Neuchatel values were provided by D. Goy-Eggenberger, T Adatte, J. Richard and B. Kübler and represents results from their original Philips 1011 diffractometer.

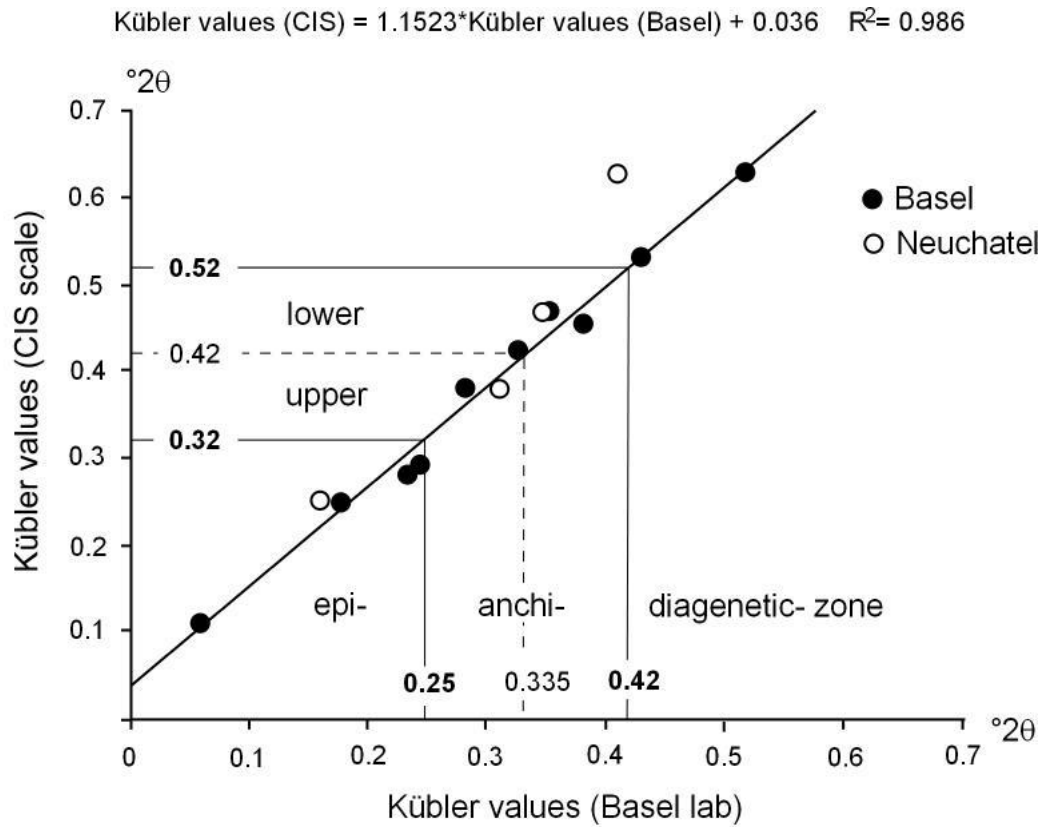


Figure 1. Correlation plot of Kübler index values determined by using the CIS scale and the experimental values provided by the laboratories of Basel (M. Frey and W.B. Stern) and Neuchâtel (Kübler and coworkers). Küblers anchizonal limits of 0.25° and 0.42°, translate into 0.32° and 0.52° for the CIS scale based on the Basel correlation.