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Recommendations for Kübler Index standardization

L. N. WARR[1,*] AND R. FERREIRO MÄHLMANN[2]

[1] *Institut für Geographie und Geologie, Ernst-Moritz-Arndt Universität Greifswald, 17487 Greifswald, Germany*
[2] *Institut für Angewandte Geowissenschaften, Technische Universität Darmstadt, 64287 Darmstadt, Germany*

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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 Kübler's (1967) anchizone, the upper and lower boundary limits of the Crystallinity Index Standard (CIS) scale are adjusted appropriately from 0.25°2θ and 0.42°2θ to 0.32°2θ and 0.52°2θ. 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 has occurred between laboratories, which 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). 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 known commonly as the Kübler Index (Kübler 1967, 1968, 1984) or the Árkai Index (Árkai, 1991) standardization. Such profile-broadening XRD standards contrast with the 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 was not successful in reproducing Kübler's (1967) original scale of measurement that was used to define the anchizone (Kisch *et al.*, 2004; Ferreiro Mählmann & Frey, 2012; see also the review by 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 that needed to be reached was 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

* Email: warr@uni-greifswald.de
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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 have 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 being replaced currently by a new set of samples, partly collected from the same localities. A total of nine samples will be available shortly for calibration purposes, which can be requested free of charge by academic institutions from 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 to 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 does not have a secure future and continuous availability is not guaranteed (Ferreiro Mählmann & Frey, 2012). Consequently, as most of the original Kübler–Frey–Kisch (KFK) standards are now lost, some loss of scientific information has occurred. Some Kübler-Frey (KF) standards are, however, still available, but are 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, we refer in the next section to CIS and KF standards only 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 Society Source Clays Repository (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 be supplied by various laboratories or institutions. Generally speaking, the more standards used for calibration purposes the better. Such standards should be: (1) suitable for calibration purposes; (2) available in large quantities; (3) homogenized effective prior to distribution; (4) measured sufficiently to produce precise and representative Kübler Index values; (5) have 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 discussion was the need to maintain the original working definition of the anchizone as defined by Kübler (1967), which was not reproduced successfully by the CIS scale that attempted to reproduce it using polished rock chips as 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 Kübler's 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 consistency 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 data sets that have been made available through 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, Fig. 1). Four data points are available for Kübler's 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 Kübler's 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

TABLE 1. Kübler index (KI) values of Crystallinity Index Standards (CIS) prepared using air-dried textured preparation of the <2 μm fractions.

Standard	MF1c	SW1	SW2	SW4	SW6	ILC1	ILC2	ILC3	ILC4	ILC5
KI-CIS[a]	0.11	0.630	0.470	0.380	0.250	0.424	0.282	0.533	0,293	0.453
KI-Basel[b]	0.06	0.518	0.353	0.283	0.178	0.327	0.234	0.430	0.244	0.380
KI-Neuchâtel[c]	-	0.410	0.350	0.310	0.160	-	-	-	-	-

[a]KI-CIS values are after Warr & Rice (1994). [b]KI-Basel values were provided by M. Frey and W.B. Stern as results from their D5000 Bruker/Siemens diffractometer (Cu-anode, 40 kV and 30 mA, step increment 0.05°, count time 30 s per step, primary slits 3° to –3°, receiving slits of 1°–0.05°–0.15° and no anti-scatter slit). The narrowest FWHM value measured on a muscovite standard was 0.05° and the sharpest reflection measured for a sample sedimented on a slide was 0.15°. The textured XRD slides were prepared by sedimentation of the separated Ca-saturated <2 μm fraction with a concentration of 4 mg/cm^2. [c]The KI-Neuchatel values were provided by D. Goy-Eggenberger, T. Adatte, J. Richard and B. Kübler and represent results from their original Philips 1011 diffractometer.

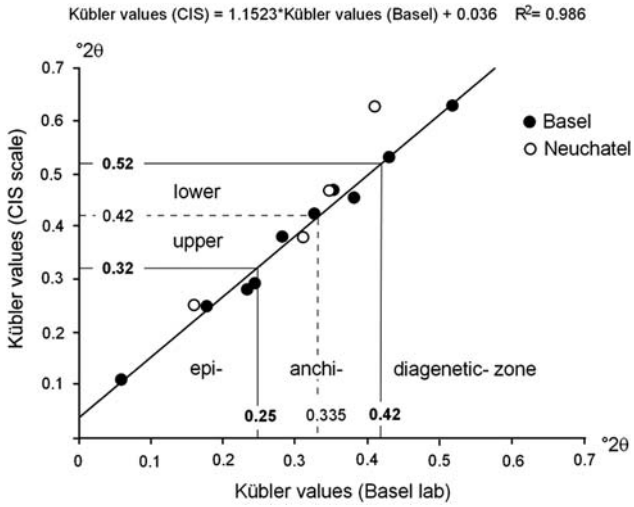

FIG. 1. Correlation plot of Kübler Index values determined using the CIS scale and the experimental values provided by the laboratories of Basel (M. Frey and W.B. Stern) and Neuchâtel (Kübler and coworkers). Kübler's anchizonal limits of 0.25°2θ and 0.42°2θ, translate into 0.32°2θ and 0.52°2θ for the CIS scale based on the Basel correlation.

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 the best line of correlation.

After evaluating the available data sets during the round-table discussion, it was agreed that the Basel correlation is the most appropriate method to use to reconstruct Kübler's anchizonal boundaries set at 0.25 and 0.42°2θ, for the upper and lower limits, respectively. Using the linear regression presented (Kübler Index 'CIS' = 1.1523 × Kübler index 'Basel lab' + 0.036), the equivalent working boundary limits of the anchizone measured using the CIS scale are 0.32 and 0.52°2θ (Fig. 1). The boundary between the low- and high-grade anchizone placed at 0.335°2θ on the KF scale is

equivalent to KI = 0.42°2θ when CIS calibrated. These revised limits are therefore 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 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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