Applied Clay Science 162 (2018) 261–267

Contents lists available at ScienceDirect

Applied Clay Science

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

Research Paper

Crystallite size as a function of kaolinite structural order-disorder and kaolin chemical variability: Sedimentological implication

Mahmoud E. Awad[a,b,c,*], Alberto López-Galindo[b], Rita Sánchez-Espejo[b], Claro Ignacio Sainz-Díaz[b], Mahmoud M. El-Rahmany[a], César Viseras[b,c]

[a] *Department of Geology, Faculty of Science, Al Azhar University in Cairo, 11884, Egypt*
[b] *Instituto Andaluz de Ciencias de la Tierra (IACT), CSIC-Universidad de Granada, Spain*
[c] *Departamento de Farmacia y Tecnología Farmacéutica, Universidad de Granada, Spain*

ARTICLE INFO

Keywords:
Kaolinite order-disorder
Index of compositional variability
Average crystallite size
Azhar-IACT chemo-structural index
Abu Zenima kaolin

ABSTRACT

The present study aims to propose a new relationship on the thickness of fundamental kaolinite particles determined by XRD crystallite size (D_{001}) as controlled by its structural order-disorder degree and the kaolin chemical variability (KCV). The average crystallite size (D_{001}) values of 29 kaolinite-rich samples, belonging to two different geologic ages and depositional conditions, show similar positive correlations with the KCV multiplied by the structural order-disorder degree determined by Hinckley (HI) and Liétard (R2) indices ($R^2 = 0.863$ and 0.853), respectively. This relationship is given by the empirical equations: $D_{001} = 99.35$ (HI × KCV) + 28.42 and $D_{001} = 141.50$ (R2 × KCV) + 24.65. The obtained values are proposed as a new chemo-structural index, named "*Azhar-IACT Index*".

1. Introduction

Kaolinite is the most chemically stable at low pH conditions amongst all the clay minerals (Carroll and Starkey, 1971) and widely distributed in all continents of the Earth's crust in variable abundances, ranged from kaolinitic siliciclastic rocks ($>50\%$ kaolinite) to high grade kaolin deposits ($>75\%$ kaolinite). Kaolinite exhibits remarkable positions in the stratigraphic sequences of the geologic sedimentary record. Khidir and Catuneanu (2009) found that the abundances of kaolinite in non-marine siliciclastic fluvial successions increase, as an observed pattern, towards unconformity surfaces reaching their maximum contents directly below the sequence boundaries. Hence, the position of kaolinite in stratigraphic sections is a powerful marker or proxy to delineate such sequence surfaces, produced by subsequent uplift and subaerial erosions prevailing in non-marine settings in the geologic record.

Kaolinite exhibits a relatively simple structure (1:1 layer type, dioctahedral character) and chemical formula ($Al_2Si_2O_5(OH)_4$), and crystallized as a periodical arrangement of the T-O layers by stacking along the c-axis, forming fundamental particles of a certain crystallite size (nm) that can be examined by transmission electron microscopy (TEM). These nano-sized fundamental particles are normally agglomerated, yielding aggregates of platy pseudohexagonal micromorphology that can be observed by scanning electron microscopy (SEM). Hence, the primary or fundamental clay mineral particle is the thinnest unit that can be formed for a clay mineral and capable of yielding a high arrangement degree by face-to-face aggregation with adsorbing exchangeable cations in the interface surfaces of adjacent particles (Nadeau, 1985). The crystallite size (D_{00l}) of a fundamental particle is a parameter introduced by Mering and Oberlin (1971) to describe the domain thickness of coherent interference by the X-rays scattering due to stacking of the platy phyllosilicate layers. Meanwhile, the structural order-disorder is the perfection degree of the phyllosilicate layers stacking, and it can be calculated for kaolinite by suitable structural indices selected based on the whole-rock mineralogical composition (Aparicio and Galán, 1999).

Murray and Lyons (1959) observed a positive strong correlation between kaolinite "crystallinity" and total iron and titanium oxides contents in kaolins. Hinckley (1965) also noticed that the soft kaolins, located at the upper coastal plain areas of Georgia and South Carolina, showed higher structural order degree and lower Fe_2O_3 contents than the hard kaolin deposits, and attributed these differences to changes in depositional conditions. He suggested that soft kaolins were deposited in a fresh water environment, with suitable pH conditions for kaolinite platelets stacking into booklets, whereas the hard kaolins were deposited in saline depositional conditions which aid on more particle flocculation that stabilize the suspended clay flakes, accompanied by a higher compaction with low permeability, and hence leading to a lack

---

* Corresponding author at: Department of Geology, Faculty of Science, Al Azhar University in Cairo, 11884, Egypt.
E-mail address: mawad@azhar.edu.eg (M.E. Awad).

https://doi.org/10.1016/j.clay.2018.06.027
Received 28 March 2018; Received in revised form 16 June 2018; Accepted 18 June 2018

of recrystallization and crystal growths. Moreover, he added that the saline water conditions are suitable to chemical precipitation of associated iron minerals like hematite. Mestdagh et al. (1980) also found positive correlations between kaolinite structural disorder degree and both, structural iron in kaolinite and total iron content in the bulk kaolin samples, and concluded that the iron associated with the internal signal of the electron paramagnetic resonance (EPR) spectrum is the only factor responsible for the structural disorder of kaolinite.

Significantly, the kaolinite crystallite size, its structural order-disorder and the kaolin purity (that is, the kaolin chemical variability) are some of the most important technological quality parameters for the industrial applications of kaolins. These parameters could also be applied for the interpretation of sedimentological and stratigraphic observations (for instance, they could be helpful to discriminate depositional environments, diagenetic conditions and/or to make correlations between relevant kaolin-bearing sedimentary facies in the stratigraphic record). It is worth of mention that the lower sediment size limit on the Wentworth (1922) is defined as " < 4 μm", and hence the classical sedimentological textural parameters defined by Folk and Ward (1957) cannot be normally applied for kaolin samples as the clay particles usually appears in aggregations; besides, the particle size distribution of such agglomerated clay particles (when determined by the Stock's method or even by laser techniques) is not actually representative to the in situ deposited clay fundamental particles. Hence, the measurement of the kaolinite crystallite size (D_{001}) and its controlling factors could be a useful tool trying to solve some sedimentological problems.

The biostratigraphic, lithofacies analysis and palynologic studies made by Kora and Schultz (1987) and Kora (1995) on Egyptian Abu Zenima kaolins suggested that the Lower Carboniferous (Upper Viséan) kaolin deposits were deposited under subtropical epicontinental fluviatile conditions through the continuous regression of the Tethys Sea. Based on the regional and global palynologic correlations, they concluded that the depositional conditions of these non-marine clastic sedimentary facies are similar to relevant Upper Viséan sediments distributed in all the northern African and Sinai, and in communication with other sedimentary successions recorded in Europe, Western Australia and eastern North America, deposited under rather uniform conditions through the early Carboniferous period. On the other hand, Kora and El Beialy (1989) suggested that the Lower Cretaceous (Neocomian) kaolin deposits were deposited in fluvial continental and fresh water shallow lakes environments, similar to the depositional conditions prevailing in the Laurasian realm of the southern Europe. The differences in age, sedimentary siliciclastic facies and depositional conditions should be reflected by a strong influence on the degree of structural stacking perfection of kaolinites, either during the pre-depositional formation processes or the diagenetic recrystallization conditions.

Kaolinite crystal growth or recrystallization is influenced by paleoenvironmental and diagenetic conditions (Lanson et al., 2002). Hence, the kaolinite stacking perfection could be used as an effective proxy in sedimentology for predicting the predominant depositional conditions of different sedimentary facies showing kaolinite contents from 20 to 50%, or intercalated by beds of silty or sandy-kaolins (50–75% kaolinite) or kaolins (> 75% kaolinite). The present study aims to characterize the influence of the kaolinite structural order-disorder degrees and the kaolin chemical variability on the average crystallite size, and to deduce their empirical relationship, which could be used in sedimentological facies analysis.

2. Materials and methods

Two sedimentary successions of similar lithofacies, composed of kaolinitic beds intercalated with sandstone layers, but related to two different stratigraphic rock units (Lower Carboniferous, Abu Thora Formation, and Lower Cretaceous, Malha Formations, Abdallah et al., 1963; Kora, 1989) have been sampled. The outcrops of these successions are distributed within the same sedimentary basin at west-central and southwest Sinai Peninsula at El Tih plateau and Abu Zenima district. They are in strong stratigraphic correlations with their equivalent units outcropped in the northern regions of Sinai Peninsula and northern parts of the Eastern desert, as well as exposed at the southern parts of the Western desert and extended subsurface units (from the core data of oil-well drillings) at the northern regions of the Western desert (Kora and El Beialy, 1989; Soliman and Wanas, 2004; El Beialy et al., 2010).

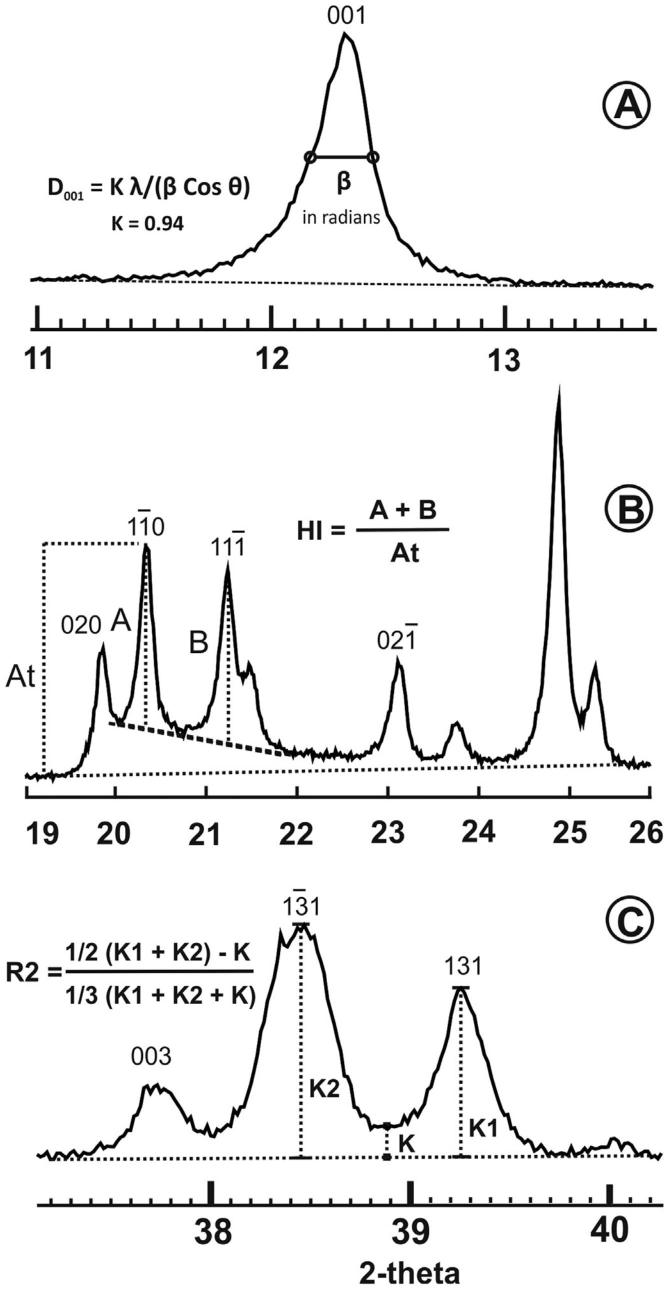

Fig. 1. A) Measurement of kaolinite crystallite size; B) Measurement of Hinckley Index; C) Measurement of Liétard Index.

Twelve Carboniferous soft kaolin samples (K, H and N) and seventeen hard Cretaceous kaolin samples (D and F), all of them with > 75% kaolinite, were collected from Abu Thora and Malha Formations outcropped at the Egyptian Abu Zenima district (West-Central Sinai Peninsula). The precise sampling locations, as well as the methodology used for determining the mineralogy and chemistry of the samples, is described in Awad et al. (2017, 2018).