Growth mechanisms of low-grade illites based on shapes of crystal thickness distributions

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Abstract

Crystallite thickness distributions (CTDs) of fundamental illite particles have been determined for a set of pelitic samples from Palaeozoic rocks. Observed CTD shapes are of two main types, asymptotic and lognormal, and these shapes evolve systematically with increasing metamorphic grade. The shapes of the CTDs are explained by two growth stages; (1) an early stage of simultaneous nucleation and growth, during which the asymptotic profiles of CTDs were established, and (2) a later stage of surface-controlled growth without further nucleation, giving rise to the lognormal shapes. The transition from the diagenesis zone to the anchizone, as determined from the Kübler index, is marked by a change in CTD shape from asymptotic to lognormal.

Keywords: Illite, growth mechanisms, crystal thickness distributions.

1. Introduction

Evolution of the illitic material (*sensu* ŚRODOŃ, 1984) has been widely used to assess the evolution of pelitic material during diagenesis and low grade metamorphism. In most studies, illite crystallinity (= Kübler index, see GUGGENHEIM et al., 2002) has been employed despite the limitations of the method (KISCH, 1983; BLENKINSOP, 1988; FREY, 1987; FREY and ROBINSON, 1999; KÜBLER and GOY-EGGENBERGER, 2001 and references therein). Alternative methods have been proposed based mainly on the determination of crystallite thickness by either TEM or XRD (EBERL and VELDE, 1989; MERRIMAN et al., 1990; NIETO and SÁNCHEZ-NAVAS, 1994; MERRIMAN et al., 1995 a, b; LANSON et al., 1995, 1996; ARKAI et al., 1996; EBERL et al., 1996, 1998a, b; DRITS et al., 1998; JABOYEDOFF et al., 2001).

The present study is an attempt to apply the Bertaut-Warren-Aberbach (BWA) method (DRITS et al., 1998), using the MudMaster computer program (EBERL et al., 1996), to evaluate illite thickness evolution in shales during the diagenesis to low grade metamorphism transition. Crystal thickness distributions (CTDs), thus obtained, have distinctive shapes which can convey information about crystal growth history (EBERL et al., 1998b). These shapes can be used in combination with the computer program GALOPER (EBERL et al., 2000) to establish a model for crystal growth of the minerals. Such information may help to unravel the physical and chemical conditions in the rocks that are associated with increasing temperature.

2. Materials and methods

A set of illite-containing pelitic samples from Palaeozoic rocks of the Cantabrian Zone, the external part of the Iberian Variscan belt (NW Spain), ranging in metamorphic grade from diagenesis to high anchizone, were selected for this study. The ages of the rocks range from Cambrian to Carboniferous. Cambrian to Westphalian A-B rocks belong to a pre-tectonic succession, deposited prior to the Variscan deformation, whereas the Westphalian C-D and Stephanian strata are syn-tectonic and were deposited while the Variscan deformation was taking place. Results from previous studies (BRIME and PÉREZ-ESTAÚN, 1980; BRIME, 1981, 1985; GARCÍA-LÓPEZ et al., 1997; BASTIDA et al., 1999; BRIME et al., 2001b) showed that maximum temperatures were attained dur-

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ing sedimentary burial previous to folding. Temperatures, assessed using conodont colour alteration index and its correlation with temperature as established by EPSTEIN et al. (1977) and REJEBIAN et al. (1987), varied in different parts of the area, but never exceeded 350 °C (GARCÍA-LÓPEZ et al., 1997, BASTIDA et al., 1999; BRIME et al., 2001b).

Samples were lightly crushed and disaggregated in distilled water with an ultrasonic probe. Then they were saturated with Na, and the <2 µm size fraction separated by centrifugation. Polyvinylpyrrolidone-(PVP-) intercalated samples were prepared according to EBERL et al. (1998a) and X-rayed on single crystal Si-wafers.

Samples were analyzed in Boulder, Colorado, using a Siemens D500 XRD system with a diffracted beam graphite monochromator, CuKα radiation and a scintillation counter. Samples were scanned from 4 to 10 °2θ using a tube current and voltage of 30 mA and 40 kV, respectively. The step size was 0.02 °2θ with a count time normally of 5 s per step, but up to 20 s per step was also used for some samples.

The resulting 001 XRD peaks for illite were measured for mean thickness and thickness distribution by the BWA method (DRITS et al., 1998) using the computer program MudMaster (EBERL et al., 1996). Although the options are included in the program, removal of the $K_{\alpha 2}$ radiation and correction for instrumental broadening were not performed, because such corrections are unnecessary in our experimental setup if the crystallite thickness is less than about 25 to 30 nm, and if the 2θ for the peak is less than about 50° (EBERL et al. 1996). Relations between crystal growth mechanism and the shapes of CTDs is based on the methods described by EBERL et al. (1998b) and ŚRODOŃ et al. (2000).

Shapes of crystal thickness distributions were simulated using the computer program GALOPER (EBERL et al., 2000). Comparison between simulated and measured crystallite distributions were made with the Kolmogorov-Smirnov statistical test. A significance level >1% was considered to be a match.

Table 1 Parameters of PVP dispersed illite samples.
α_{MM} and β^2_{MM}—lognormal parameters for the distribution of fundamental particle thicknesses measured by the Bertaut-Warren-Aberbach method using MudMaster; α_{G1} and β^2_{G1}—lognormal parameters for the distribution of fundamental particle thicknesses obtained during crystal thickness distribution simulations using GALOPER; N + SCG—calculation cycles of early stage of nucleation and surface-controlled growth; SCG—calculation cycles of late stage of surface controlled growth without nucleation; KS test %—level of significance of the Kolmogorov-Smirnov statistical test in comparing GALOPER simulated with MudMaster measured illite thickness distributions. (*)—samples from the syn-tectonic sequence.

Sample age	Sample reference	IC Kübler °2θ	α_{MM}	β^2_{MM}	mean size nm	CTD shape	N + SCG no cycles	SCG no cycles	α_{G1}	β^2_{G1}	KS test %
Ordovician	B73	0.24	2.53	0.43	15.6	LN	4	4	2.62	0.46	1 to 5
Cambrian	B612	0.29	2.71	0.34	17.8	LN	3	4	2.79	0.39	1 to 5
Silurian	B12	0.36	2.01	0.41	9.3	LN	4	2	2.04	0.32	>10
Ordovician	I309	0.40	2.11	0.43	10.2	LN	5	2	2.22	0.43	>10
Cambrian	S20	0.42	2.21	0.36	11.0	LN	4	3	2.25	0.27	1 to 5
Ordovician	I222	0.45	1.95	0.41	8.7	LN	5	1	2.04	0.33	1 to 5
Silurian	I310	0.42	2.33	0.33	12.1	LN	4	3	2.41	0.37	1 to 5
Ordovician	S1	0.43	1.29	0.41	4.7	Asymp	5	0	1.46	0.39	1 to 5
Lower Devonian	S12	0.47	1.20	0.34	4.1	Asymp	4	0	1.28	0.24	>10
Carboniferous	I248	0.52	1.34	0.43	4.9	Asymp	5	0	1.46	0.39	>10
Lower Devonian	I306	0.57	1.46	0.47	5.6	Asymp	5	0	1.45	0.38	>10
Ordovician	I234	0.61	1.41	0.40	5.1	Asymp	5	0	1.45	0.38	>10
Upper Silurian	B70	0.62	1.47	0.45	5.6	Asymp	5	0	1.46	0.39	>10
Carboniferous	I214	0.65	1.25	0.38	4.4	Asymp	4	0	1.28	0.24	1 to 5
Carboniferous	I282	0.66	1.31	0.38	4.7	Asymp	5	0	1.46	0.39	1 to 5
Lower Devonian	I308	0.72	1.28	0.36	4.4	Asymp	4	0	1.28	0.24	1 to 5
Lower Devonian	I307	0.74	1.23	0.36	4.3	Asymp	5	0	1.46	0.39	>10
Lower Devonian	B24	0.75	1.17	0.31	3.9	Asymp	5	0	1.46	0.39	>10
Upper Devonian	I256	0.76	1.18	0.31	3.9	Asymp	4	0	1.28	0.24	1 to 5
Carboniferous	I299	0.84	1.19	0.33	4.0	Asymp	4	0	1.28	0.24	1 to 5
Carboniferous*	H5	0.26	1.86	0.70	9.4	Asymp	7	0	1.84	0.70	1 to 5
Carboniferous*	H12	0.33	1.53	0.53	6.4	Asymp	5	0	1.48	0.40	1 to 5
Carboniferous*	H7	0.35	1.51	0.61	6.5	Asymp	5	0	1.47	0.38	1 to 5
Carboniferous*	H4	0.41	1.50	0.50	6.1	Asymp	5	0	1.46	0.39	1 to 5
Carboniferous*	H24	0.54	1.44	0.48	5.6	Asymp	5	0	1.46	0.39	1 to 5

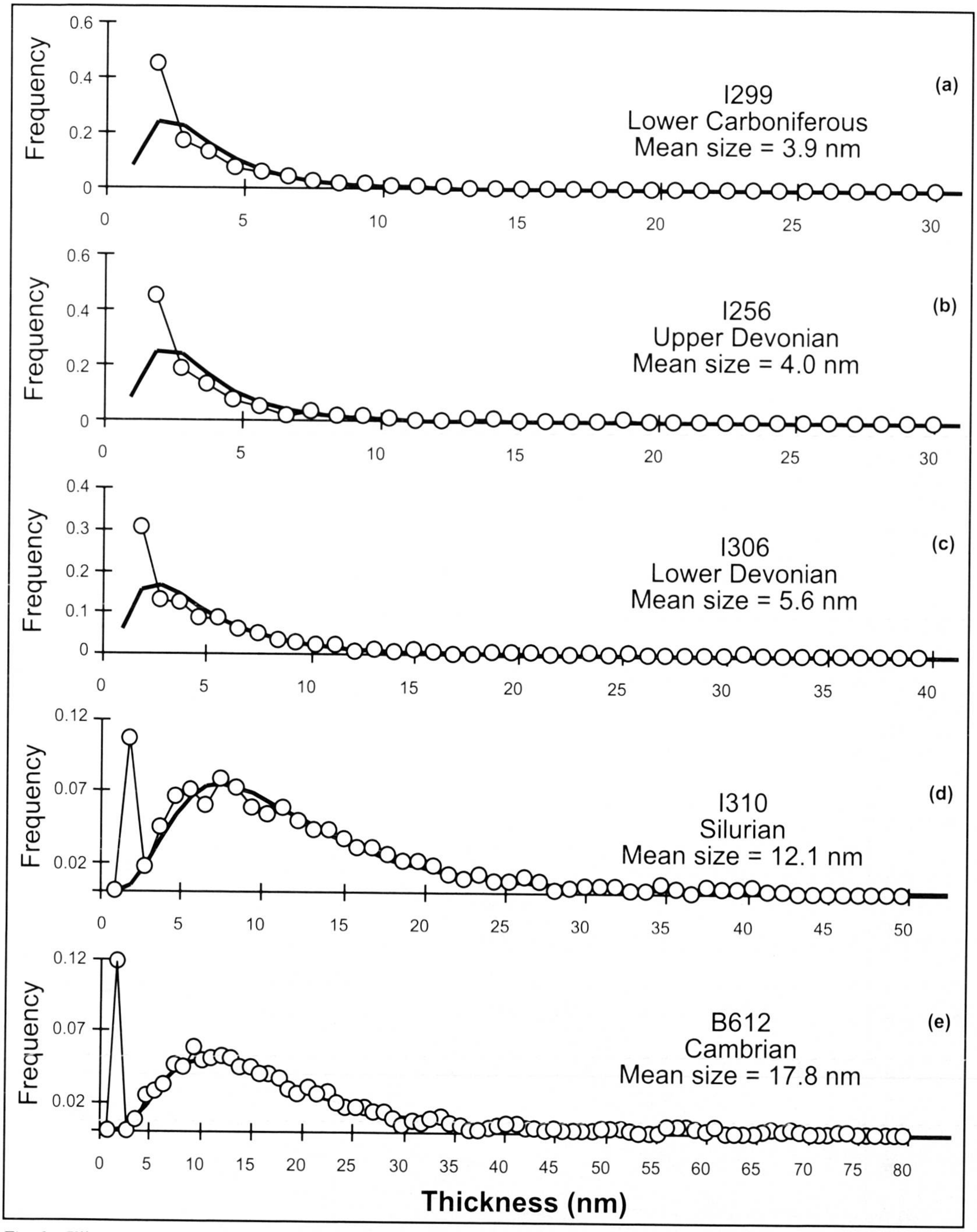

Fig. 1 Illite crystallite thicknes distributions. (a–c) Asymptotic shape; (d–e) Lognormal-like shape. The solid lines are lognormal fits to the data.

X-ray diffraction analyses of the <2 µm fraction for determination of the Kübler index were done in Oviedo, Spain using a Philips 1710 diffractometer equipped with graphite monochromator and using CuKα radiation. Preparation of samples and Kübler index determinations followed the recommendations of the IGCP294 working group (KISCH, 1991). The values of Kübler index obtained have been converted to Kübler scale, with anchizone limits between 0.42° and 0.25 °2θ, using a set of nine samples provided by H.J. Kisch.

3. Results

Results of the XRD thickness measurements for PVP intercalated illite samples, together with Kübler index, are indicated in Table 1. Mean thickness measurements range between 3.9 and 17.8 nm (Table 1). Thickness roughly correlates inversely to the Kübler indices ($r^2 = 0.5$).

Measurement of the 001 peak of illite yielded two main types of crystal size distributions, asymptotic and lognormal (Fig. 1). Asymptotic shapes (Figs. 1 a–c) correlate with diagenetic rocks, as indicated by measurement of Kübler indices greater than 0.42 °2θ, whereas lognormal distributions (Figs. 1 d–e) correlate with anchizonal values (with Kübler indices less than 0.42 °2θ, Table 1).

Lognormal distributions are characterized by a spike at very small sizes, the nature of which was uncertain, but which could be an artifact of the MudMaster calculation. To check this possibility, theoretical XRD patterns were calculated with the NEWMOD computer program (REYNOLDS, 1985) using lognormal and asymptotic CTDs in the calculations. CTDs then were determined from the calculated patterns using MudMaster. The crystallite thickness distributions used in NEWMOD calculated XRD patterns did not contain spikes. Upon analysis, the spike is not present in MudMaster analysed NEWMOD patterns that used asymptotic CTDs, but is present in those calculated using lognormal CTDs. Therefore, the spike in the measured lognormal CTDs is considered to be an artifact. The spike probably results from the manner in which the hook correction is performed in the MudMaster program (EBERL et al., 1996), because this correction is better optimized in the program for the asymptotic CTD shape. Consequently the spikes shown in Fig. 1 were removed from lognormal CTDs measured for the samples, using a smoothing power of 1 in the MudMaster program, prior to further analysis.

Crystallite thickness distributions can be characterized using parameters α and β^2 that describe the mean and variance of the natural logarithms of the crystal thickness (EBERL et al., 1998b), respectively (Table 1, Fig. 2). The growth pathways for the samples can be simulated with the aid of an alpha-beta squared diagram and the computer program GALOPER (EBERL et al., 2000). On this diagram, line 1–7 indicates the path for continuous nucleation and growth in open sys-

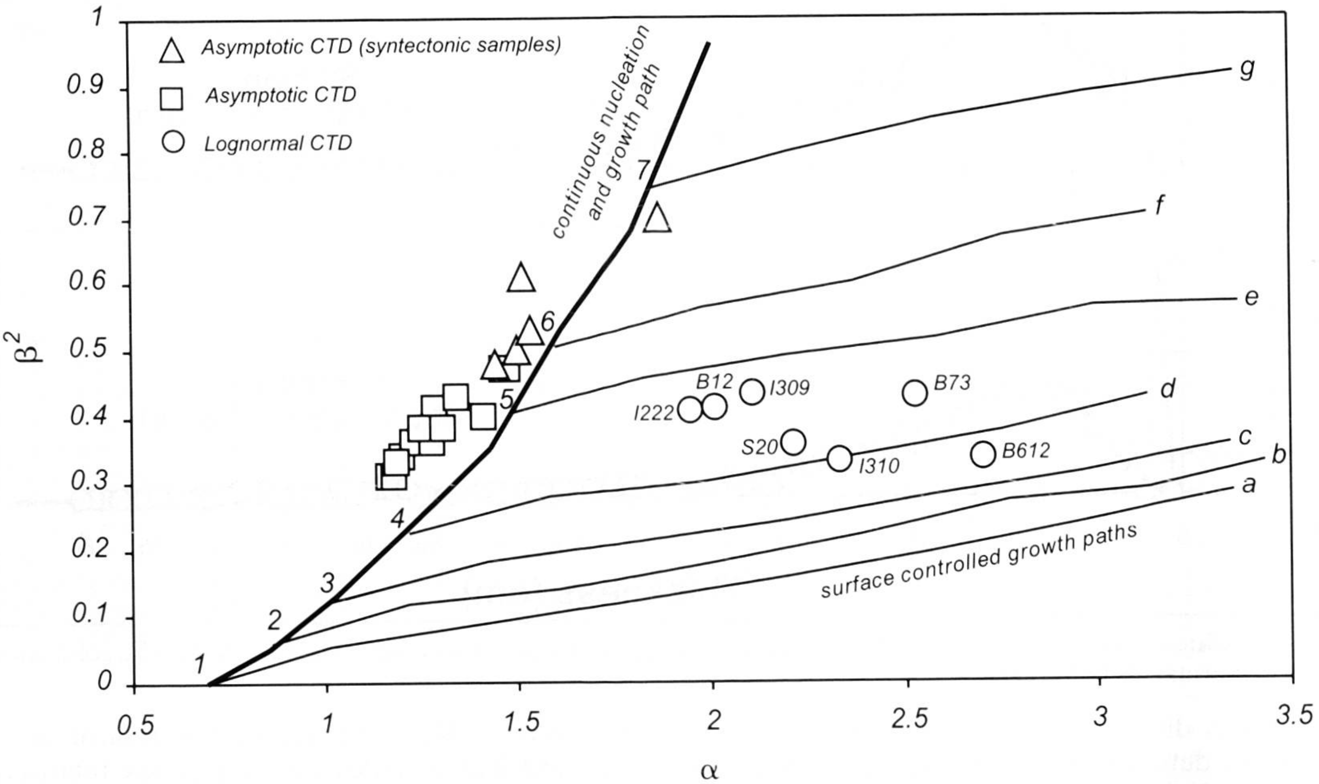

Fig. 2 α vs β^2 diagram determined on the samples using the MudMaster program. 1–7, path for simultaneous, constant-rate nucleation and growth; a–g, paths for surface-controlled growth without simultaneous nucleation.

tems, and lines a–g indicate paths for surface-controlled growth in open systems (EBERL et al., 1998b). Numbers 1 to 7 correspond to the number of cycles used by the GALOPER program to reach that position in the alpha-beta squared diagram. Lines a–g correspond to the various paths followed by the surface controlled growth of particles of different initial size (smaller in a, and bigger in g). The distribution of the studied samples (Fig. 2) shows that most asymptotic samples are distributed in an area roughly parallel to line 1–7, whereas samples with lognormal CTDs are located in the field to the right of it, between lines c–e. Both results are predicted by crystal growth theory (EBERL et al., 1998b; ŚRODOŃ et al., 2000).

Samples with asymptotic distributions have been modelled with a growth mechanism of constant rate nucleation and growth (path 1–7 of Fig. 2). According to EBERL et al. (1998b), this crystal growth mechanism is characterized by crystals nucleating with the same crystal thickness (2 nm in this case) and then growing according to the Law of Proportionate Effect as more crystals nucleate at a constant rate. In this model, β^2 increases exponentially with α. If this nucleation and growth event is followed by a surface-controlled growth without nucleation, the asymptotic distribution is transformed into a lognormal one (Fig. 1). The path followed by particles growing according to this model would be 1-4-d (Fig. 2).

4. Discussion

GALOPER simulations indicate that illites with asymptotic CTDs evolved by a mechanism of constant-rate nucleation and growth. These crystals must have formed in highly supersaturated solutions that could sustain nucleation (EBERL et al., 1998b). This behaviour is shown by the Devonian and younger rocks. Similar asymptotic shapes are obtained for samples with a big proportion of detrital material (DUDEK, 2001; ŚRODOŃ et al., in press), but the fact that the samples closely parallel and approach the theoretical curve in the α–β^2 space for nucleation and growth, lead us to favour this mechanism. However, the presence of various amounts of detrital components could cause the samples to have a larger β^2 than is predicted from crystal growth theory, and therefore cause them to plot to the left of theoretical curve 1–7 in Fig. 2.

In contrast, GALOPER simulations indicate that illites with lognormal-like CTSs grew initially by a mechanism of nucleation and growth followed by surface-controlled growth without nucleation as the level of supersaturation decreased. Nucleation is favoured by elevated supersaturation (e.g. LASAGA, 1998), and therefore a decrease in supersaturation, as nuclei appear and grow, would hamper nucleation. This mechanism is consistent with these samples showing the smaller Kübler index values. All of the lognormal CTDs are pre-Devonian.

The behaviour of the syntectonic Carboniferous samples (triangles on Fig. 2) is noteworthy. Although they have a low value of the Kübler index, indicating high anchizone for most of them, their CTDs are asymptotic, and organic indicators such as coal rank or pallinomorph alteration, indicate that diagenetic conditions prevailed in the area (CASTRO et al., 2000a, b). The disagreement between Kübler index and both stratigraphic position of the samples (thermal increase is mostly due to burial) and organic indicators, has been interpreted as the signature of detrital micas inherited from the rapidly uplifting Variscan chain. These micas probably avoided any significant chemical weathering throughout their short transport history (BRIME et al., 2001a). Incorporation of detrital phyllosilicates into the <2 μm fraction of sediments is a well known feature of low-grade shales (KÜBLER et al., 1991; WARR et al., 1996; NIETO et al., 1996; LANSON et al., 1998; GHARRABI et al., 1998), and would tend to narrow the XRD peak at half width. Therefore, it seems that CTD shape may better reflect crystallite evolution than the measurement of the Kübler index, particularly if some detrital components are present in the samples. Whereas the Kübler index may indicate anchizonal and even epizonal conditions, CTDs would not show the lognormal shapes characteristic of the onset of metamorphism.

5. Conclusions

The illites studied are characterized by distinct CTDs that seem to evolve in thickness systematically with increasing grade. The shapes of the CTDs are best explained by two growth stages,

1) an early stage of nucleation and growth, during which the asymptotic profile of CTDs was established; and, for crystals larger than a certain critical size,

2) a later stage of surface-controlled growth without further nucleation.

According to the results presented here, the critical thickness for the change from growth stage (1) to stage (2) is close to 5 nm (Fig. 2), a thickness which marks the change in CTD shape from asymptotic to lognormal, and which lies at the diagenesis-anchizone boundary. Therefore, at least in the rocks studied here, this boundary marks an important qualitative change in the mode of crystal growth. Location of this boundary by CTD shape rather than by mean crystallite thickness (determined either by XRD or TEM) may be less subject to measurement errors.

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