On the shape of the first 'illite' X-ray diffraction-reflection, crystallinity, and incipient metamorphism

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ABSTRACT

In a profile along the Swiss Alps 88 lithologically different sedimentary rocks, formed under diagenetic, low- and high-anchimetamorphic conditions, were sampled from 41 outcrops and prepared under normalized conditions to obtain <2μ fractions. The samples were analyzed chemically by non-destructive X-ray fluorescence analysis, and X-ray diffractometry (air-dried, glycolated); from all specimens temperatures ex-fluid inclusions in authigenic quartz had been determined previously. The XRD evaluation comprised: **a-** half-width determination of the complex, unresolved 10Å basal reflection (Kübler width); **b-** deconvolution of this complex reflection using Pearson functions for the three reflections of illite-muscovite, smectitic phase/smectite-illite mixed-layer, and chlorite in the angular range of 3-13°2θ (CuKα radiation, automatic divergence slit, optimized counting statistics by slow motion measurement); **c-** domain size determination after Warren-Averbach using a muscovite single crystal (002) reflection as a reference. The 10Å complex reflection is formed by the first illite basal reflection and in diagenetic/low-anchimetamorphic specimens by an additional mineral phase, expandable under glycol, and labelled here 'smectitic phase'. This phase has not been identified so far, but may be a mixed-layer mineral consisting of chlorite, illite,..,smectite. Though there exists for certain specimens a clear correlation between temperature ex-fluid inclusions and **a-** the overall half-width (Kübler width), but also **b-** the half-width, the curve exponents (curve form=Gauss- or Cauchy-like) and the peak positions of the deconvoluted illite and smectitic phase, this correlation is neither in all diagenetic, nor in all anchimetamorphic specimens preponderant. Domain sizes of coexisting air-dried illites and smectitic phases are, however, significantly correlated (r=0.93, N=88), as are the half-widths and d- spacings from the smectitic phase (r=0.90, N=88), on which both temperatures depend, at least trendwise. Several reasons are responsible for the sometimes weak interdependence of peak shape and illite crystallinity/incipient metamorphism: the general shape of the clay 10Å complex reflection is influenced by the height, position, half-width, symmetry and form of its contributors (e.g., illite-muscovite, smectitic phase, chlorite) on the one hand, and by instrumental, preparational, and specimen-related factors on the other. As a consequence, neither the overall half-width (Kübler width), nor the deconvoluted illite half-width is necessarily linked with illite crystallinity and incipient metamorphism alone. Notably, the grinding impact on sheet silicates during sample dressing may influence the symmetry of their basal reflections and half-widths, as can be demonstrated experimentally. But the chemical composition of the specimen may contribute also, for specimens from one and the same outcrop display, in some cases, different half-widths of illite and smectitic phase together with a strong chemical difference of the <2μ fractions involved.

Key words: Clay minerals, Crystallinity, X-ray diffraction.

RESUMEN

La forma del primer pico de difracción de rayos X de 'illita', cristalinidad y metamorfismo incipiente. En un perfil a lo largo de los Alpes suizos, se muestrearon 88 rocas sedimentarias, litológicamente diferentes, formadas bajo condiciones de diagénesis y de alto y bajo grado de anquimetamorfismo de 41 afloramientos y se prepararon bajo condiciones normalizadas con el objeto de obtener fracciones de <2μ. Las muestras se analizaron químicamente por medio de fluorescencia de rayos X no destructiva y por difractometría de rayos X (secadas al aire, glicoladas); de todas ellas se había determinado previamente las temperaturas según inclusiones fluidas en cuarzo autígeno. La evaluación con difracción de rayos X comprendió: **a-** determinación del ancho a media altura de la difracción basal compleja a 10Å no resuelta (ancho de Kübler); **b-** la descomposición de esta difracción compleja usando las funciones Pearson para las 3 difracciones de illita-muscovita, fase esmectítica/esmectita-illita interestratificada y clorita en el rango angular de 3-13°2θ (radiación CuKα, ranura de divergencia automática, estadística de conteo optimizada por medición de movimiento lento); **c-** determinación de dominios de tamaño según Warren-Averbach, usando la difracción (002) de un monocristal de muscovita como referencia. La difracción compleja a 10Å está formada por la primera difracción basal de illita y en especímenes diagenéticos/anquimetamórficos de bajo grado por una fase mineral adicional, expandible en glicol y llamada aquí 'fase esmectítica'. Esta fase no ha sido identificada, pero puede ser un mineral interestratificado que consiste en clorita, illita,..., esmectita. Aunque existe, para ciertos especímenes, una clara correlación entre la temperatura de inclusiones fluidas y **a-** el ancho a media altura general (ancho de Kübler), pero también **b-** con el ancho a media altura, los exponentes de curva (forma de curvas-Gauss o tipo Cauchy) y las posiciones de los picos de illita y de la fase esmectítica descompuestos, esta correlación no es preponderante ni en todas las muestras diagenéticas ni en todos las anquimetamórficas. Los dominios de tamaño de las illitas secadas al aire y de las fases esmectíticas coexistentes están, sin embargo, correlacionados en forma significativa (r=0,93, N=88), como lo están los anchos a media altura y los espaciados de la fase esmectítica (r=0,90, N=85), de las cuales dependen ambas temperaturas, al menos, desde el punto de vista tendencial. Varias causas son responsables de la, en ciertos casos, débil interdependencia entre la forma de los picos y la cristalinidad de la illita/metamorfismo incipiente: la forma general del pico complejo a 10Å de la arcilla está influenciada por la altura, posición, ancho a media altura, simetría y forma de sus contribuidores (por ejemplo, illita-muscovita, fase esmectítica, clorita) por un lado, y por factores instrumentales, preparacionales y relacionados con los especímenes, por el otro. Como consecuencia, ni el ancho a media altura general (ancho de Kübler) ni el ancho a media altura de la illita descompuesta están necesariamente ligados sólo con la cristalinidad de la illita y el metamorfismo incipiente. Notablemente, el impacto de la molienda en los filosilicatos durante la preparación de las muestras puede influenciar la simetría de sus difracciones basales y sus anchos a media altura, como puede ser demostrado experimentalmente. Pero la composición química del espécimen puede contribuir también, ya que especímenes del mismo afloramiento exhiben, en algunos casos, diferentes anchos a media altura de illita y de fase esmectítica junto con una diferencia química en las fracciones de <2μ.

Palabras claves: Minerales de arcilla, Cristalinidad, Difracción de rayos X.

INTRODUCTION

Along the northern slope of the Swiss Alps 41 sedimentary outcrops have been sampled for temperature determinations on fluid inclusions in authigenic quartz (Mullis, 1987; Mullis *et al.*, 1991) representing the diagenetic and anchimetamorphic realm with temperatures ranging from slightly below 200°C to 280°C. The rock samples were treated according to normalized procedures of preparation for clay minerals. Decarbonated, $CaCl_2$ saturated <2μ fractions were sedimented on glass slides maintaining 5 mg/cm².

MEASUREMENTS

The air-dried clay mineral fractions were analyzed by means of non-destructive energy-dispersive X-ray fluorescence spectrometry (ED-XFA, Stern, 1985), subsequently measured with X-ray diffraction (XRD), then glycolated and measured again with XRD (Table 1).

Since the diffractograms had to serve two purposes-identification of the mineral phases present, and deconvolution of the first complex reflection at

TABLE 1. INSTRUMENTAL CONDITIONS.

	XRD		
Equipment	Siemens Diffractometer D-500		
Excitation	Cu- radiation, 40 Kv, 30 MÅ		
Apertures	Automatic divergence slit, 3° opening angle slit configuration 3° primary side, 1°, 0.05, 0.15 mm, secondary side. Graphite secondary monochromator		
Scanning	From 3 to 15°2θ increment 0.05°, time 30 seconds		
	15 to 42°2θ	0.02	1 second
	42 to 48°2θ	0.02	10 seconds
Computer	Sicomp 32-20, Syquest external hard disc		
Software	Diffrac AT version 3.1 by Socabim, Siemens 1992		
	Win-Crysize by Sigma-C, version 1.0 1991		
	JCPDS-sets 1 to 43 for phase idetification		
	Graphics, evaluation LOTUS 1-2-3, version 3.1		
	Windows version 3.1		
	ED-XFA		
Equipment	Tracor/Spectrac Spectrace-5000		
Elements	light	medium	heavy
Tube anode	W	W	W
Excitation	4kV 0.50 mA	10 kV 0.05 mA	25 kV 0.20 mA
Filter	no	cellulose	silver
Time, sec.	100	200	100
	Na Mg Al	Si S Cl K Ca ti V Cr Mn Fe	Zn Rb Sr Zr Nb
Vacuum	+	+	+
Collimator	10 mm	10mm	10mm
Specimen	sedimented <2 micron 5mg/cm^2, same as for XRD		
Computer	IBM PS/2 80-386, 300 Mb hard disc		
Software	Spectrac version 1.35		
	Fundamental parameter correction routine /GL-III		
	Graphics, evaluation LOTUS 1-2-3, version 3.1		

10Å- the entire angular range from 2 to 48°2θ (Cu radiation) was recorded, but split into three sections with different angular increments and measuring times in order to obtain adequate counting statistics, a prerequisite for mathematical peak deconvolution, the overall measuring time being $3^1/_2$ hours for one sample. The raw data were stored electronically for further evaluation.

The first slow scan ranges between 2 and 13°2θ containing the often unresolved complex, together with chlorite (001), 'smectitic phase/mixed-layer', and illite-muscovite (001) was deconvoluted by means of a fairly complex fitting programme (Diffrac AT, version 3.1 of Socabim 1986/92 and Siemens 1992). The term 'smectitic phase' is chosen here, because its often unresolved main reflection expands under glycolation, but never reaches 17Å. In air-dried <2μ fractions it never replaces illite, but represents always an additional reflection well developed in diagenetic specimens, and forming a marked tailing on the short angle side of illite in anchimetamorphic specimens. The term 'illite/smectite mixed-layer' is not used here, since the identity of the possibly present minerals chlorite, illite, smectite was not clarified.

For deconvolution, the following steps had to be performed on the display: **a-** background subtraction using a minimal curvature only; **b-** choice of the appropriate fitting function among Gauss, Lorentz, Pseudovoigt, Pearson 7 and Split-Pearson options. In general, strong X-ray reflections can be described by Gaussian curves, whereas weak reflections with broad base lines, like the ones of clay minerals, are best fitted by Pearson functions which display the strong advantage in modelling Gauss-like and Cauchy-like curves by adapting their curve exponent (Wang, 1994). This exponent is high for Gauss-like reflections of well crystallized sheet silicates, and small (near 1) for poorly crystallized phases, and represents,

therefore, an essential variable when studying incipient metamorphism; **c-** identification of the involved peaks, usually three belonging to chlorite (001), smectitic phase, and illite-muscovite (001), and setting the cursor at the respective peak apex; **d-** fixing the background at ze-o level, since it had been subtracted already; **e-** performing a first tentative fit, comparing the obtained curve envelope with the measured curve, and controlling the reliability percentage given by the programme; **f-** in case of a good reliability (percentage e.g., below 5) the results (peak positions, d-spacings, heights, half-widths, areas and exponents) were stored electronically for further use, like graphical display under LOTUS, or domain-size determination after Warren-Averbach; **g-** in case of insufficient reliabilty, steps 4 and 5 had to be repeated and optimized by varying the peak positions of the smectitic phase and illite. Reliability figures above 10 were accepted only, when explained by *e.g.*, poor counting statistics (low concentration of sheet silicates in the clay mineral fraction). The reliability percentages were also stored as an essential indication on the fitting quality.

Though it is in principle, possible to improve the reliability figure by introducing additional reflections, this approach is acceptable only, when there exists mineralogical evidence for further phases present in the <2μ fraction.

RESULTS

For certain specimens a clear interdependence between the shape of the 10Å complex and incipient metamorphism exists, (Fig. 1), Stern *et al.* (1991, 1993). The half-width of the unresolved reflection (Kübler width) and the temperature ex-fluid inclusions correlates well, as do the deconvoluted half-widths of the smectitic phase and illite, the curve exponents -a new criterion, neglected so far in clay mineral studies,- and the d-spacings of the smectitic phase, (Fig. 2). As stated by Mullis *et al.* (1993), however, a large scattering is present when the illite crystallinity of air dried samples is plotted against the homogeneization temperature of methane-bearing, water-rich fluid inclusions in quartz.

Several reasons may be claimed, why half-width and temperature are not always closely correlated:

- The shape of complex reflection around 10Å does not depend on illite crystallinity solely, but on instrumental, preparational and specimen related factors as well (Table 2).

TABLE 2. FACTORS INFLUENCING THE OVERALL SHAPE OF THE CLAY MINERAL 10Å COMPLEX.

	OVERALL SHAPE				
Source	**Height/Area**	**Position/d-value**	**Half-Width**	**Symmetry**	**Form Gauss/Cauchy**
Instrumental					
Construction	+		+	+	+
Tube, anode	+	+			
kV, mA	+				
Collimators	+		+	+	+
Apertures	+		+		
Mineral Assemblage					
Present phases	+	+	+	+	+
Mass fractions	+				
Preferred orientations	+				
Mineral chemical	+	+			
Crystallinity	+		+		+
Mixed layering	+	+	+		
Sample Preparation					
Rock dressing	+		+	+	
Slide preparation	+		+		

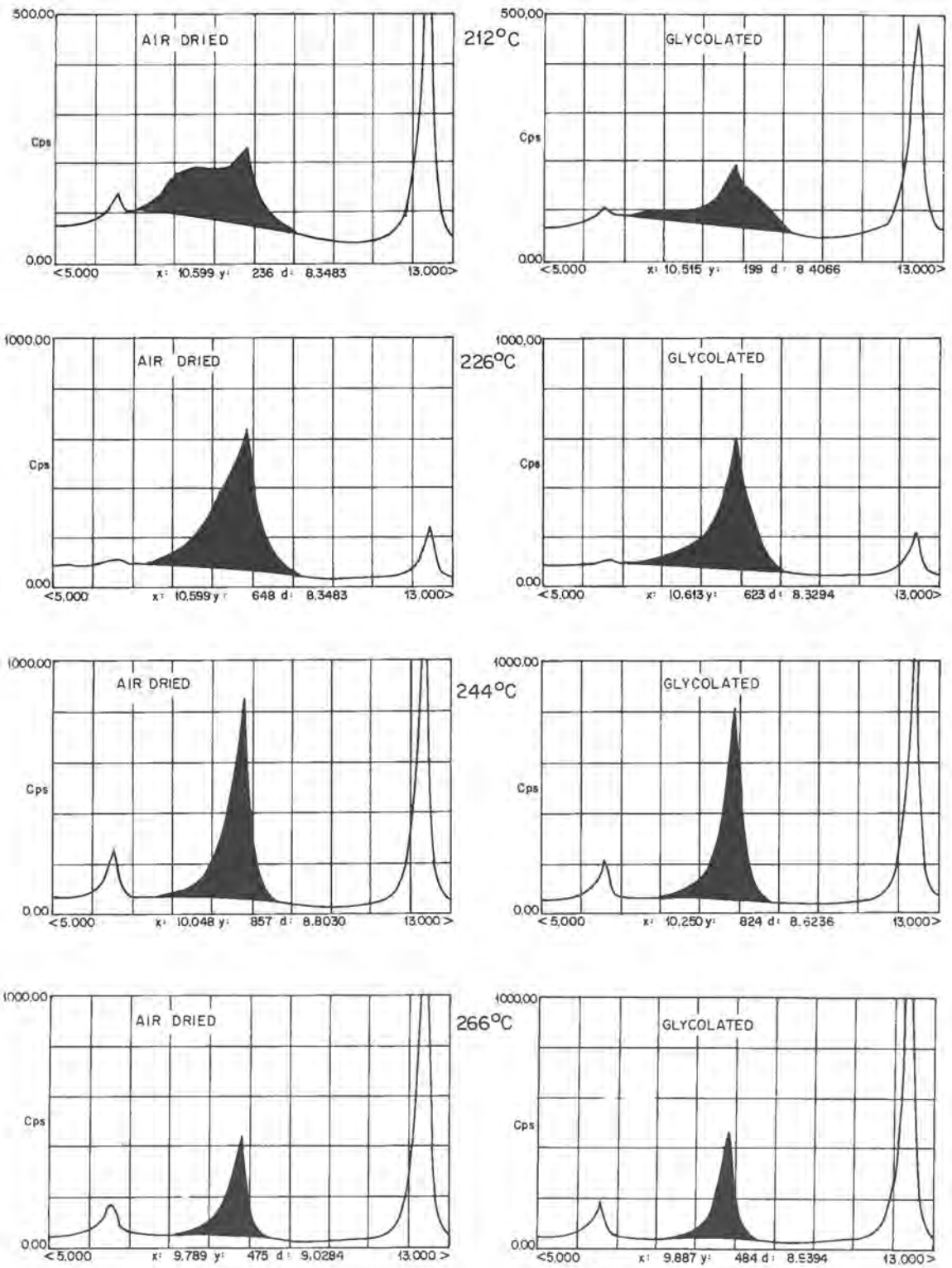

FIG. 1. Diffractograms of four <2μ fractions 5 mg/cm² (air-dried left, glycolated right), temperature ex-fluid inclusion measurements on quartz. The unresolved first clay mineral basal complex around 10Å is marked in black.

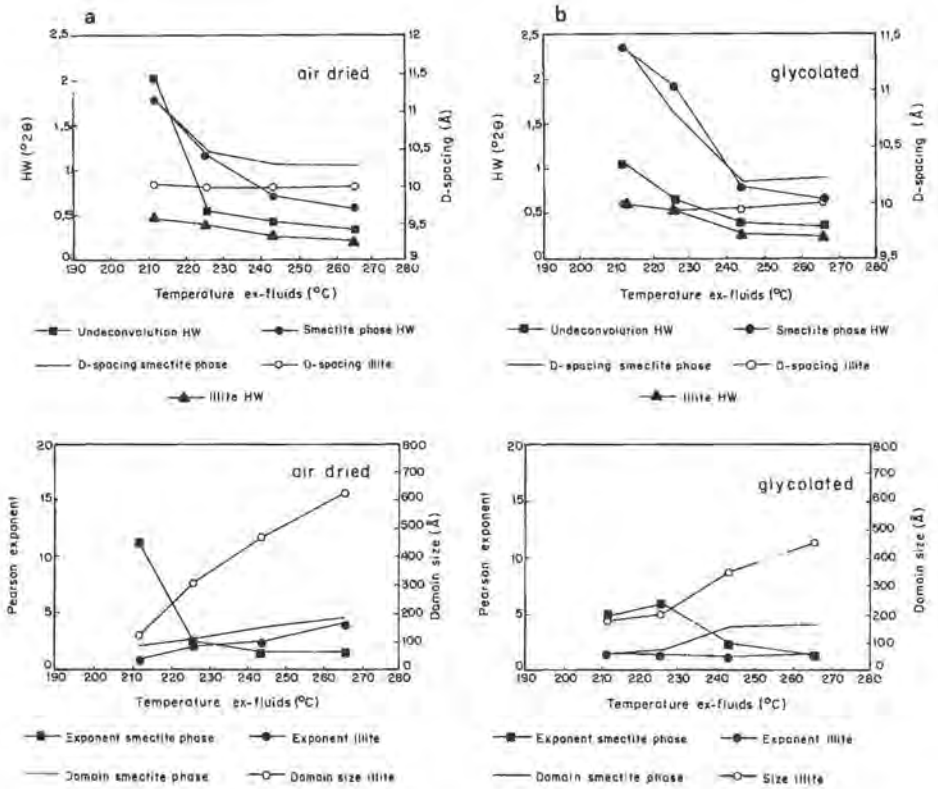

FIG. 2. Half-widths and d-spacings of the same four diffractograms, obtained by deconvolution using a Pearson curve fitting, air dried (2a), glycolated (2b). The d-spacings of illite do not change with temperature, their half-widths (HW) change weakly in contrast to the smectitic phase. The curve exponents are highly correlated with temperature: illite becomes Gauss-like with incipient metamorphism (rising exponent), whereas the smectitic phase becomes Cauchy-like (dropping exponent).

Instrumental factors play an important role when data of different sources are compared, but are neglectable when the results are considered which were collected with the same standardized analytical routine on the same diffractometer.

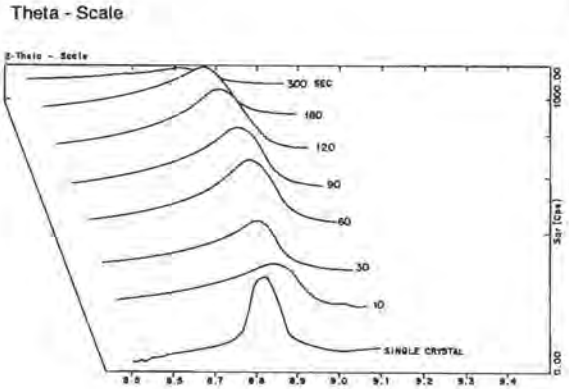

FIG. 3. The effect of grinding on muscovite (002) basal reflection. The strong, symmetric peak of the muscovite single crystal shrinks after short grinding in a disc mill, its half-width broadens, and a tailing on the short angle side appears, possibly due to the mechanical impact of grinding on the sheet silicate platelets.

Preparational factors are important when samples of different brittleness are treated, for grinding a rock specimen has an impact on the sheet silicates present: basal reflections may display a marked asymmetry or tailing after short grinding times (20 s disc mill), (Fig. 3). This tailing is not observed when the rock specimen is cleft, and the untreated surface measured with XRD.

Specimen-related factors, like the mineral proportions, preferred orientation of certain minerals, have an influence on the overall curve shape.

- The chemical composition of the <2μ fraction may have an impact on the half-widths of the sheet silicates present. Different samples from the same outcrop, treated and measured individually, may display quite different half-widths, though the temperature ex-fluid inclusions is the same. If the half-widths of illite and the smectitic phase are different, then the chemistry of the <2μ fraction is different also (Fig. 4).

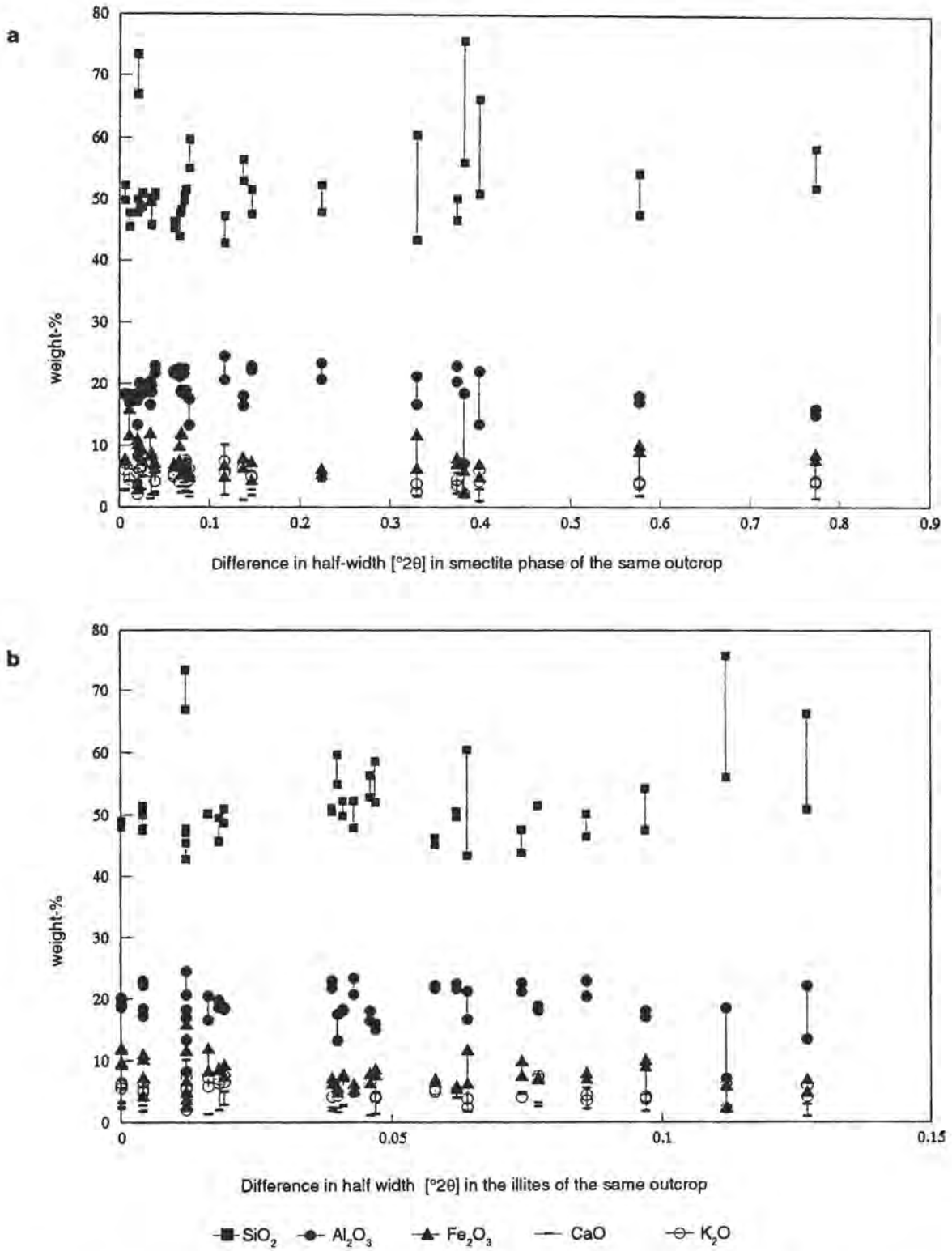

FIG. 4. The difference of half-width (air-dried) of a- smectitic phase and b- illite specimens from the same outcrop *versus* the chemical composition of the <2μ fractions involved. A strong difference in half-width is generally linked with a strong chemical difference in either SiO_2, Al_2O_3, Fe_2O_3 K_2O or CaO.

The deconvolution of the complex reflection around 10Å reveals, that behind the correlation of the unresolved half-width (Kübler width) with incipient metamorphism, a series of variables connected with crystallinity exists, like d-spacing, curve exponent, peak area and half-width of the smectitic phase, curve exponent, area and half-width of illite. All variables together are responsible for the shape and the half-width of the unresolved complex.

Some of the mentioned variables are closely correlated with each other, like d-spacings and half-widths of the smectitic phase, (Fig. 5). Diagenetic samples (code C, 1, 2) plot in a large compositional field, whereas anchimetamorphic specimens (code 4-7) occupy a restricted field only. The deconvolution of the smectitic phase reflects merely the ripening under diagenetic conditions.

From both, smectitic phase and illite, domain sizes after Warren-Averbach can be derived by using a perfectly crystallized single crystal of muscovite as a reference. Domain size, sometimes called crystallite size, must not be interpreted as grain size, for it is defined as the size of a microdomain that diffracts 'in phase'. Diffraction is sensitive to such diffraction units and not to the particle size. By evaluating a (001) basal reflection, the domain size reflects parts of the crystallographic c-direction, the thickness of a sheet silicate grain, and not the a-b plane, *i.e.*, the flake diameter.

The domain sizes of illite and smectitic phase are highly correlated with r=0.932, N=88, diagenetic specimens displaying expectedly small sizes (code 0, 1, 2 +-3), and anchimetamorphic specimens, larger ones, with 400-700Å for illite, and 80-160Å for smectitic phases, (Fig. 6).

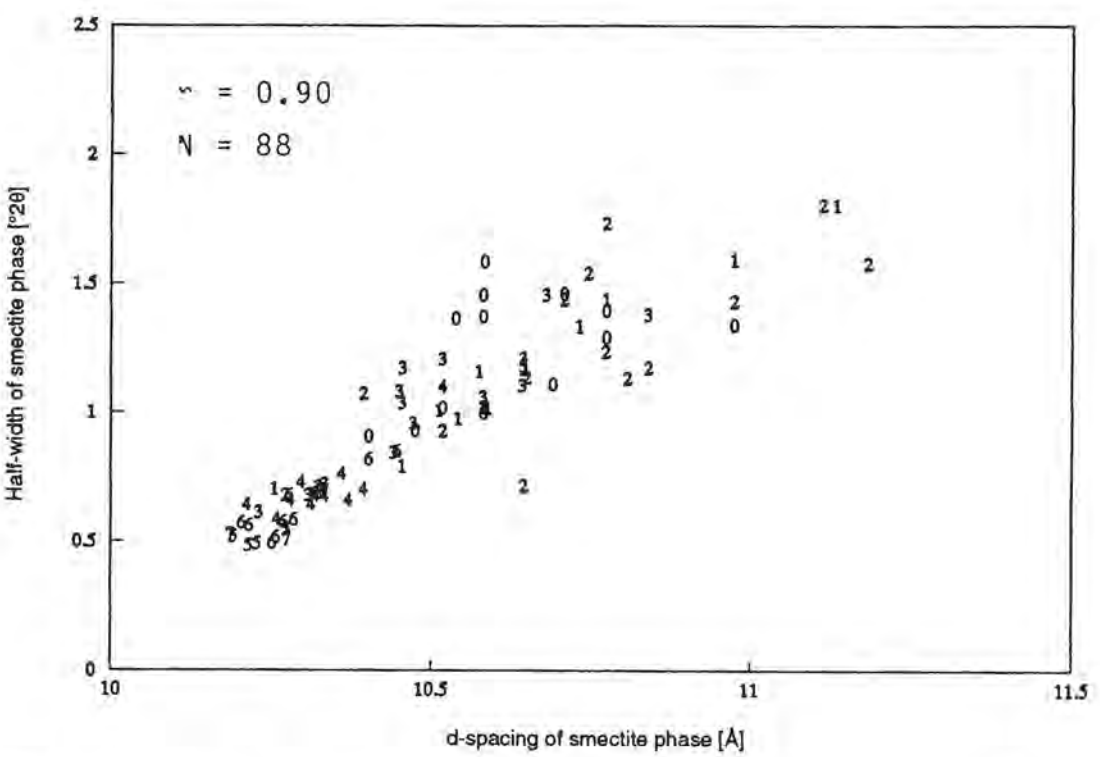

FIG. 5. Half-width *versus* d-spacing of air-dried smectitic phase. Diagenetic specimens (temperature code 0 to 2, ±3) occupy a field in contrast to anchimetamorphic samples (temperature code 3-7).

Code for temperatures from fluid inclusions (°C) [for figures 5 and 6]

0- below 209 1- 210-219 2- 220-229 3- 230-239 4- 240-249 5- 250-259 6- 260-269 7- 270-279

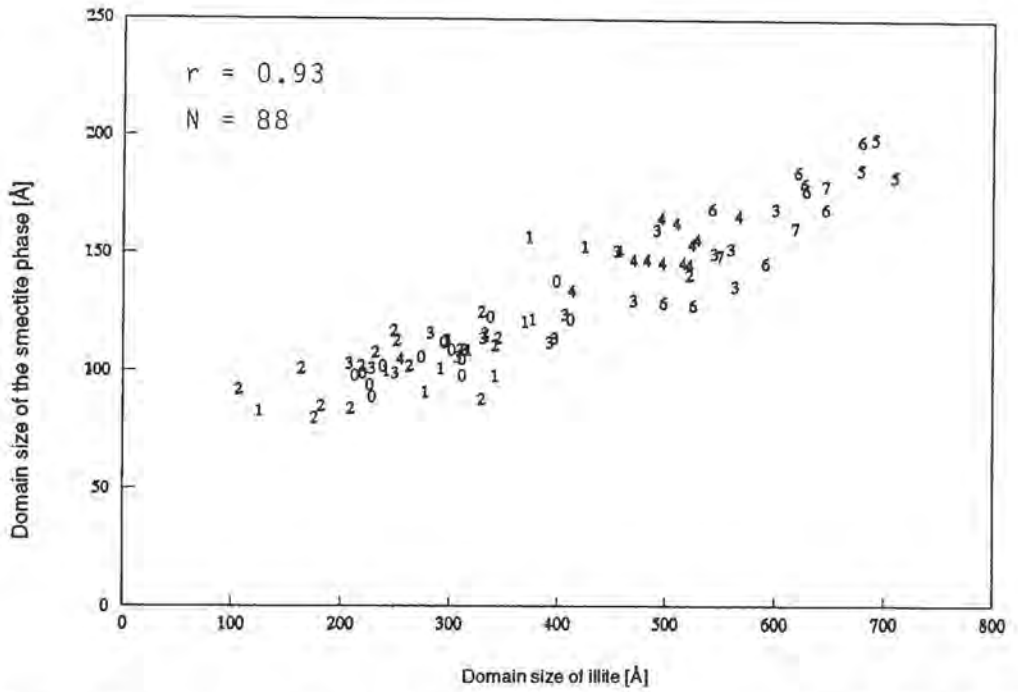

FIG. 6. Domain size after Warren-Averbach of air dried illite and smectitic phase. Diagenetic specimens (temperature code 0 to 2, ±3) display much smaller domain sizes (80-160Å for smectitic phases, and 100-400Å for illite) representing a low degree of ordering in contrast to anchimetamorphic samples (120-200Å for smectitic phases, and 400-700Å for illites).

ACKNOWLEDGEMENTS

This paper was presented at the IGCP 274 Low Temperature Metamorphism Symposium, Santiago, Chile, October 1993.

The authors are indebted to Drs. C. Brime and H. Kisch for critical reading and helpful suggestions.

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Manuscript received: January 5, 1994; accepted: December 5, 1994.