1 XRD-based $^{40}\text{Ar}/^{39}\text{Ar}$ age correction for fine-grained illite, with
2 application to folded carbonates in the Monterrey Salient
3 (northern Mexico)

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9 **ABSTRACT**

10 Due to their minute size, $^{40}\text{Ar}/^{39}\text{Ar}$ analysis of illite faces significant analytical challenges,
11 including mineral characterization and, especially, effects of grain size and crystallography on
12 ^{39}Ar recoil. Quantifying the effects of ^{39}Ar recoil requires the use of sample vacuum
13 encapsulation during irradiation, which permits the measurement of the fraction of recoiled ^{39}Ar
14 as well as the ^{39}Ar and $^{40}\text{Ar}^*$ retained within illite crystals that are released during step heating.
15 Total-Gas Ages (TGA) are calculated by using both recoiled and retained argon, which is
16 functionally equivalent to K-Ar ages, while Retention Ages (RA) only involve retained Ar in the
17 crystal. Natural applications have shown that TGA fits stratigraphic constraints of geological
18 processes when the average illite crystallite thickness (ICT) is smaller than 10 nm, and that RA
19 matches these constraints for ICTs larger than 50 nm. We propose a new age correction method
20 that takes into account the average ICT and corresponding recoiled ^{39}Ar for a sample, with X-
21 Ray Corrected Ages (XCA) lying between Total-Gas and Retention ages depending on ICT. This

correction is particularly useful in samples containing authigenic illite formed in the anchizone, with typical ICT values between 10 and 50 nm.

In three samples containing authigenic illite from Cretaceous carbonates in the Monterrey Salient in northern Mexico, there is a range in TGAs among the different size-fractions of 46-49, 36-43 and 40-52 Ma, while RAs range from 54-64, 47-52 and 53-54 Ma, respectively. XCA calculations produce tighter age ranges for these samples of 52.5-56, 45.5-48.5 and 49-52.5 Ma, respectively. In an apparent age vs ICT or %2M illite plot, authigenic illite grains show a slope that is in general slightly positive for TGA, slightly negative for RA, but close to zero for XCA, with thinner crystallites showing more dispersion than thicker ones. In order to test if dispersion is due to a different formation history or the result of retention capability, degassing spectra were modeled for site XCA averages and overall XCA average. Modeling shows that local site age average best match the measured spectra, instead of a global average age, indicating that illite growth reflects local deformation, and is not the result of regional metamorphism. Modeling also shows that Ar-degassing spectra are very sensitive to grain size, such that age interpretation based on Ar-plateaus is meaningless for most fine-grained clays.

KEYWORDS: Ar-Ar dating, illite, XRD, crystallinity

1. INTRODUCTION

$^{40}\text{Ar}/^{39}\text{Ar}$ illite dating is commonly used to analyze the timing of various geological processes in the upper crust, including diagenesis and hydrocarbon formation (Pevear, 1999; Dong *et al.*, 2000; Clauer *et al.*, 2011; 2012), low grade metamorphism (Dong *et al.*, 1997; Merriman and Peacor, 1999; Verdel *et al.*, 2011), epithermal ore formation (Hall *et al.*, 1997 and 2000), faulting (e.g., van der Pluijm *et al.*, 2001; Solum and van der Pluijm, 2005; Haines and

van der Pluijm, 2008; Osborn *et al.*, 2014), and folding (Fitz-Díaz and van der Pluijm, 2013; Fitz-Díaz *et al.*, 2014a). Illite is one of the few K-bearing minerals that form under diagenetic and anchizonal conditions (Fig. 1a) and has the capacity of retaining radiogenic argon ($^{40}\text{Ar}^*$) in its structure after natural recoil (i.e., $^{40}\text{Ar}^*$ nm-scale displacement during ^{40}K spontaneous radioactive decay, Zimmermann and Odin, 1982; Szczerba *et al.*, 2015) at low temperature (Hassanipak and Wampler, 1996; Clauer *et al.*, 1997; Sletten and Onstott, 1998).

$^{40}\text{Ar}^*/^{39}\text{Ar}$ dating is a variant of the K-Ar dating method that allows for the analysis of small amount of samples with high precision (van der Pluijm *et al.*, 2001; Clauer, 2012). The K-Ar dating technique is based on the decay of the rare ^{40}K isotope into ^{40}Ar and radiogenic ^{40}Ar is typically designated $^{40}\text{Ar}^*$. Such a transformation involves a low energy process, known as electron capture, that retains most of the $^{40}\text{Ar}^*$ in the parent ^{40}K site after decay (Fig. 1, Beckinsale and Gale, 1969). Recently, Szczerba *et al.* (2015) demonstrated, using molecular dynamics simulations, that some dislocation of $^{40}\text{Ar}^*$ is possible within illite due to the decay of ^{40}K , but the net loss is expected to be very small for all but the smallest of illite particles ($<0.02\mu\text{m}$ in diameter and less than five illite fundamental layers). For $^{40}\text{Ar}^*/^{39}\text{Ar}$ dating, the K content is estimated by producing ^{39}Ar in a nuclear reactor using the fast neutron reaction ^{39}K (n,p) ^{39}Ar (Merrihue and Turner, 1966). Assuming a constant $^{39}\text{K}/^{40}\text{K}$ ratio, one can then use ^{39}Ar as a proxy for ^{40}K (McDougall and Harrison, 1999). The $^{40}\text{Ar}/^{39}\text{Ar}$ age equation is given by:

$$t = \frac{1}{\lambda} \ln \left(1 + J \frac{^{40}\text{Ar}^*}{^{39}\text{Ar}} \right) \quad (1)$$

where λ is the total decay constant for ^{40}K and J is a conversion constant determined by analyzing mineral standards of known K-Ar age, as neutron flux monitors.

In fine-grained samples, such as illite, many studies have shown that the effects of ^{39}Ar recoil can be significant (Turner and Codogan, 1974; Halliday, 1974; Hall, 2014). Onstott *et al.*

(1995) calculated a mean recoil range of 162 nm for the reaction $^{39}\text{K}(\text{n}, \text{p})\text{-}^{39}\text{Ar}$, which explains why small flake-shaped crystallites of illite (Fig. 1b), often smaller than 2000 nm in diameter and 30 nm in thickness, lose significant amounts of ^{39}Ar during irradiation. Seidemann (1976) devised a method of vacuum encapsulation of fine-grained samples during irradiation, and after opening the sample capsule within the fusion system (i.e., a vacuum line where the sample is heated for thermal degassing) to directly measure the release of ^{39}Ar that occurred during neutron irradiation. The technique has since been applied with considerable success by several laboratories (e.g., Hess and Lippolt, 1986; Foland *et al.*, 1992; Smith *et al.*, 1993), and has been routinely used at the Argon Geochronology Laboratory of the University of Michigan since the mid-1990's.

Total-Gas Ages (TGA, Fig. 2a) are calculated from Equation 1 by using both recoiled and retained argon after breaking the silica capsule, while Retention Ages (RA, Fig. 2b) only involve retained Ar in the crystal (Dong *et al.*, 1995). The Total-Gas Age model considers that K is absent in the two exposed half interlayers (top and bottom, Fig. 2a) and that ^{39}Ar in the recoil fraction has escaped from the interlayers (gray area, Fig. 2a) during neutron irradiation. Since the unbound or exposed half interlayers (i.e., K bearing surface bounding TOT fundamental particles of illite, Fig. 1) do not contribute to the total ^{39}Ar inventory, all of the ^{39}Ar measured, both retained and recoiled, is included in the age calculation, hence the name Total Gas Age. On the other hand, the retention age model considers that K is present in all non-retentive sites (two exposed half layers, smectite layers and dislocations, Aronson and Douthitt, 1986, Fig. 2b), and that ^{39}Ar in the recoil fraction (f_{recoil}) comes from such layers. Since radiogenic $^{40}\text{Ar}^*$ would have already escaped the exposed interlayers, that component of the total ^{39}Ar inventory should be omitted from the age calculation.

Empirical observations have shown that TGAs are in excellent agreement with stratigraphic constraints of geological processes when illite crystallite thickness (ICT, see Kübler, 1968; Eberl and Velde, 1989) are smaller than 10-15 nm (e.g., Hnat and van der Pluijm, 2014), while RAs better match stratigraphic constraints when illite crystallites are thicker (e.g., Dong *et al.*, 1995, 1997, 2000; Hall *et al.*, 1997; Verdel *et al.*, 2011; Fitz-Díaz *et al.*, 2014a, Fig. 2a-b). Illite crystals with illite crystallite thickness >50 nm tend to have total gas and retention ages that are close to each other, and when crystallites are larger than 150 nm the ages are identical within the analytical error (Hall, 2014). However, samples with illite crystallite thickness between 10 and 50 nm might have intermediate ages between TGAs and RAs, but there is currently no quantitative method to calculate such an age, which is the focus of this paper.

The XRD-derived illite crystallinity (IC) provides a measure of average illite crystallite thickness (*ICT*) in nm, here considered as the average number of TOT fundamental units of illite, which are 1 nm thick (Fig. 1). The average number of TOT layers or *ICT* (in nm) in a sample also contains the same number of K-bearing interlayers. $^{40}\text{Ar}/^{39}\text{Ar}$ step-heating analysis gives the average fraction of recoil in the samples. This is the fraction of ^{39}Ar released after breaking the sample quartz capsule and prior to heating and this recoil fraction does not include Ar retained within illite crystals. According to Dong *et al.* (1995), this can be visualized as an average number of Ar-retentive TOT interlayers, here is indicated as n_a , where $n_a = 1/f_{\text{recoil}}$. The average recoil distance in silicates for ^{39}Ar is 162 nm, or roughly the equivalent of 162 TOT layers. ^{39}Ar concentration can be assumed to have been thoroughly homogenized within illite crystals, so ^{39}Ar will only be retained if the recoiled atom ends up in a bound interlayer (Fig. 2c). See the methods section for further discussion.

We test our approach in natural samples containing dominantly authigenic discrete illite that was formed during a single deformation event, thereby allowing us to characterize the effects of ICT on $^{40}\text{Ar}/^{39}\text{Ar}$ illite age. XRD studies were performed on four clay-size-fractions (1-2, 1-0.2, 0.2-0.05, and $<0.05\ \mu\text{m}$) of three illite-dominated samples. Mineralogical composition of the samples, as well as crystallographic properties such as illite crystallite thickness (ICT) and polytype quantification were obtained. We tested our new XCA calculation with synthetic age spectra based on Monte Carlo simulation outlined in Hall *et al.* (1997, 2000), which successfully reproduces experimental age spectral patterns. By comparing experimental and modeled degassing patterns, we show that our new age correction method matches theoretical prediction. Our results have implications in understanding the effect of grain size on Ar-Ar age interpretations, and on the meaning of (absent) plateaus in illite degassing spectra.

2. GEOLOGICAL SETTING

The studied samples were collected in the Monterrey Salient (Fig 3a), which is a curved sector of the Mexican Fold-Thrust Belt in northeastern Mexico (Padilla y Sánchez, 1982; Campa-Uranga, 1983; Chávez-Cabello *et al.*, 2005). The Mexican Fold-Thrust Belt (MFTB) is mostly a thin-skinned thrust belt that involves a thick package of Cretaceous carbonates (Eguiluz de Antuñano *et al.*, 1999; Fitz-Díaz *et al.*, 2011). Lateral and vertical facies variations of carbonates exert controls on deformation styles, which are fold-dominated in stratified deep-water carbonate successions and thrust-dominated in massive, shallow-water carbonate platforms (Fitz-Díaz *et al.*, 2012). Shortening in the MFTB was progressive and episodic from west to east and occurred in a time span between 86 and 43 Ma in central Mexico (Fitz-Díaz *et al.*, 2014a).

In the Monterrey Salient, the sedimentary cover is constituted by a horizon of Middle Jurassic evaporites, which is hundreds meters of thick (Minas Viejas Fm.) and carbonates (Zuloaga Fm.), covered by Late Jurassic terrigenous units (La Casita and Taraises formations). These, in turn, are overlain by a succession of thickly bedded shallow-water Cretaceous carbonates interbedded with bentonitic shale (Cupido, La Peña and Aurora fms.), covered by Late Cretaceous terrigenous units (Agua Nueva, San Felipe and Mendez fms. Fig. 3b-c). The successions show a thin-skinned deformation style, dominated by a train of upright, symmetrical, km-scale, buckle folds, detached above a thick horizon of evaporites (Fig. 3c, Padilla y Sánchez, 1982; Carmelo 1998; Chávez-Cabello *et al.*, 2005). Balanced cross-section analysis provided an estimate of a minimum of 33% of horizontal shortening by folding (Marrett and Aranda, 1999). According to physical models on folding of carbonate sequences above a very weak detachment, deformation is likely synchronous in all folds along the train (e.g., Dixon, 2004). Therefore, we expect that illite formation is contemporaneous in both limbs of a fold (Fitz-Díaz and van der Pluijm, 2013), which we test by dating two limbs in two folds and a hinge of a fold in between. We collected samples of bentonitic shale in three folds, Sample 1 on the forelimb of the Los Muertos Anticline, in the northern front of the Monterrey Salient; Sample 2 in the hinge of Los Nuncios Anticline to the south; and Sample 3 in the backlimb of the Clavelillas Anticline, farther south (Fig. 3c and 4). The timing of deformation in the area can be constrained from the age of deposition of syn-tectonic units in La Popa Basin (foreland basin to the north of the Monterrey Salient, Fig. 3a), indicating that fold-related uplifts in the area occurred in the Paleogene (Lawton *et al.*, 2009; Gray and Lawton, 2011).

Samples were collected from strongly sheared shale layers associated with a single event of folding (Fig. 4a-b). SEM and XRD analysis in this study show that samples consist mostly of

illite, with minor amounts of calcite, quartz, kaolinite and iron oxides. Illite crystals are very homogeneous in size (few microns in diameter), and show a strong alignment with bedding-parallel, shear-related foliation. The fact that almost all illite grains show similar size and morphology (lath shape), and the absence of overgrowth of hairy shaped alteration illite, suggests only one generation of illite present in the sample (Fig. 4c-e).

3. METHOD

Based on field considerations, such as the evidence of only one generation of folding and no secondary alteration in the samples, we centered our analysis on samples 1, 2 and 3 in the forelimb, hinge and backlimb of a train of folds in the northernmost front of the Monterrey Salient in Aptian limestone successions, as shown in Figure 3. We collected 200 grams of shale sample, from which four grain-size fractions were separated by centrifugation, in order to concentrate illite from other phases in the sample. Illite concentrates were characterized with XRD, dated with the Ar-Ar vacuum-encapsulation method (Dong *et al.*, 1995; van der Pluijm *et al.*, 2001). We obtained illite crystallinity (ICT), fraction of recoil, traditional Total Gas Ages (TGA) and Retention Ages (RA), and determined corrected ages (XCA) from our new method that were tested with Monte Carlo simulations.

3.1 Clay Characterization

Illite concentration included rock crushing, dispersion of powder in de-ionized water in an ultrasonic bath, separation of four clay size-fractions ($<0.05\ \mu\text{m}$, fine; $0.05\text{--}0.2\ \mu\text{m}$, medium-fine; $0.2\text{--}1\ \mu\text{m}$ –medium-coarse; and $1\text{--}2\ \mu\text{m}$, coarse) by centrifugation, and sample drying. Randomly oriented preparations of the $<2\ \mu\text{m}$ clay size-fraction samples were created to

characterize the mineralogy by scanning from 2° - 50° 2θ (Cu $K\alpha$) at a rate of 1° per minute, which verified that no other phases containing potassium or hydrogen are present in the clay size-fractions. Oriented clay slurry mounts with a concentration of at least 4 mg/cm^2 of the five size-fractions were prepared by sedimentation onto glass slides and measured from 2 to 30° 2θ under air-dried and glycolated conditions. Air-dried samples were measured at a rate of $1^{\circ}/\text{min}$, while XRD measurements of glycolated preparations were carried at a speed of $1^{\circ}/20$ seconds. Mineralogical identification, the presence of discrete illite and smectite, interlayered with illite and/or chlorite, was identified by comparing XRD patterns in air-dried and glycolated preparations as described by Moore and Reynolds (1997), see Appendix 1.

We measured the illite crystallinity (IC) or Kübler index (Kübler 1967) of clays, which is a measure of the ordering/thickness of illite crystallites, but has also been attributed to the temperature of formation (Kübler, 1968). The illite crystallinity (IC) corresponds to the full width ($\Delta 2\theta$ angle) at the half maximum of the 001 basal reflection of the $10 \text{ \AA}$ or 1 nm peak of illite in the XRD pattern of an oriented preparation. Calibration of the IC followed the procedure of Warr and Rice (1994). With calibrated IC and using the Scherrer equation we obtain the illite crystallite thickness (Patterson, 1939), see Figure 5a.

The proportions of illite polytypes, $2M_1$ (detrital) and $1M_d$ (authigenic), in the samples (Fig. 5b) were determined by comparing XRD patterns measured in randomly-oriented powder samples with high-resolution patterns measured on standards. XRD patterns of Owl Creek muscovite clay-size powder is a proxy for $2M_1$ (detrital) illite, and the $1Mt_1$ standard of the Clay Mineralogical Society is a proxy for $1M_d$ (authigenic) illite (Haines and van der Pluijm, 2008). The patterns from end-member standards are numerically mixed and compared in an Excel spreadsheet, and best-matched with measured patterns. This allows for the estimation of the ratio

of detrital to authigenic illite for different size-fractions within a few % (Ylagan *et al.*, 2002; Solum and van der Pluijm, 2007, Appendix 2).

Scanning Electron Microscopy (SEM) offered high-resolution imaging of sample fabrics. Minerals and their textural expression were studied in rock-chips coated with gold and analyzed in the secondary electron mode; mineral phases were analyzed by Energy Dispersive X-ray Spectroscopy (EDS). SEM images showed the distribution of large clay grains (i.e., pieces of which could be present in the clay size-fractions analyzed) with respect to cleavage (Fig. 4c-e).

3.2 $^{40}\text{Ar}^*/^{39}\text{Ar}$ Illite Dating

Around 10 milligrams of illite concentrates of different grain size-fractions were mixed with deionized water in 2 mL centrifuge tubes, and centrifuged at 10,000 rpm for 30 minutes, in order to concentrate illite particles in a condensed pellet. After drying the illite pellets were cut in tiny, 0.5-1 mg cubes that were then placed inside thin silica tubes (1mm inside diameter and 5 cm long). Each tube was attached to a vacuum line, atmospheric air was pumped out while the sample region was immersed water and then the tube was necked and fire cut (Hall, 2014). The vacuum encapsulated sample was packed and sent to the McMaster Nuclear Reactor for neutron bombarding for a duration of 90 MWh. After irradiation the silica capsule is placed in a glass vacuum line connected to a VG1200S mass spectrometer. The capsule was broken with a steel ball that was manipulated with a magnet, with the ^{39}Ar released accounting for the recoiled fraction (f_{recoil}). Then the sample was step heated with a 5W continuous Ar-ion laser. Total Gas Ages (TGA) include recoiled and retained (released during heating) ^{39}Ar in the age calculation (see eq. 1) while model-based retention ages (RA) only consider retained Ar within the illite structure (Dong *et al.*, 1995).

The new XRD correction ages, or XCA, consider an illite stack comprised of a number of TOT layers, which is equivalent to the illite crystallite thickness (ICT in nm, Figs. 1 and 2c). Non-retentive interlayers within the stack (i. e. when $n_a < ICT$) are assumed to possess K in the same concentrations as internal retentive layers. As ICT approaches n_a , the correction method approaches the TGA. Thus, n_a , ICT and TGA are used to determine XCA according to the equation below (Fig. 2c).

$$XCA = \left(\frac{TGA \times (ICT - 1) \times n_a}{(n_a - 1) \times ICT} \right) \quad (2)$$

where $TGA = e^{\lambda \cdot TGA} - 1$ and TGA is proportional to $^{40}\text{Ar}^*/^{40}\text{K}$.

XCA error is a weighted average with respect to RA's and TGA's analytical errors.

Illite dating was applied to the samples from the Monterrey area in northern Mexico. This method is based on the fact that $2M_1$ (detrital) illite is concentrated in coarser size-fractions, while much finer $1M_d$ illite grew during subsequent diagenesis or deformation. In order to examine provenance, we plot Ar-illite ages vs. % $2M_1$ (detrital) illite of multiple grain size-fractions from a single sample and calculate the ages at 0 and 100% of $2M_1$ illite by using York regression (Mahon, 1996). Intersection at 100% of $2M_1$ corresponds to the detrital illite age, while intersection at 0% of $2M_1$ is the age of authigenic illite. York regression considers standard errors in both Ar ages and composition, of which the latter are much greater, resulting in extrapolated ages with errors that are larger than those from individual Ar ages. Note that negative slopes might reflect Oswald ripening growth of illite (Verdel *et al.*, 2012), while horizontal trends imply that all illite size-fractions and polytypes were (trans)formed at approximately the same time (Fitz-Díaz *et al.*, 2014a).

3.3 Monte Carlo argon diffusion model

In order to model expected ages for studied samples, we use results of a random walk Monte Carlo simulation that was outlined in Hall *et al.* (1997) and Hall *et al.* (2000). In the latter study, Ar atoms were individually positioned randomly on a hexagonal grid that was used to mimic the geometry of expected K or Ar locations within illite interlayers. The grain size used has a diameter of 200 unit cells and the simulation was repeated 100,000 times to approximate a uniform initial Ar concentration profile within the interlayer. For each time step, an atom could attempt to move in one of 8 directions, either vertically up or down into a bounding TOT layer, or alternatively, along one of 6 possible directions along the interlayer hexagonal grid (Fig. 6). In the case of all $^{40}\text{Ar}^*$ atoms and those ^{39}Ar atoms that are bound by at least two TOT layers in both vertical directions, any attempt to move through a TOT layer is unsuccessful and therefore transport is solely in the plane of the interlayer. Such Ar atoms can only exit the crystal by moving beyond the edge of the hexagonal grid. ^{39}Ar atoms fitting this category are here referred to as being “internal” ^{39}Ar atoms. For ^{39}Ar atoms bounded by one TOT layer whose other side is a crystal surface, it is assumed that a point defect through the TOT layer exists adjacent to the starting location of the ^{39}Ar atom. Such a defect is the result of crystal damage during ^{39}Ar recoil (Hall *et al.*, 1997, 2000). For such ^{39}Ar atoms, there is a 50% chance that the atom can escape through a bounding TOT layer if the atom is at its original coordinates in the hexagonal grid. This scenario does an excellent job of simulating the enhanced loss of ^{39}Ar at low temperatures, which in turn can explain why apparent $^{40}\text{Ar}^*/^{39}\text{Ar}$ ages for illite invariably start at or near a value of zero (Dong *et al.*, 1995; Hall *et al.*, 1997, 2000).

As shown in Hall *et al.* (2000), the loss of Ar as a function the number of time steps almost perfectly matches what would be expected for diffusion in an infinite cylinder (Crank,

1979). In the case of diffusion in a continuum, the fraction f of gas lost is a function of $x = \int D/a^2 dt$, where D is the temperature dependent diffusion coefficient for Ar and a is the radius of the diffusing mica layer. There is an excellent linear fit between the simulation time step number and x , using a uniform initial Ar concentration for $^{40}\text{Ar}^*$ and ^{39}Ar atoms in a circular disk (i.e. infinite cylinder geometry), which indicates that a simple random walk model is an accurate proxy for diffusion of Ar along illite interlayers.

An additional feature was introduced in Hall *et al.* (1997, 2000) to model the stereotypical “hump-shaped” pattern frequently seen in illite age spectra. Specifically, those interlayers bound on one side by only one TOT sheet were assumed to be less rigid, leading to enhanced diffusion of both ^{40}Ar and ^{39}Ar . It was arbitrarily assumed that diffusion coefficients along such interlayers are 50% higher than for internal, more rigid interlayers.

For a given n_a , the model assumes that the sample is made up of crystallites with thicknesses n_{a1} and n_{a2} , which are integers such that $\mathbf{n}_{a1} \leq \mathbf{n}_a \leq \mathbf{n}_{a2}$. The fraction of crystallites with thicknesses of n_{a1} and n_{a2} are f_1 and f_2 respectively where $f_2 = (1/f_{\text{recoil}}) - n_{a1}$ and $f_1 = 1 - f_2$. In order to model specific age spectra, the value of time steps for each gas fraction for the distribution of crystallite’s release of ^{39}Ar is determined that matches the actual release pattern for ^{39}Ar .

4 RESULTS

Table 1 summarizes the results from the analysis of the samples. On the left-most columns the results from XRD analyses are presented. Illite polytype characterization based on XRD measurements of randomly oriented powders finds only two illite polytypes in the samples, $2M_1$ and $1M_d$, and quantifies the % $2M_1$ and $1M_d$ polytypes (Haines and van der Pluijm, 2008 and

Fitz-Díaz *et al.*, 2014). %2M₁ varies between 10 and 100% in Sample 1, between 0 and 100% in Sample 2 and between 0 and 65% in Sample 3 (second column of Table 1 and Appendix 2). Comparison of XRD patterns of air-dried and glycolated oriented preparations allows estimates of the percentage of interlayered smectite (Moore and Reynolds, 1997), with less than 5% of smectite in some of the finer fractions and no detectable smectite in coarser fractions (third column of Table 1 and Appendix 1). Measurements of air-dried, oriented preparations provides illite crystallinity (IC) values, which were calibrated using Warr and Rice's (1994) approach (IC*), with $\Delta 2\theta$ ranges of 0.97-0.29, 0.75-0.29 and 0.69-0.34, among the different grain size-fractions of samples 1, 2 and 3, respectively. Smaller IC* corresponds to coarser size fractions, while bigger IC* corresponds to finer size fractions (fourth column of Table 1). There is good correlation between IC*, %2M₁ illite and % interlayered smectite, where more crystalline has the highest proportion of 2M₁ illite and the least presence of smectite.

Considering IC*, Bragg's angle for the 001 reflection of illite, the X-Ray wavelength ($\lambda=0.154$ nm for a Cu XRD tube) and the shape factor in Scherrer Equation (~ 1 , Fig. 5a), illite crystallite thicknesses are calculated for all size-fractions, providing *ICT* ranges of 8.2-27.3, 10.3-27.3 and 11.5-23.6 nm, for S1, S2 and S3. By dividing *ICT* values by 1.0 nm, the average number TOT fundamental particles of illite are obtained (Fig. 1). Such *ICT* number corresponds to the amount of potassium-bearing interlayers (Table 1), with smaller values for finer size-fractions and bigger values for coarser fractions. The value of *ICT* was used along with the number of Ar-retentive interlayers ($n_a = 1/f_{recoil}$) and total gas ages (TGAs) to determine X-Ray Corrected Ages (XCA; Fig. 2). In all cases, TGAs are younger than RA in finer size-fractions, and total gas ages are also significantly younger in the finest grain size-fraction of the samples. Except for Sample 3, RAs are slightly younger in the coarser fractions than in finer fractions

(Fig. 7). XCAs in the finest fractions give closer sample averages than TGAs and RAs. Values of TGAs, RAs and XCAs are compiled Table 1 and Fig. 7.

5 DISCUSSION

5.1 Illite sources and conditions

Unlike most clastic deposits, bentonitic layers interbedded with reefal limestone are alteration units that contain negligible amounts of detrital illite (tiny muscovite flakes) and are mostly volcanic material and glass (Grim and Guven, 1978). The bentonitic shale layers (<10 cm) are interstratified in much thicker layers (≥ 140 cm) of Aptian limestone, which were deposited after the worldwide sea rise that affected most of the Mexican region (Goldhammer, 1999) and was contemporaneous with extensive volcanism in western Mexico. Illite in the samples was formed from volcanic material, together with calcite, quartz and traces of kaolinite and chlorite, as are commonly found in anchizonal bentonitic layers (Hower *et al.*, 1976; Sucha *et al.*, 1993). We find that illite grains are 90% of the sample and most of them with similar shape and size, aligned with a strong cleavage subparallel to bedding (Fig. 4c-e). Such a cleavage is related to bedding-parallel shear during flexural folding (Fitz-Díaz *et al.*, 2012 and 2013; Fitz-Díaz and van der Pluijm 2013; Wang *et al.*, 2016) which in the study area occurred during one major folding event (Padilla y Sánchez, 1982; Camerlo, 1998; Chávez-Cabello *et al.*, 2004; Higuera-Díaz *et al.*, 2005).

Illite orientation with a strong shear-related cleavage is dominantly the result dissolution of diagenetic grains and precipitation, and less a result of grain rotation, since no evidence of kinking or bending of larger grains was observed in SEM (Ho *et al.*, 1995). In fact, dissolution-precipitation is the dominant illite reorientation mechanism in anchizonal-epizonal conditions

(van der Pluijm *et al.*, 1998). These conditions occurred in this area during folding, based on temperatures of homogenization (above 200°C) of fluid inclusions trapped in calcite and quartz of fold-related veins (Gray *et al.*, 2001; Fischer *et al.*, 2009). This temperature range is also consistent with the dominant illite grain size, with >90% of illite has grains >1µm and IC* <0.4, which represents anchizonal-epizonal conditions (Merriman, 2005).

5.2 Ar-degassing spectra, argon diffusion and Ar-age plateaus

Since the landmark paper by Merrihue and Turner (1966), $^{40}\text{Ar}^*/^{39}\text{Ar}$ step-heating experiments have been used to provide information on the spatial distribution of radiogenic argon in the samples, as the release of argon is controlled by intracrystalline diffusion. Hassanipak and Wampler (1996) investigated the effect of diameter and potassium content in illite and glauconite on Ar release during stepwise heating and concluded that particle diameter was less relevant than K content. However, Dong *et al.* (1995, 2000) noticed that in shale samples from the Gulf Coast basin containing different illite polytypes/generations, particle size indirectly affects illite composition, with concentration of younger (authigenic) 1M_d illite in finer particles and older (detrital) 2M₁ polytypes in coarser fractions. According to these authors, 1M_d illite produces staircase shape spectra during the first steps of degassing because of its poorly organized structure and because it has a lower K content (and hence $^{40}\text{Ar}^*$), while 2M₁ illite degassing at higher temperatures is constituted by discrete (detrital) illite with higher K content in coarser fractions, producing flatter degassing patterns (“plateaus”) such as those common in metamorphic muscovite (Hall, 2014). However, such “plateaus” can be much higher than the upper step of the initial staircase pattern when detrital illite is much older than authigenic illite. Similar observations and interpretations were described by Kirschner *et al.* (1996) in Ar-Ar

analyses of larger grains of white mica (2-6 μm in diameter), which is essentially coarse 2M_1 illite, grown during multiple phases of mylonitic deformation developed in the Helvetic nappes.

To a first approximation, our Monte Carlo simulations explore the effects of grain thickness, examining the effect of the f_{recoil} derived Ar-retentive illite crystallite thickness (n_a) on the shape of Ar-degassing spectra patterns. Based on results from our samples, in which Ar-degassing patterns significantly vary with grain size, we use XCA averages per site (54.6, 46.5 and 51.1 for sample 1, 2 and 3, respectively) and global averages (50.7 My), and assume homogeneous K and Ar concentration illite particles for model spectra. Similar shapes as in experimental patterns of Figure 7, result for constant XCA and a range of n_a or f_{recoil} . As f_{recoil} increases, there are greater distortions to the age spectra that are caused by recoil artifacts in combination with the distribution of n_{a1} and n_{a2} values. In this suite of models, all of the crystallites are assumed to have a single diameter. In the more realistic case where there is a range of grain sizes (typically over a factor of 5), even greater distortions of the age spectral shapes would be expected.

Age spectra shape variations can be evaluated by comparison of: (1) f_{recoil} , (2) steepness of staircase degassing pattern at low temperature (first half of the spectrum), and (3) hump-shaped (as opposite to flat-shaped) spectra at higher degassing temperatures (second half of the spectrum). In illite samples, $^{40}\text{Ar}^*/^{39}\text{Ar}$ ratio variations can be affected by illite crystallite thickness in different ways. For instance, in smaller illite crystallites the surface area to volume ratio is greater, increasing the proportion of non-retentive sites Ar relative to retentive sites (Fig. 1b), which reduces the chance for recoiled ^{39}Ar to be retained within the crystallites during neutron bombarding, thereby increasing f_{recoil} . A large surface area also increases spontaneous loss by diffusion of weakly bounded radiogenic $^{40}\text{Ar}^*$ on the edges of illite crystals (Huneke,

1976) occasionally due to recoil during ^{40}K - $^{40}\text{Ar}^*$ decay (Zimmermann and Odin, 1982). This phenomenon has also been observed in large crystallites of standard quality silicates (Hall, 2014), and produces smaller $^{40}\text{Ar}^*/^{39}\text{Ar}$ ratios (*i. e.* ages) at lower temperature degassing steps. In our model, Ar diffusion occurs from the surface (i.e., damaged external half layers and spontaneously $^{40}\text{Ar}^*$ depleted crystal edges) crystallite layers by Ar random walk along the interlayers (Fig. 6), thus giving markedly younger ages in early heating steps and biasing to older ages with temperature increase (Figs. 7 and 8). These abrupt age variations are purely due to recoil artifacts that are revealed by temperature induced Ar-diffusion. Thicker illite crystallites show smaller f_{recoil} , more rapid age increases, defining a steeper staircase in the first steps of heating, and similar ages in the following steps due to grain homogeneity. This defines a flat or a slight hump pattern shape that resembles an Ar age plateau (McDougall and Harrison, 1999).

Synthetic patterns of Fig. 8 resemble the same shape variations observed in experimental patterns in the natural samples (Fig. 7). In all analyzed samples, illite degassing spectra show similar spectra variations with grain size, with smaller f_{recoil} and flatter shape spectra in coarser fractions (particle diameter $>0.2\ \mu\text{m}$ and $\text{ICT}>15\ \text{nm}$) and larger f_{recoil} and prominent hump shaped spectra in finer fractions (particle diameter $<0.2\ \mu\text{m}$ and $\text{ICT}<15\ \text{nm}$). By comparison of synthetic and experimental spectra variations and considering textural observations, we confirm that the studied samples most likely contain one generation of illite with different grain size-fractions, which might partly be induced during sample preparation. Thus, both illite polytypes present in the samples (2M_1 and 1M_d) are authigenic, since all ages are Paleogene-Eocene and always significantly younger than deposition (Aptian-Albian). 2M_1 illite, typically considered as detrital, in this particular case is authigenic because deformation took place at relatively high temperature conditions.

Patterns with $f_{recoil} > 0.2$ do not define meaningful plateau ages in synthetic or experimental Ar-degassing spectra (figs. 7 and 8), even after applying the recoil-weighted age correction to the degassing pattern, as proposed by Clauer *et al.* (2012). By comparing model and experimental Ar-spectra and using f_{recoil} as a common denominator, we find that illite age interpretations based on plateaus significantly overestimate the true age of samples containing one generation of illite with particle diameters smaller than 1 μm (1000 nm). Thus, illite age determinations from Ar-spectra plateaus may be in error for samples containing fine-grain illite, especially if samples contain different generations of illite.

5.3 Illite age analysis and timing of folding.

We use standard illite dating procedures (Haines and van der Pluijm, 2008) that plot ages (TGA, RA and XCA) vs. %2M₁ illite, with errors for the upper and lower intercepts from York regression (Mahon, 1996). Results are shown in Figure 9 a-c, for samples 1, 2 and 3, respectively. We find positive slopes in TGA vs. %2M₁ plots, with larger errors (shaded in yellow) compared to RA and XCA plots. RA vs. % 2M₁ regression shows a negative slope for samples 1 and 2, and a slightly positive slope for Sample 3. In general these plots have small age errors. XCA vs. % 2M₁ plots show flatter regression lines, with a very small negative slope in samples 1 and 2 and a slightly positive slope in Sample 3. XCA's regression gives more closely clustered ages and a better linear correlation with %2M₁ compared to TGA's and RA's. Even the finest grain size-fractions (<0.05 μm), which show more dispersion in TGA and RA plots, align with ages of coarser grain size-fractions. Consequently, if samples contain one generation of illite, $^{40}\text{Ar}/^{39}\text{Ar}$ age determination depends mostly on illite crystallite ordering and size. The X-Ray corrected age (XCA) better defines illite ages and is in general more accurate and precise

than RA and TGA for illite grain size-fractions with equivalent sphere diameters greater than 50 nm and crystallite thickness between 10 and 50 nm.

Fig 9d plots ages for all three samples vs. ICT, in which, similar to plots of age vs. %2M₁ illite, XCA's show an almost horizontal regression line, negative slope for RA's and positive slope for TGA's, with higher age dispersion in finer grains and age convergence of all samples in coarser grains. These patterns show that ICT is more important than illite polytypes (which gives a measure of 3D ordering and K content, although both vary linearly) and particle diameter for the determination of true ages.

While ages of the three samples are very close to each other, we can test the conclusion that all illite is contemporaneous or differing within a few Myr by modeling. We produced synthetic patterns for each grain size fraction, considering grain size and two ages: site average and global average, representing by red and black synthetic degassing patterns, respectively (Fig. 8). In samples 1 and 2, the site age average clearly differs from the global age average, while in Sample 3 they are about the same within analytical error. With one exception (sample 1FM), age site average (red synthetic pattern) better matches the experimental degassing patterns, which implies that illite samples may have precipitated during slightly different times in the same folding event that occurred during a time span between 55 and 47 Ma, corresponding to the XCA averages of the oldest and youngest sample. We note that this time range is in excellent agreement with deformation timing constrained by stratigraphy in the area (Lawton *et al.*, 2009 and Gray and Lawton, 2011).

CONCLUSIONS

Three bentonitic samples in a succession of platform carbonates were affected by strong bedding-parallel shear during the formation of km-scale folds. We analyzed four clay grain-size fractions from illite-dominated samples that were collected along essentially the same folded stratigraphic horizon (Fig. 3). XRD analysis shows that finer grain size-fractions ($<0.2\ \mu\text{m}$) dominantly contain weakly-ordered illite (1Md polytype), while coarser fractions contain mostly muscovite-like ($2M_1$) illite. Illite crystallite thickness increases (ICT) with degree of crystallographic order of illite and particle diameter. All Ar-Ar illite ages are younger than the depositional age, reflecting that illite in the samples is authigenic and, supported by stratigraphic constraints, formed from alteration during a single folding event. Indeed, SEM observations of rock fabric and systematic variations in experimental and synthetic ^{40}Ar - ^{39}Ar degassing patterns with ICT indicate that samples were formed about the same time under anchizonal conditions (Table 1). This implies that Total Gas Ages underestimate the illite age, while Retention Ages (Dong *et al.*, 1995) overcorrect. Our XRD-based age correction method considers crystallite thickness and the recoil fraction over a critical range of grain sizes that reflect the physical properties of these illites, which provides ages between TGA and RA, with increased precision and accuracy (error is smaller), especially when the finest grain-size fraction is excluded. On this basis, we recommend analyzing illite grain size-fractions no less than 50 nm for most accurate results and using XCA in the illite crystallite thickness (ICT) range of 10-50 nm.

A set of synthetic spectra of TGA and RA for grain populations with different f_{recoil} but the exact same age show significant differences in degassing patterns as the grain size changes from thick to thin crystallites. Staircase pattern at low temperature degassing steps was related to natural Ar loss during K-Ar decay on the edges of illite crystals (Huneke, 1976). In such a tiny particles it is unlikely to have hydrothermally induced Ar-loss only affecting crystallites edges

and not the cores of nanoparticles (*i. e.* Turner *et al.*, 1966). Thus, age determination from Ar-age plateaus would overestimate true age in these samples, as we see in multiple prior studies of illite dating.

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FIGURE CAPTIONS

Figure 1. Fundamentals on illite crystallography. (a) Crystalline structure of illite, a phyllosilicate constituted by two silica tetrahedral sheets (T) with an octahedral sheet unit (O) in between. The three layers together (TOT), along with the cation (potassium) connecting them, constitutes the fundamental particle of illite, which has an average thickness of 1 nm (Grim, 1968). (b) Multiple TOT units constitute illite crystallites, which have an average thickness determined by the number of stacked fundamental units, also known as illite crystallite thickness (*ICT*). Illite stacks also commonly contain interlayered smectite and imperfections (i. e., dislocations and vacancies; Peacor, 1992), which cannot retain argon.

Figure 2. Total-Gas Age or TGA (a), Retention Age or RA (b) and the X-Ray Diffraction, recoil fraction based Age (XCA). For example, in a sample with an average *ICT*=10 nm and a fraction of recoil (f_{recoil}) of 0. 25, $ICT=10$, $na=1/0. 25=4$ and $XCA=(40/33)TGA$ (see Table 1).

Figure 3. Geological setting of samples. (a) Landsat and Google Earth images northern Mexico and the Monterrey Salient, respectively, showing the location and geomorphological expression of regional folds in the study area. (b) Synthetic geological map of the study area showing the location of sampling sites (based on map Padilla y Sánchez, 1982). (c) Cross section showing the geometry of the studied buckle folds and the relative of sampling sites (based on cross section by Padilla y Sánchez, 1982). S1=Sample 1, S2=Sample 2 and S=Sample 3.

Figure 4. (a) Cupido Fm. outcrop on the back limb of Clavelillas Anticline. (b) Close up to sampling site where we see highly sheared reddish shale layers interbedded with thickly

bedded limestone. Below, SEM secondary electron images showing textural aspects of the studied samples: (c) surface of Sample 1 (S1) showing a homogeneous granular texture and continuous cleavage with illite grains oriented parallel; (d) close-up of cleavage domains in Sample 3 (S3), again, illite grains show homogeneous size and disposition across the samples; (e) illite grains of Sample 3 with a view perpendicular to that in (d) also showing homogeneous grain size of illite flakes. I=illite, C=calcite.

Figure 5. XRD sample characterization. (a) Schematic representation that shows how calibrated illite crystallinity (IC, Warr and Rice, 1994) can be used in the Scherrer Equation (Patterson, 1939) to determine average illite crystallite thickness with $\lambda=0.154$ nm for a Cu XRD tube and the shape factor $K \sim 1$ (Moore and Reynolds, 1997). (b) Sketch showing the structure of $2M_1$ and $1M_d$ illite polytypes and their XRD patterns (modified from Haines and van der Pluijm, 2008).

Figure 6. Schematic representation of premises for the argon diffusion model in illite based on work by Hall *et al.* (1997, 2000). Note that Ar is assumed to randomly walk along the interlayers and escapes from the most external layers during degassing.

Figure 7. $^{40}\text{Ar} / ^{39}\text{Ar}$ -degassing spectra obtained in the four different clay size-fractions from samples that were collected in three folds. Total gas ages (TGA), retention ages (RA) and fraction of recoil (f_{recoil}) are indicated for each aliquot. Degassing patterns of fine-grained samples are indicated in yellow, fine-medium in orange, medium-coarse in red and coarse in deep-red.

Figure 8. Comparison of experimental (color-coded for the samples according to Table 1) and synthetic degassing patterns considering f_{recoil} , as well as XCA's, site average age (54.9, 46.5 and 51.1 Ma, for samples 1, 2 and 3, respectively) and global average age (50.8 My),

red and black synthetic degassing patterns, respectively. Note that red (age average per site) patterns provide a better fit to the experimental patterns. All of the synthetic age spectra use a single grain size and the ICT distribution above. The model age spectra are scaled so that they have either a site specific XCA or a globally averaged XCA. In spite of the simplicity of the model used, the concordance between measured age spectra and model age spectra is remarkable, especially for site averaged XCAs, which supports the hypothesis that site averaged XCAs represent the time of illite formation during folding.

Figure 9. Illite Dating. (a), (b) and (c) show TGA, RA and XCA vs. $2M_1$ plots for samples 1, 2 and 3, respectively. York regression errors for upper and lower intersection are shown in blue for TGA, in pink for RA and in grey for XCA (following procedure in Mahon, 1996). (d) XCA vs. ICT showing that age dispersion is more important in smaller grain size-fractions compared to samples with thicker crystallites. Symbols in pale-green correspond to Sample 1, pale-blue to Sample 2 and pale-orange to Sample 3.

Table 1: Results from all analytical tools applied to the studied samples, including illite crystallographic properties and Ar-Ar illite age (TGA, RA and XCA) determined in illite concentrates.

Table 1

Table 1. Results from all analytical tools applied to the studied samples, including illite crystallographic properties and Ar-Ar illite age (TGA, RA and XCA) in illite concentrates.

Sample	%2M ₁	%Sm	IC* ($\Delta 2\theta$)	ICT(nm)	TGA (Myr)	RA (Myr)	f_{recoil}	n_a	XCA (Myr)
1-F	10±2	<5%	0.97	8.2	46.4±0.22	63.6±0.31	0.28	3.6	55.9±0.27
1-FM	18±3	<5%	0.86	9.2	49.1±0.22	62.±0.28	0.22	4.6	55.9 ±0.25
1-MC	35±5	~0%	0.46	17.2	49.3±0.21	57.5±0.24	0.15	6.8	54.3±0.23
1-C	100±5	~0%	0.29	27.3	49.2±0.25	54.5±0.27	0.10	10.3	52.5±0.27
2-F	0±2	<5%	0.75	10.7	36.1±0.23	50.4±0.32	0.29	3.4	45.7±0.29
2-FM	30±4	~0%	0.59	13.5	42.4±0.25	51.9±0.30	0.19	5.3	48.4±0.29
2-MC	80±5	~0%	0.37	21.4	43.5±0.21	48.7±0.24	0.11	9.2	46.5±0.22
2-C	100±5	~0%	0.29	27.3	43.6±0.28	47.3±0.30	0.08	13.2	45.5±0.29
3-F	0	<5%	0.69	11.5	39.7±0.23	53.1±0.30	0.26	3.9	48.9±0.28
3-FM	16±2	~0%	0.50	16.0	45.6±0.18	54.6±0.22	0.17	5.8	51.5±0.20
3-MC	40±3	~0%	0.38	20.8	49.3±0.18	53.7±0.19	0.09	11.8	51.4±0.19
3-C	65±3	~0%	0.34	23.6	51.8±0.17	54.4±0.18	0.05	19.6	52.6±0.17

%2M₁=fraction of 2M₁ illite polytype wrt 2M₁+1M_d polytypes; %Sm= smectiteproportion in illite-smectite; IC*=Illite crystallinity calibrated according to Warr and Rice (1994); ICT= average illite crystallite thickness; TGA=Total Gas Age; RA=Retention Age; f_{recoil} =fraction of recoil; n_a = average number of continuous Ar retentive TOT layers; XCA=XRD based corrected age.

Figure 1

Figure 1

Figure 2

Figure 2

Figure 3

Figure 3

Figure 4

Figure 4

Figure 5

Figure 5

Figure 6

Figure 6

Figure 7

Figure 7

Figure 8

Figure 8

Fraction of ^{39}Ar released

Figure 9

Figure 9