

Fibrous illite in oilfield sandstones – a nucleation kinetic theory of growth

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ABSTRACT

Fibrous illite is one of the most important cements that grows within sandstones during burial, and the only one which is commonly dated using the K–Ar age technique. A small quantity of illite can dramatically reduce porefluid flow rates within a sandstone, thus making oil recovery uneconomic. Illite ages potentially correspond to geological events such as hydrocarbon filling of a sandstone reservoir, providing calibration to basin models. Yet the fundamental processes controlling fibrous illite growth are not understood. This contribution

presents a new theory for illite growth within sandstones that explains the fibrous morphology of illite, the restricted range of illite K–Ar age dates compared to the age of the host sandstones, and the lack of 0-Myr-old illite reported. The growth of fibrous illite as an authigenic cement may be controlled by nucleation kinetics, and not by thermodynamic or growth kinetic considerations as has been previously assumed.

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Introduction

The importance of illite, to the oil industry and academics, is illustrated by the extensive data set of illite K–Ar ages measured from petroleum reservoirs worldwide (e.g. Hamilton *et al.*, 1992). Despite an extensive literature, the fundamental controls upon fibrous illite growth have not been determined, and the significance of the K–Ar ages remains open to debate. Attempts at understanding the significance of illite age dates have relied upon the calculated conditions of illite stability (Bjørlykke and Aagaard, 1992; Berger *et al.*, 1995) and by a consideration of processes likely to control the rate of growth such as: porefluid flow velocity (Darby *et al.*, 1997; Swarbrick, 1994); solute supply (Hamilton *et al.*, 1992) and temperature or reaction kinetics (Ehrenberg and Nadeau, 1989; Berger *et al.*, 1995; Lanson *et al.*, 1996). Although progress has been achieved using these approaches, they do have limitations. Low-temperature systems are characterized by the metastability of phases and by porefluid supersaturation which does not lead to mineral precipitation (Fig. 4 of Bjørlykke, 1998). These nonequilibrium features cannot be modelled thermodynamically.

Problems with thermodynamic data for clays, especially for stability constants, are discussed by Langmuir (1998; p. 338). Nonequilibrium systems are sometimes described in terms of growth kinetics (e.g. Bjørlykke, 1998), but modelling of sandstone-like systems shows that reaction kinetics are very rapid, and not rate-limiting (Berger *et al.*, 1997).

Any model for illite growth in sandstones should offer explanations for the following observations:

1 Illite ages are usually clustered, i.e. apparently record 'events'. These events are of short duration compared to the age of the sandstone (Hamilton *et al.*, 1989).

2 Authigenic illite is frequently of fibrous morphology, an indication of rapid growth (Mullin, 1961).

3 There is no recorded authigenic illite of recent age (< 1 Myr old, Berger *et al.*, 1995; Lanson *et al.*, 1996) despite porewaters in many present-day sandstones being supersaturated with respect to illite (e.g. Bjørlykke, 1998).

Nucleation models

Mineral growth is only one of two processes required to form a crystal. For fine-grained precipitates such as clays, crystal nucleation is also important. It will be shown below that nucleation kinetics can explain some features of authigenic illite growth that are not easily explained by thermodynamics or growth kinetics. The use of nucleation models is uncommon in geology (review in

Eberl *et al.*, 1998), although the basic theory is well understood (e.g. Berner, 1980, p.93; Putnis *et al.*, 1995; Lasaga, 1998). The most important concept is that of a critical nucleus (Fig. 1): this is a collection of molecules of such a size that, if a single molecule is removed, then the 'embryo' becomes thermodynamically unstable and prone to spontaneous dissolution. Conversely, if a single molecule is added to the critical nucleus, it becomes thermodynamically stable, and prone to spontaneous growth into a crystal. In order to precipitate a mineral within a sandstone, critical nuclei must form to initiate crystal growth.

In a solution, ions of solute are constantly forming pairs and larger clusters. These may spontaneously increase or decrease in size, according to the frequency of encounters with other ions or embryos, amongst other factors. The probability of these encounters leading to nucleation depends, in turn, upon a number of factors, including the concentration of the solute and the size of the critical nucleus.

Critical nucleus models

Modelling the formation of a critical nucleus is complicated by the shape of the embryo, which is generally unknown, and the possible influence of pre-existing surfaces. The simplest model involves the formation of a spherical embryo in free solution, i.e. without the interference of any pre-existing surfaces. This model, termed

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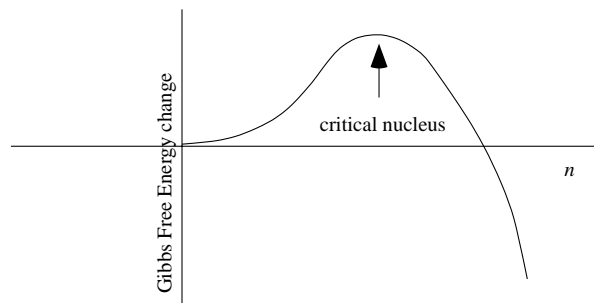


Fig. 1 The nucleation process from a solution, measured in the Gibbs Free Energy change as the number of atoms/molecules (n) in the incipient crystal increases. Groups, pairs and larger aggregates of atoms/molecules are continually colliding, forming incipient crystals. However, these very small crystals (termed ‘embryos’) are less stable (have a higher Gibbs Free Energy) than separate atoms/molecules in solution, owing to the very high surface area of the embryo compared to the volume. Each extra atom/molecule added makes the embryo even less stable (higher Gibbs Free Energy). Hence, the embryo is likely to dissolve back into individual atoms/molecules in the parent solution. At a critical size (the critical nucleus), the addition of additional atoms/molecules starts to decrease the Gibbs Free Energy of the crystal, so that growth is spontaneous. (After Lasaga, 1998, fig. 6.4.)

homogeneous nucleation, is realistic for the growth of crystals of simple salts from highly supersaturated solutions (Nielson, 1964), but has little application to geological systems. It is the simplest case mathematically, and has consequently appeared within the geological literature (e.g. Berner, 1980; Putnis *et al.*, 1995; Lasaga, 1998). For mineral growth within a sandstone, nucleation will be heterogeneous, i.e. involve a pre-existing mineral surface. Most pores will have quartz, feldspar and detrital and/or authigenic clay minerals adjacent to them.

The shape of the embryo is also unknown. In a heterogeneous system a spherical embryo is not likely, as this cannot be closely attached to a surface. However a hemispherical shape is possible, as are a cuboid or a layer of single unit-cell thickness (termed a ‘pancake’ by Lasaga, 1998, for a layer with circular geometry). For a sheet silicate such as illite, the layer model with the (001) face parallel to the mineral surface seems a sensible choice, given that the (001) surfaces of illite and other mica crystals are known to be stepped (Inoue and Kitagawa, 1994). At the nanometer scale, surface free energy considerations prevent the formation of crystal faces. This is demonstrated by irregular or spiral steps upon (001) surfaces on the $1M_1$ illite polytype (Inoue and Kitagawa, 1994), of which all fibrous illite is composed (Srodón and Eberl, 1984).

Method: simple model for nucleation of illite

The heterogeneous ‘pancake’ model of Lasaga (1998; p.512) is here modified for illite nucleation on pre-existing ‘illite’ (001) surfaces. In a sandstone these surfaces would be either detrital illite–smectite (Whitney and Velde, 1993), detrital muscovite, or earlier formed authigenic illite. The model assumes a rectangular geometry to the

embryo crystal (with an equal number of unit cells per side, Fig. 2), which is an acceptable approximation to the crystallographic form or a circle, given the uncertainty in the shape discussed above. Note that the choice of nucleus shape does not significantly alter the results of the model. The growth of a layer one unit cell thick is modelled herein, a realistic assumption for a mineral in which enlargement parallel to a face is easy compared to nucleation upon this face. This is considered reasonable for illite because TEM photomicrographs show 10 Å steps upon (001) illite crystal faces (Fig. 3), which correspond to single unit cell thickness. Equation (1) derives the Gibbs free energy for the layer model from the Gibbs free energy of reaction (ΔG_n) and the surface free energy term, and is modified from Lasaga (1998; p. 512).

$$\Delta G_r = n\Delta G_n + 2n^{1/2}(a + b)c\sigma_{100} \quad (1)$$

where ΔG_r is the Gibbs Free Energy of the embryo/nucleus, n the number of atoms and ΔG_n the Gibbs Free Energy per atom. Other terms are in Table 1 and Fig. 2. Note that the surface free energy of the (001) face is not involved, because the new surface area on top of the layer simply replaces the old surface area below. From this equation the relationship between

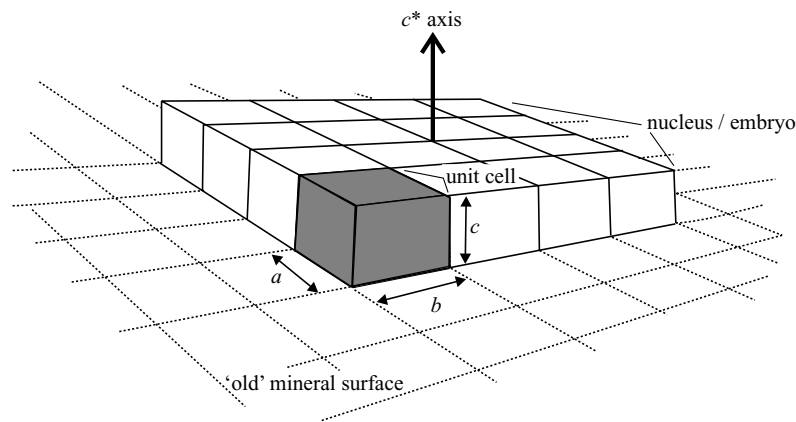


Fig. 2 Cartoon of the single layer nucleation model, showing unit cells as cuboids. The embryonic illite nucleus/embryo (solid lines) forms on an existing (001) illite surface (dotted lines), which could be authigenic or detrital. The embryo is only a single unit cell in thickness parallel to the c -axis. The shape of the embryo in the (001) plane is unknown, and is modelled as square for convenience, although hexagonal (the crystallographic shape) or circular (minimum surface energy) shapes are likely in nature. However, the results of the calculations are not affected significantly by the exact shape of the embryo.

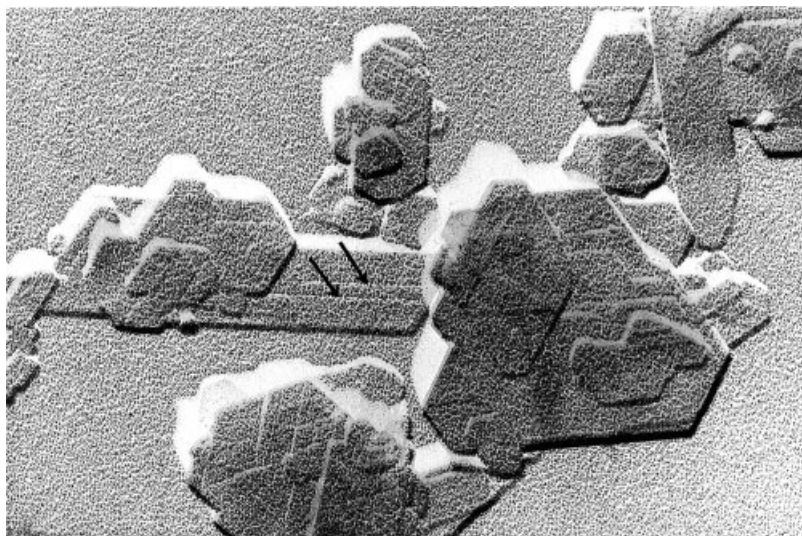


Fig. 3 Transmission electron micrograph of illite fundamental particles showing 10 Å (single unit cell) steps on (001) faces (arrowed). The sample has been 'shadowed' with platinum, which builds up on the sample surface where relief is present. Because the angle of the deposit is known, the thickness of the illite particles can be calculated. Field of view is 1500 nm across.

ΔG_n and the size of the critical nucleus can be calculated for any combination of fluid supersaturation and temperature. Because surface free energy is unknown for illite, the value for gibbsite (100) is used for the (100) and equivalent faces (Lasaga, 1998). Constants are listed in Table 1.

In order to calculate the size of the critical nucleus for a specified set of physical conditions, (1) is differentiated with respect to n , and $d(\Delta G_r)/dn$ is set to 0 (for the turning point as Fig. 1; Ω is the porefluid supersaturation).

$$n_c = [\sigma_{100}c(a+b)/k_B T \ln \Omega]^2. \quad (2)$$

Results

Calculated critical nucleus size vs. fluid supersaturation is shown for three common authigenic cements at 298 K (Fig. 4). The critical nucleus size is smallest for calcite, and largest for illite. For comparison, porefluid supersaturations are shown as controlled by common geological phases (Bjørlykke *et al.*, 1995; Langmuir, 1998).

Discussion

Although paragenetic sequences vary widely between sandstones, several generalizations can be made. Carbon-

ate cements can occur very early ($< \approx 20$ °C; Wollast, 1971), quartz overgrowths are rare below ≈ 80 °C and authigenic illite is uncommon below ≈ 100 °C. Although this could be a consequence of the thermodynamic stability of the minerals, it is apparently not the case: quartz is thermodynamically stable at surface temperatures (although the situation is complicated by the existence of opal) and illite can be modelled as stable at temperatures at least as low as 50 °C (Bjørkum and Gjelsvik, 1988). It is suggested herein that the discrepancy between thermodynamic stability and actual mineral growth is caused by the kinetics of nucleation. Thus, calcite – which is very easy to nucleate – can form at very low temperatures, while illite – which is more difficult to nucleate – requires higher

temperatures. Hence, having thermodynamic conditions for illite stability is not a sufficient condition for illite growth. Instead, it has been shown empirically that illite formation is a geologically uncommon event, associated with relatively unusual conditions, e.g. oil charging into a sandstone reservoir (e.g. Hamilton *et al.*, 1992), influx of highly concentrated or highly acidic fluid (Zwingmann *et al.*, 1998), or high porefluid flow rates (e.g. Swarbrick, 1994; Darby *et al.*, 1997). These unusual geological conditions overcome the kinetic barrier to illite nucleation, allowing illite growth to proceed.

'Zero-age' illite

The North Sea is one of the most intensively explored regions of the world for hydrocarbons, and there are many (< 100) published illite ages from sandstones. While the ages span a wide range (≈ 20 –100 Myr; Bjørlykke *et al.*, 1995), there are no samples that have yielded recent ages (< 1 Myr), despite the fact that porewaters within buried sandstones are frequently over-saturated with illite (Bjørlykke and Aagaard, 1992; Berger *et al.*, 1995). Assuming that recorded illite ages represent the youngest illite in a rock (Hamilton *et al.*, 1989), then it can be concluded that illite formation is not taking place at present, despite the thermodynamic conditions for illite stability being satisfied, and the presence of sources of ions for illite growth (e.g. dissolving K-feldspar, kaolinite). This is in contrast to the formation, for example, of quartz overgrowths, where models based upon empirical data show that overgrowth formation is continuous once started (Walderhaug, 1996) and is continuing at present day within many

Table 1 Symbols and values of constants used in calculations

Constant	Value	Source
Surface free energy of:		
Calcite	9.7×10^{-6} mol cm ⁻²	Lasaga (1998)
Quartz	3.5×10^{-5} mol cm ⁻²	Lasaga (1998)
Illite (100) σ_{100}	4.83×10^{-5} mol cm ⁻²	Lasaga (1998)
Unit cell dimension illite:		
a	5.20×10^{-8} cm	Deer <i>et al.</i> (1966)
b	9.00×10^{-8} cm	Deer <i>et al.</i> (1966)
c	1.00×10^{-7} cm	Deer <i>et al.</i> (1966)

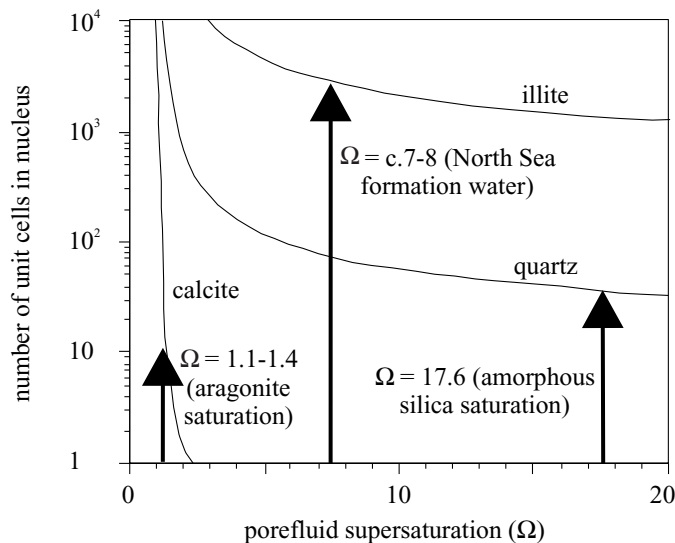


Fig. 4 Critical nucleus size for common cements in sandstones at 298 K vs. porefluid supersaturation (Ω), along with levels of porefluid supersaturation typical of subsurface sandstones (arrows). Importantly, illite has a much larger critical nucleus size than quartz or calcite, so that nucleation of illite is much more difficult than for these common geological cements. As nucleation is unlikely if the critical nucleus size exceeds 10–1000 atoms (Lasaga, 1998), then calcite will nucleate very easily, quartz less readily, and illite only under unusual geological conditions. This fits well with the observation that calcite cements grow at low temperatures during diagenesis, while quartz overgrowths begin to grow at $\approx 80^\circ\text{C}$, and illite growth is episodic and controlled by geological events such as oil emplacement or fluid flow. Although the presented values are calculated using a homogeneous spherical model (Lasaga, 1998) for ease of comparison, the relative results are independent of the nucleation model.

North Sea sandstones, unless interrupted by oil emplacement. Again, this is consistent with the critical role of crystal nucleation in the process of illite growth. Having conditions sufficient for illite crystal stability (as calculated thermodynamically) is not sufficient to cause illite growth. In passive sedimentary basins, such as those in the northern North Sea, there is little seismic pumping of fluids, and most potentially oil-bearing structures are already filled and/or breached. In other words, there are probably very few ‘events’ occurring today which could trigger illite growth.

The role of fundamental particles

The reason for the anomalous behaviour of illite, compared to other common authigenic cements, lies in the unusual ultrastructure of an illite crystal. SEM and TEM photomicrographs of authigenic illite show fibrous crystals with a normal maximum dimension of 10–100 μm and with a length-to-width ratio of several

tens to hundreds (Lee *et al.*, 1989). These crystals are believed to be composed of sheet-like subcrystals termed ‘fundamental particles’ with thicknesses measured in nanometres (Nadeau *et al.*, 1994), which can be imaged by TEM (e.g. Clauer *et al.*, 1997). From published studies (e.g. Nadeau *et al.*, 1994), and from the present authors’ data, there is an upper limit to fundamental particle size which is of the order of hundreds of nanometres. This limitation on the dimensions of the fundamental particles is a direct result of the atomic structure of illite, where strain energy makes ‘large’ crystals unstable (Radoslovich, 1959). This contrasts with the unstrained structure of muscovite, where crystal size can exceed one metre. As a consequence, once all the fundamental particles within an illite crystal are at, or near to, their maximum size, then growth cannot continue without the nucleation of new fundamental particles. It is because the conditions for illite nucleation are geologically more unusual than the conditions for crystal

enlargement that the formation of fibrous illite is an episodic process.

Given the difficulty of nucleating illite, it is not surprising that there is a strong substrate control upon illite formation. SEM observations of reservoir sandstones indicate that fibrous illite grows almost exclusively upon either detrital illite/smectite (Pollastro, 1985; Whitney and Velde, 1993), muscovite or kaolinite. All of these substrates have a similar molecular surface configuration to illite so that the interfacial energy between the growing nucleus and the substrate is minimized. The nucleation control upon illite growth is the cause of the fibrous morphology of the crystals. A sufficient degree of porefluid supersaturation to promote nucleation represents a considerable driving force for crystal growth, which is consequently rapid. It is well established that rapid growth favours an elongate morphology (Mullin, 1961).

Conclusions

The growth of fibrous illite within sandstones is limited by the kinetics of nucleation, and not by thermodynamic or kinetic controls, as has been assumed previously. Illite nucleates less readily than other common authigenic cements, and the unusual ultrastructure of its crystals limits the size of fundamental particles to hundreds of nanometres. Once each fundamental particle has grown close to maximum size, then an illite fibre can enlarge only by nucleating more fundamental particles. This requires unusual geological conditions, which are more rigorous than those required for simple crystal growth, such as abnormally high porefluid supersaturations, high porefluid flow velocities, high temperatures, or a catalyst.

This theory explains several key observations of illite occurrence:

1 Fibrous illite growth within sandstones is episodic, as determined by K–Ar age measurements. This is because the conditions for illite nucleation require high degrees of porefluid supersaturation or other unusual conditions that are satisfied only for short durations relative to the age of a typical sandstone.

2 The lack of ‘zero-age’ illite. Many sandstones from the UK North Sea

contain porefluids which are supersaturated with respect to illite, and would hence be expected to contain recent illite. Despite extensive sampling, such a recent illite has not been located. This is because the conditions for illite nucleation are more rigorous than for growth and are geologically rare, such that illite is not growing under present conditions.

3 The fibrous morphology of much authigenic illite. Because the chemical conditions required for nucleation are substantially more rigorous than those required for stability, when nucleation does occur then crystal enlargement is very rapid as a result of high degrees of porefluid supersaturation. Rapid growth results in fibrous crystals.

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