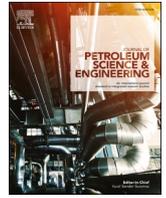




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How do chlorite coatings form on quartz surface?

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ABSTRACT

Chlorite-coats on quartz surfaces are ubiquitous in various sedimentary environments. Chlorite-coats shield the surface of quartz from quartz cement overgrowths, thus preserving anomalously high porosity in deeply buried sandstone reservoirs. The inhibition of the quartz cement implies that the chlorite-coats on the surface of quartz grains can significantly influence the physicochemical behavior of the quartz grains. Therefore, failure to notice the initial thin microscale coatings forming during deposition can have serious consequences for modeling several geochemical reactions occurring at liquid-solid interfaces. Despite this huge implication, the fundamental mechanisms involved in chlorite-coat formation is not well understood. Here we present an experimental study to determine the parameters that control chlorite-coat formation on the surface of quartz grains. The batch experiments were conducted in a concoction of quartz and chlorite under different conditions of ionic strength, pH, and presence of humic acid (HA), iron- (Fe) and aluminum (Al) oxides. HA, Fe- and Al oxides are suggested to aid the emplacement of chlorite-coat precursors. At pH 7, the quartz-chlorite and quartz-chlorite-Fe/Al-oxides mixing experiments performed in saline and non-saline solution result in equal chlorite-coat coverages, suggesting neither salinity nor Fe and Al-oxides explain the mechanisms of chlorite-coat formation. At pH 5 and 9, however the chlorite-coat coverage was superior only in saline solution, indicating differences in coat coverage may be caused by variable electrokinetic charge distribution due to the distribution and transport of dissolved salt. The chlorite-coat barely formed in experiments that contain HA in quartz-chlorite mixtures regardless of ionic strength and pH. Against a long-standing notion, the presence of organic matter cannot necessarily be prerequisites for binding chlorite on the surface of quartz grains. The dynamic interactions between solution chemistry and surface chemistry of solid phases (quartz, chlorite, HA, Fe and Al oxides) can result in changing the electrokinetic properties in a region near the solid phases and at mineral-solution interfaces. We therefore propose that the electrokinetic response that arises in heterogeneous systems may explain the mechanisms of chlorite-coat formation.

1. Introduction

Chlorite is an Fe-containing phyllosilicate with a 14 Å unit, which is ubiquitous in deltaic and fluvial depositional settings as grain-coatings on the surface of sedimentary grains (Dowey et al., 2012; Moore and Reynolds, 1997). The chlorite-coats are believed to originate due to the alteration of precursor clay minerals such as berthierine – a 7 Å chlorite (Aagaard et al., 2000), kaolinite (Boles and Franks, 1979) and smectite (Chang et al., 1986). The iron-rich precursor clay minerals form in near-shore settings associated with major riverine input. In modern settings, these coatings comprise several clays (odinite, odinite-rich mixed-layer clay, different detrital minerals and ferric chloritic minerals) whereby iron is dominantly ferric (Odin and Gupta, 1988). These modern precursor coating mineral forms in sediments buried to a few cm

beneath the sediment-water interface (Odin and Gupta, 1988).

Detrital clay-coat formation in various sedimentary environments i. e. continental, coastal and marine has been explained in terms of (i) infiltration and bioturbation (Bloch et al., 2002; Dowey et al., 2017; Matlack et al., 1989; Moraes and De Ros, 1992; Wilson, 1992), (II) surface-based hydrological processes (Wooldridge et al., 2018), (III) benthic diatoms produced biofilms of exopolymers (Duteil et al., 2020; Virolle et al., 2019; Wooldridge et al., 2017), (IV) a reduction of flow velocity at sand-grain contacts (Cao et al., 2018), and (V) sediment dewatering in deep-marine turbiditic systems (Houseknecht and Ross, 1992; Porten et al., 2019). On the contrary to this dewatering process, a recent study has shown that the origin of chlorite coats in deep-marine sediments are inherited precursor chlorite coatings remobilized from shallow marine environments (Hansen et al., 2021). This remobilization

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hypothesis for the origin of chlorite-coats is reasonable as the clay-coats can resist abrasion (Verhagen et al., 2020).

Most studies on chlorite-coats on the surface of sedimentary particles have been carried out from the perspective of preservation of open pore networks in deeply buried sediment (Dowey et al., 2012; Haile et al., 2018; Line et al., 2018). Chlorite-coats inhibit quartz cement by isolating the quartz grain surfaces from silica-saturated pore fluids so anomalously high reservoir quality can be preserved at deeper burial depths. This scenario shows that the chlorite-coats can also have considerable potential to mask other reactions at sediment grain surfaces. For example, clay-coated quartz control methane gas (CH₄) wettability and thus methane recovery in shales (Pan et al., 2019). Understanding how chlorite-coats form on the surface of sediment is therefore central to understand various geochemical processes, including biogeochemical cycles of many elements, underground storage of nuclear waste, subsurface CO₂ storage and fate and transport of contaminants.

Despite its ubiquity and implications for numerous environmental surface and interface reactions, chlorite-coat formation in the context of other geosystems than petroleum prospect sedimentary rocks has not been given much attention. Even though numerous case studies have been conducted in the context of reservoir quality, to date, much remains unknown regarding how chlorite precursor particles attach on the surface of the sedimentary grains and the factors that control the attachment pathways. The evidence for where these clays form and what controls this process is not clear-cut, and mostly conjectural.

It is therefore essential to explore the mechanisms and variables that control chlorite-coat formation to predict various processes that occur at the interface between water and solid phases, especially in fluvial and deltaic settings. Because 1) clay-coats on the surface of sediment grains are abundant in fluvial and deltaic settings (Dowey et al., 2012) and 2) the fluvial and deltaic settings are the most environmentally and economically important geosystems whereby the human population within 100 km of these systems is growing (Arto et al., 2019; Cazarro et al., 2018; Lauria et al., 2018). The population within such systems was 2.1 billion in 1990 and is expected to grow to 3.2 billion in 2030 (Kummu et al., 2016). This population increase will result in massive human activities that have enormous potential to modify the affected drainage basins through marked anthropogenic induced changes. Human activities can increase the influx of terrestrially driven contaminants such as toxic heavy metals and emerging contaminants (e.g., microplastics, fertilizers and pharmaceuticals) into the rivers and deltas and ultimately the oceans. It is therefore indispensable to understand how clay-coats form on the surface of sediment grains, as it is fundamental in several natural and human induced phenomena, not only in the fields of petroleum geology, but also aquatic chemistry, soil chemistry, environmental chemistry and hydrogeology. The main objective of this study is therefore to unravel how clay-coats form on the surface of quartz grains.

2. Materials and methods

Laboratory batch experiments were conducted to unravel under which conditions clay-coating occurs, where iron/aluminium-oxides and humic acid were added to quartz – clay suspensions. All mixing experiments were conducted at room temperature (~20 °C) and all chemicals used were of analytical-grade quality while aqueous solutions were prepared using ultrapure water i.e. Milli-Q water (resistivity 18 MΩ/cm). Metal oxides (Al₂O₃ and Fe₂O₃) and salt (CaCl₂·2H₂O) with purity (≥99.0%) were purchased from MERCK. Aluminium (Al) - and iron (Fe) oxide were chosen as they represent a ubiquitous and highly reactive component of the inorganic particles in fluvial and estuary systems. We also used a Ca²⁺ solution, as it is the dominant cation in freshwater and important in the fluvial-marine transition. Humic acid (HA) in the form of crystalline powder purchased from Alfa Aesar was used without further purification. We used HA as it represents the

fraction of naturally occurring terrestrial derived organic matter commonly found in sediments and soils (Hayase and Tsubota, 1983). The natural chlorite (ripidolite CCa-2) rock chip from Flagstaff Hill, California, USA, was purchased from the Clay Minerals Society. This natural Fe-bearing trioctahedral chlorite was chosen because it represents the commonly found Fe-rich clay mineral in a spectrum of depositional environments including deltaic and fluvial settings as coatings on the surface of sediments (Dowey et al., 2012; Worden et al., 2020). The clay rock chip was first smashed and crushed into smaller fractions. Subsequently, the crushed clay fraction was wet micronized using ethanol for 12 min using the micronizing mill.

We used clean industry standard quartz as a sediment model as it is one of the most abundant components of sediment and soil. To remove any residual contaminants, if any, from the surface of quartz, the quartz grains were soaked overnight in 2 M HCl and washed thoroughly using Milli-Q water. The grain size distribution was determined using the Beckman coulter LS 13 320 Laser Diffraction Particle Size Analyzer. The quartz grains used in all experiments have a grain size distribution ranging from 63 to 500 μm representing very fine to medium sand.

All experiments were conducted in two type solution media, one-saline water (saline solution of 0.01 M CaCl₂) of ionic strength slightly higher than river water (estuary conditions) and other Milli-Q water (non-saline solution) representing low ionic strength conditions. The mixing experiment was performed to study how detrital clay coatings form on the surface of quartz. Varying solution chemistry, inorganic and organic materials under conditions relevant in natural settings are considered (Table S1). The procedure employs a heterogeneous mixture of quartz–ripidolite, including Fe- and Al oxides, and HA. The aqueous solutions were prepared at various initial pH values (5, 7 and 9). The pH of all experimental solutions was adjusted by the dropwise addition of a solution of 1 M NaOH and 1 M HCl and concurrently measured using a Metrohm 702 SM Titrimetric coupled pH meter. The batch experiments were conducted grounded on the presence and absence of supposedly binding agent/s into quartz–clay mixtures: Fe oxide, Al oxide, a mixture of Fe/Al oxide, HA, a mixture of HA and Fe/Al oxide and without the presence of the binding agents at the two aqueous conditions selected. Experiments from each category were conducted in duplicate to make certain that the results are repeatable.

First, quartz, ripidolite, HA, Fe- and Al oxide were weighed and added in 25 mL experimental tubes according to experimental categories. Second, 15 mL of the mixing solution prepared at a desired pH and salinity was added to the batch mixing tubes consisting of solid materials. The mixing tubes were quickly stoppered, and the mixtures were positioned on a horizontal axis on a mechanical shaker. The mixtures were shaken continuously at 250 rpm in the back-and-forth mode to simulate current agitated condition of coastal settings over a period of 48 h. Later, the mixtures were left for a week without any disturbances because in a natural setting, aggregates or flocs of clay particles are expected to be settled for example on sand bars during high and low tides slack water conditions. Therefore, our experimental configuration attempts to mimic environmental processes associated with sedimentary environments at the continental-marine transition. After a week, the quartz grains were sampled from each experimental mixing tube. Afterward, the samples were rinsed with Milli-Q water and the fluid was evaporated by placing the wet samples in an oven for 12 h at 60 °C. After drying, samples were loaded on individual stubs (sample holders) for analysis using Hitachi SU5000 field emission gun scanning electron microscope (FEG-SEM) at the Department of Geosciences, University of Oslo. Furthermore, wet quartz grains (without drying) were examined for the clay-coat formation using the Nikon SMZ18 binocular stereomicroscope. This investigation was done to show that the emplacement of the clay particles was not due to the drying process.

The extent of clay-coat coverages was quantified, using SEM micrographs of quartz grains. A semiquantitative coat coverage estimation was obtained for each sample by randomly selecting three representative grain surfaces from each SEM micrograph of each experiment. In

total, 108 quartz grains were analyzed. Based on the analysis of SEM micrographs using Python and the image processing library scikit-image, the extent of average clay-coat coverage was calculated (Van der Walt et al., 2014; VanRossum, 1995). Gray scale segmentation was performed on representative quartz surfaces in order to separate clean quartz surfaces from ripidolite particles using their differences in the shades of gray. As we used stub samples, the quantification results cannot be considered a perfect representation of the extent of clay-coating coverage. Because the gray scale, which is used to separate quartz grains from ripidolite particles, to some degree depends on the orientation of the selected grain surfaces. It is however, a more reliable way of estimating coating coverage compared to the commonly used visual qualitative classification method.

3. Results and discussion

The batch clay-coat experiments were conducted using a mixture of quartz–chlorite (Fe-bearing clay) in the absence and presence of initially solid phases (HA, Al- and Fe oxide), which are ubiquitous in soil and sediment deposited in fluvial and deltaic systems. These systems have been reported as common places for the Fe-rich clay-coat formation (Dowey et al., 2012). The results of the batch mixing experiments are presented and discussed below.

3.1. Solid phase control on clay-coat formation

Figure S1 shows representative SEM micrographs of quartz–ripidolite mixtures from batch mixing experiments conducted in saline and Milli-Q water at various pH values (5, 7, and 9) without the presence of HA, Fe and Al oxides (solid phases). Figures S2–S6 show representative SEM micrographs of quartz–ripidolite mixtures with the presence of HA, Fe- and Al oxides. Chlorite particle attachments were formed on the surface of quartz grains as coatings, irrespective of the absence or presence of the HA, Fe and Al oxides, though the extent of clay-coat

coverage varies (Fig. 1). Fig. 1 represents the estimated clay-coat coverage on quartz grains for six categorical batch experiments, for saline- and Milli-Q water respectively. The clay-coat coverage range from ~6% to 27% in the absence of solid phases, whereas ~1% to 32% in the presence of solid phases (Fe and Al oxide). The image processing method used for quantification of clay-coat coverage revealed a strong variation in clay-coat coverage on the surface of quartz grains. All the HA mediated experiments had very low clay-coat coverage (Figs. S2–S3), ranging from ~2% to 7% (Fig. 1).

The interparticle associations between ripidolite particles on the surface of quartz grains were largely seen to form edge-to-edge- and face-to-edge patterns rather than face-to-face stacking patterns (Fig. 2 and Figs. S1–S6). Similar types of geometrical arrangement of the clay particles have been reported in both natural environments and in laboratory formed chlorite-coats (Charlaftis et al., 2021; Haile et al., 2015). Underpinning what controls the clay staking patterns is however a difficult question as complex variables, such as the particle size distribution, mechanical forces of the physical mixing process, and different types of charges on the faces and at the edges and the heterogeneity of layer charges can regulate the clay particle stacking patterns. Generally, the interaction of clay surfaces with surrounding fluid in terms of the differences in charge characteristics of the clay basal surface and edge surface of clay minerals may explain the geometric arrangement of clay particles (Bennett and Hulbert, 1986).

The ripidolite particles in coatings are oriented parallel to quartz surfaces, which is analogous to the pattern of clay-coats on sediment surfaces that has been reported in natural environments (Haile et al., 2018; Wilson and Pittman, 1977; Worden et al., 2020; Aagaard et al., 2000). This pattern suggests that the clay-coat formation occurs by similar mechanisms in a natural setting. Also, the clay-coat attachment patterns appear similar in the presence of various types of solid substrates, suggesting that the solid substrates cannot control the mechanisms of attachment.

In all experiments (Figs. S1–S6), the attachment of clay particles on

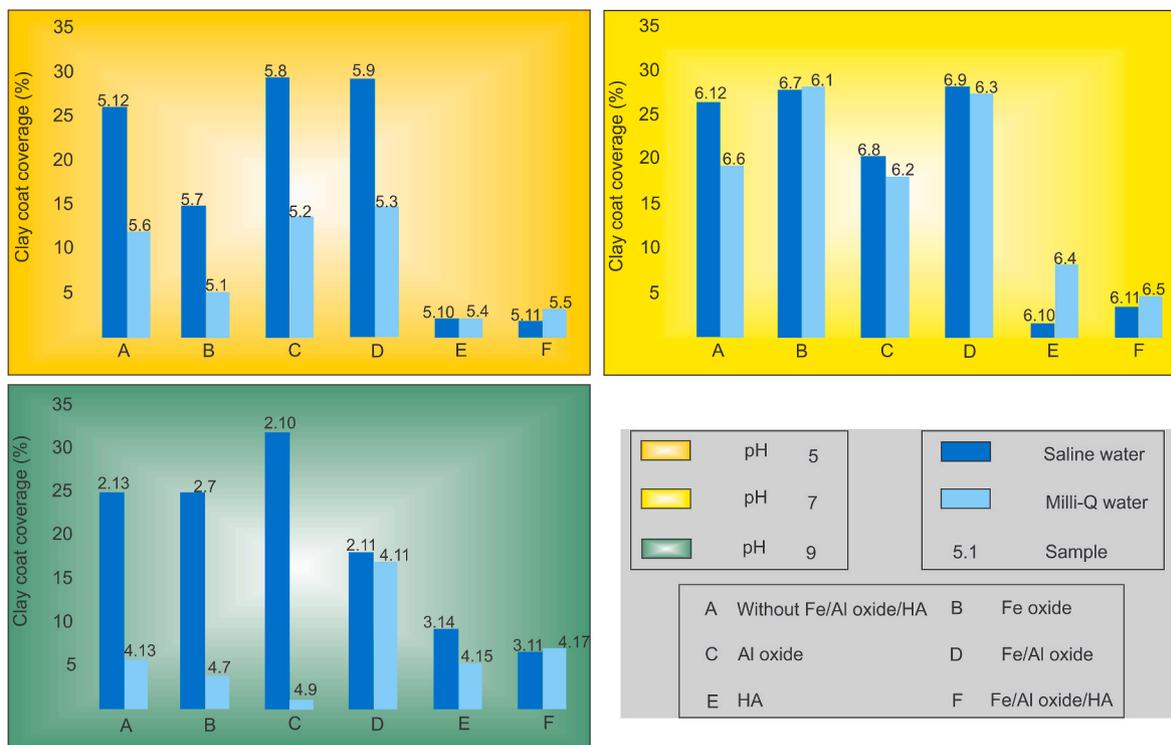


Fig. 1. Histograms showing variations of estimated clay-coat coverage on the surface of quartz grains for experiments conducted in saline- and Milli-Q water adjusted at pH 5, pH 7 and pH 9. The y-axis labels the clay-coat coverage on the surface of quartz grains, whereas the x-axis denotes types of solid substrates that constitute the six categorical experiments (A to F).

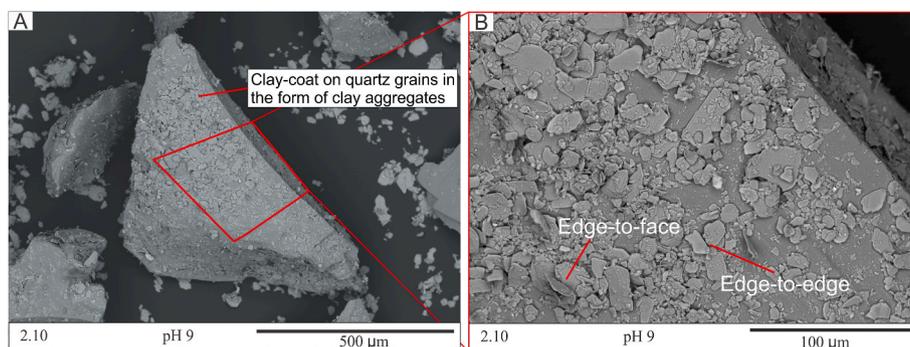


Fig. 2. Representative SEM-BSE micrographs of quartz–clay mixtures from experiment 2.10 conducted in the presence of Al oxide. A) Clay particles attach as coats in saline water of pH 9. B) Close-up view of the clay-coats marked with red rectangle on the surface of quartz grains. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

the surface of quartz grains was irregular, suggesting the surface chemistry of quartz in aqueous environments is uneven along the entire quartz surface. This observation agrees with the presence of two distinct surface groups (silanol and siloxane) that have been previously reported for the surface of quartz based on density functional theory computations (Bandura et al., 2011). These different quartz surface terminations can thus exhibit unique properties, which regulate the interactions with clay particles and attachment mechanisms.

Fig. 3A shows optical microscope micrographs of clean quartz grains before batch clay-coat experiments for comparison, whereas Fig. 3B–D shows quartz grains after batch mixing experiments. The emplaced clay and iron oxide particles on the surface of quartz grains were examined under the microscope as it was in the wet phase, i.e. before drying. Most of the quartz grains were coated with clay particles in the quartz–clay mixture (Fig. 3B) and Fe oxide particles in the quartz–Fe oxide mixture (Fig. 3C). The optical micrograph revealed that Fe oxide particles were uniformly coated on the entire surface of quartz, whereas clay particles were not in the quartz–clay–Fe oxide mixture (Fig. 3D). This result suggests that binding agent (here Fe oxide) mechanisms cannot explain clay particle attachment on the surface of quartz grains. If the metal oxide was serving as a binding agent, the clay attachment on the surface of quartz should have followed the Fe oxide attachment patterns and as a result, the entire surface of quartz should have been coated uniformly. This result is thus another supporting evidence that the presence of

binding agent mechanisms cannot explain clay coatings on the surface of quartz particles.

Nevertheless, it does not mean that the presence of so-called binding agents plays no role even though their absence does not inhibit the formation of clay-coats (Fig. 3B). For example, in a mixture of Fe and Al oxide, the surface charging behavior of Al- and Fe oxide can change in the mixture because the point of zero charge of the mixed oxides is the linear combination of the corresponding quantities of the components (Kosmulski, 2002). Such a scenario can produce a conducive environment for negatively charged clay minerals to come together to form aggregates that consequently led to settlement and ultimately attachment on the surface of quartz grains.

In the presence of HA (Fig. 4A), after the batch mixing experiments, we expected that the aggregates and/or coalescence cluster complexes of clay particles to settle on quartz grains but settling of the HA-complex did not happen (Fig. 4B). It appeared that the mixtures formed aggregates that consist of a relatively low-density, soft, jelly-like, crenulated, and spiraled, hallow loose network of grains (Fig. 4C and D). Therefore, HA remained predominantly in the aqueous phase by complexing with ripidolite particles (Fig. 4B).

The formation of the complexes in the aqueous phase inhibited sedimentation and hence the attachment of ripidolite aggregates on the surface of quartz grains. Reduction of the clay-coat coverage can be related to the potential of the HA to affect the electrokinetic properties

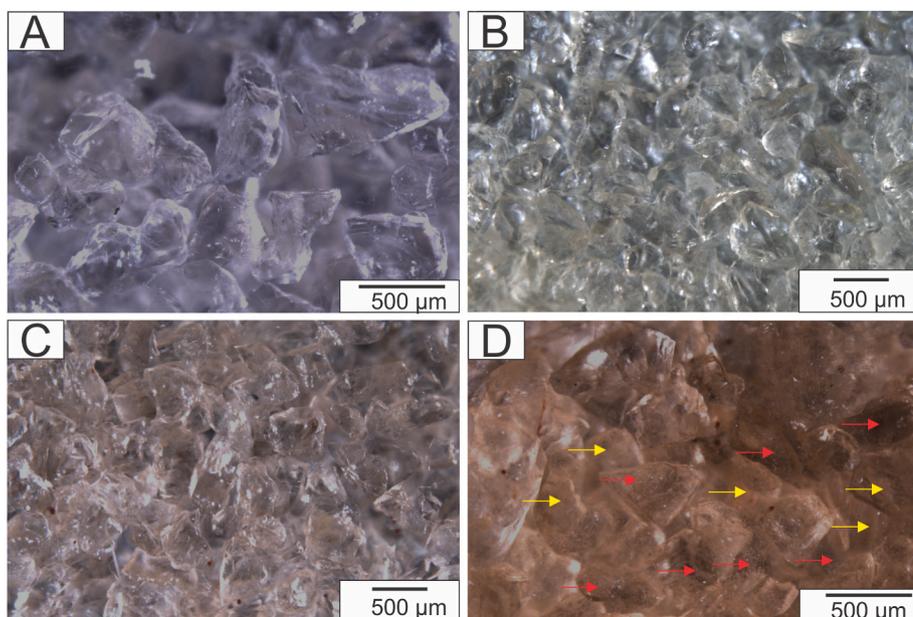


Fig. 3. Representative binocular stereomicroscope images of quartz grains. A) Original quartz grains with clean but irregular surfaces. B) Quartz grains coated in quartz–clay mixture. Most of the surfaces of quartz grains appear greenish-gray due to the clay-coats. C) Quartz grains coated with Fe oxide in quartz–Fe oxide mixture. Most of the surfaces of quartz grains appear brownish because of the Fe oxide coatings. D) Quartz grains coated in quartz–clay mixture in the presence of Fe oxide. The metallic bronze colored quartz surface indicates clay-Fe oxide mix coats (red arrows), while the brown colored indicates Fe oxide coats (yellow arrows). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

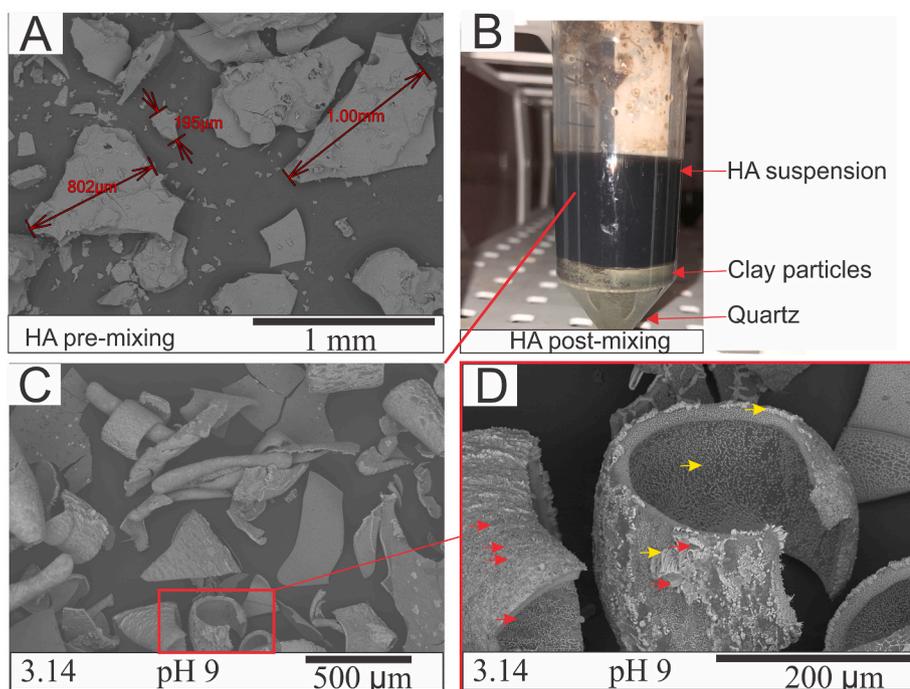


Fig. 4. Representative picture and SEM-BSE micrographs of humic acid before and after the experiments. A) Texture of initial HA. B) HA remained in suspension in the mixing tube after the batch mixing process. C) The HA displayed various textural modifications as it remained in the suspension. D) Close-up view of hollow coiled structure displayed in part C (red rectangle) showing the attachment of clay particles and salt on HA surface. Red arrows indicate clay particles, whereas yellow arrows indicate salt complexation on the surface of HA. Similar trends were observed for pH 5 and 7. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

(e.g., zeta potential) of the solid substrates, including clay particles. HA has high affinity to form complexes with Fe and Al oxide as well as clay minerals. For example, adding 50 mg/l of humic acid caused the entire zeta potential vs pH curve of hematite to become largely negative and nonresponsive to a wide pH range (3–10), resulting in the absence of a measurable isoelectronic point (Carlson and Kawatra, 2013).

The HA scavenging property for solid phases and clay particles can modify the ion distribution and association in the bulk solution and in the electric double layer. HA complexed with charged ions can thus modify physicochemical properties of the system. This modification can limit the availability of charged ions easing flocculation of ripidolite particles. As indicated in previous studies, low ionic strength solution will result in the formation of large flocs, whereas high ionic strength into small flocs (Konduri and Fatehi, 2017; Metaxas et al., 2021; Wilkinson et al., 2017). Similarly, the modification of the electrokinetic property of the coating process has resulted in the formation of large organo-clay flocs with open structures (low-density values) maximizing the possibility of the flocs to remain in the suspension. It has been shown that organic matter-mineral associations can lower the density of pure Fe and Al mineral phases (Kaiser and Guggenberger, 2007). Therefore, the scarcely observed clay-coats for quartz–clay mixtures in the presence of HA suggests that the clays, Fe- and Al oxide in the suspension have formed an interacting network with HA. This interaction can retard settling and/or attachment process. Although the fact that the interaction of organic matter with abundant hydrous metal oxides (e.g., Al and Fe oxides) dictates many important geochemical processes in aquatic systems, including rivers and deltaic settings, it has not been given the attention it deserves. This can be the reason why the interaction mechanisms of natural organic matter with mineral surfaces are not well understood (Gu et al., 1994; Kleber et al., 2021).

Unlike the results presented here, published studies suggested organic matter-related mechanisms to explain the origin of clay-coated sand grains in modern marginal marine sediments (Wooldridge et al., 2017). According to such studies, a biofilm (exopolymeric substance) that contains molecular bands fully consistent with organic-rich complex mixtures mediate clay particle attachment. Exopolymeric substances (EPS) are polyanionic large organic molecules mainly composed of polysaccharides, but they also include proteins, nucleic acids and lipids (Decho and Gutierrez, 2017). HA like EPS is a polyanionic organic

matter mainly containing abundant carboxyl and hydroxyl functional groups. Complex polysaccharides interact with mineral surface through their hydroxyl and carboxylate functional groups (Hakim et al., 2017). HA used in this study is not the same as EPS but from a functional group standpoint, we speculate that the basis for HA sorptive and adhesive properties can work also for EPS. This inference is reasonable as functional groups play a significant role in controlling physicochemical properties of the organic compounds.

This study unequivocally revealed that the attachment of clay minerals on sediment grain surfaces cannot necessarily be related to the presence of supposedly binding agents, such as metal oxides and organic matter. Therefore, our study signals the inevitability of scrutinizing the existing prevailing hypothesis about clay-coat formation i.e., the binding agent mechanisms are pivotal to form detrital clay-coats on sediment surfaces at or near the Earth's surface (Duteil et al., 2020; Virolle et al., 2021; Wooldridge et al., 2017). The prevailing hypothesis whereby the presence of binding agents explain the mechanisms of clay-coat formation in a spectrum of sedimentary environments is therefore overly simplistic.

3.2. Solution chemistry controls on clay-coat formation

Here, the potential-controlling role of changing medium salinity and pH on clay-coat formation as a function of the response of solid surfaces is presented and discussed. Detrital ripidolite particles attach on the surface of quartz grains as coats at various pH values in saline and Milli-Q water-mediated experiments (Figs. S1–S6). These results demonstrate that the clay-coats can form across different solution chemistries with a strong variation in clay-coat coverage on the surface of quartz grains (Fig. 1).

3.2.1. Ionic strength dependence of clay-coat formation

Across the pH values, the extent of the clay-coat coverage range from ~15% to 32% and ~1% to 28% related to saline- and Milli-Q water-mediated experiments (excluding HA-mixtures), respectively (Fig. 1). At ~ pH 5, the average clay-coat coverage is two to three orders of magnitude higher in saline water compared to Milli-Q water-mediated experiments (Fig. 1, S1A–B, S4, S5–S6A–B). At ~ pH 9, the average clay-coat coverage is significantly higher (> four times) in saline than Milli-Q

water-mediated experiments (Fig. 1, S1E-F, S4, and S5E-F) except for the experiments that were conducted in the presence of a mixture of Fe and Al oxides (Fig. 1, and S6E-F).

The substantial variation in the average clay-coat coverage at fixed pH (pH 5 and pH 9) levels as a function of changing the ionic strength of the solution suggests that the quartz surface chemistry in an aquatic environment responds to changes in electrokinetic charges. Therefore, the observed variation in clay-coverage in these experiments can be linked to the behavior of minerals in solution, e.g. changes in solubility and chemical speciation, which depend on the ionic strength of the solution. The formation of the observed clay-coat formation can be related to the surface configuration of the solid-solution interface of clay minerals, quartz, Fe and Al oxide sensitivity to ionic strength in aqueous environments (Tombácz et al., 2001). This observation suggests that at these pH values the zeta potential (electrokinetic property) on quartz is basically dependent on the ionic strength.

In contrast to pH 5 and 9 systems, the average clay-coat coverage is similar in both saline and Milli-Q water-mediated experiments at pH 7 environment (Figs. S1C-D, and S4–S6C-D). The pH level and solution chemistry can dictate charged species adsorption at the solid phases (e.g., quartz and ripidolite surface), surface charge and electric double layer that can regulate the chemistry and physics of charged interfaces (Chang et al., 1993; Marchuk and Rengasamy, 2011). Results observed at pH 7 indicate that the clay-coats formed irrespective of ionic strength and the presence of the types of solid substrates. The fact that the extent of clay-coat coverage is similar irrespective of salinity at pH 7, suggests that ripidolite aggregation in saline medium due to ion-bridging mechanisms cannot explain the ripidolite attachment on the surface of quartz. Salt-induced flocculation is however proposed as a major controlling mechanism for depositing suspended matter where the river meets the seawater (Manning et al., 2010; Mietta et al., 2009). However, it has also been suggested that salt mediation of flocculation is a minor factor in controlling flocculation of suspended solid particles (Eisma et al., 1991b; Thill et al., 2001). Our observation is similar to the latter studies. Similar clay-coat coverage imply that the zeta potential on quartz in contact with aqueous saline and non-saline solutions at pH 7 was independent from ionic strength. It appears that the clay-coat process at pH 7 is complex from a theoretical perspective and thus challenging to pinpoint precisely the dominant controlling parameter. Various parameters may have acted concurrently to modify the solution chemistry and thus dictate surface charges, including charged ion associations at the interfaces and in the bulk solution.

3.2.2. pH-dependence of clay-coat formation

The pH of the solution can strongly modify the surface chemistry of quartz. The presence of silanol groups on the surface of quartz is capable of adsorbing and releasing protons. The silanol group becomes deprotonated above the pH corresponding to the point of zero charge (pzc) of quartz that occurs at \sim pH 2.0–4.5 (Davis and Kent, 2018; Fuerstenau, 2005; Kosmulski, 2020). This means as the pH of the solution increases above the pzc, the number of deprotonated silanol groups and the negative charge of the surface increase. Therefore, the quartz–ripidolite or quartz–metal oxide interactions in the aqueous medium are expected to vary as a function of pH at a fixed ionic strength. Keeping salinity identical (Milli-Q water), the extent of clay-coat coverage varies a lot as function of pH values (Figs. S1 and S4–S6). For all experiments conducted with an increase in pH values ($5 < 7 < 9$) resulted in at first by an increase and then a decrease (e.g., \sim 12%, 19%, 6%) in the extent of clay-coat coverage on the surface of quartz grains (Figs. S1, S4–S6 B, D, and F). This pattern suggests that altering the pH of the solution can significantly dictate the clay-coat formation mechanisms in non-saline media. Unlike the predominantly suggested environments where clay-coats form, results of this study indicate that the formation of clay-coats is feasible in non-saline media (similar to freshwater natural environments).

In the saline water-mediated experiments, the clay-coat coverage

variations remain minor across the whole range of pH levels (Fig. 1). Since the clay-coat variations are minor as a function of pH, it can be concluded that the variations in the zeta potential of quartz as a function of pH in the saline solution were smaller. Therefore, in this case the pH level cannot be the key parameter controlling the extent of clay-coat coverage. This study underpins how the attachment of precursor clay particles happen, which will transform into authigenic chlorite coatings during burial. A direct precipitation reaction due to the dissolution of unstable rock materials, such as volcanic rock fragments, has also been proposed to form chlorite coatings in an alkaline environment (Chen et al., 2011). The direct precipitation mechanism describes only how authigenic chlorite is formed rather than the emplacement mechanism of a precursory clay phase. Still, unlike the alkaline environment proposition, hydrothermal chlorite synthesis experiments that simulated burial diagenesis have shown that authigenic grain-coating chlorites can be obtained at different pH values (Haile et al., 2015). This study indicates that previous suggestions about the emplacement of clay particles and their controls are probably too simplistic for chlorite-coat formation in a sandstone reservoir. It appears that the electrochemical environment and the physical mixing process regulate the emplacement of clay particles on the surface of sedimentary grains than only pH values.

3.3. How do clay-coats form?

Chlorite (Ripidolite) structure shows a regular alteration of negatively charged trioctahedral micaceous layers and of positively charged octahedral interlayer hydroxide sheet interacting when in contact with aqueous media. The solution chemistry and the types of solid phases in aqueous media can control ripidolite particle rearrangement via attachment, detachment and migration in sedimentary environments. Aggregates of ripidolite particles appear as irregular masses or clumps of numerous individual grains (Figs. S1–S6). The ripidolite aggregates consist of particles ranging from small (\sim 2 μ m) to large (\sim 10 μ m) and it appears that these aggregates and larger size individual ripidolite particles were attached on the surface of quartz grains.

The aggregates are mainly arranged in a chain-like structure rather than stacking in a regular pattern resembling the staircase structure. This pattern indicates that processes leading to the aggregation and settling of ripidolite particles are crucial for the coating process on the surface of quartz grains. As the aggregates get closer to the quartz surface, the strength of intermolecular binding forces that facilitate the coating process will increase. Therefore, the electrokinetic interactions that dictate the aggregation of clay particles can be regarded as possible mechanisms for sedimentation and attachment of clay particles on the surface of quartz grains. In contrast to saline water, Milli-Q water-mediated systems (pH 5 and 9) can have individual particles homogeneously dispersed forming a stable suspension. Such a process can remain virtually unchanged for long periods and will inhibit settling and thus the coating process. Although at a low rate, changes can occur in such a system, suggesting that the system is unstable in a thermodynamic sense.

A complex array of parameters that either enhance or inhibit the aggregation process can thus control the clay-coat formation. At fixed pH 5 and 9, changing the ionic strength of the solution demonstrates variations in clay-coat coverage, suggesting increasing ionic strength favors the mechanism of the clay-coat formation. In the Milli-Q water-mediated experiments (non-saline solution), aggregation can be hindered due to limited interactions between the constituent phases due to limited availability of charged ions. In contrast to the Milli-Q solution, the charged ions in the saline solution will affect the aggregate size and aggregate-settling velocity, due to the increase in the cohesive force between clay particles and other phases. These mechanisms favor the formation of aggregates of clay particles that sink many times faster than their component grains. These phenomena look like the non-equilibrium aggregation of cohesive sediments that occur in nature in turbulent type

flows through random collisions of sedimentary particles. The reason for this process is related to an increase in the mobility of the salt ions in an aqueous system affecting the electrokinetic properties, including the structure of the electric double layer and zeta potential, of quartz grains, clay particles and metallic oxides. Therefore, charged ion interactions can explain the attachment process on the surface of quartz grains.

It is obvious that clay-coats were scarcely formed under the Milli-Q water system. The exceptions tend to be experiments conducted at pH 7 (Fig. 1). This scarcity of clay-coats can be linked to a shortage of charged ions in the freshwater suspensions as the abundance of charged ions favor sticking leading into strong electrokinetic interactions. Particle attraction and association are more effective in a saline solution rather than dilute solutions (freshwater) (Dao et al., 2020; Wu and Adachi, 2018).

van der Waals attractive forces that operate between the atoms of particles can also cause particle association in saline medium. The summation of all attractive forces between all phases can result in total attractive forces between the particles. In a freshwater medium, repulsive forces between the particles can prevent particle association. The presence of such change is evident from the well-known movement of particles in an electric field system. The effectiveness of the repulsive forces can be shown to decrease with increasing ion concentration of the liquid phase in the system. Therefore, repulsive forces will prevent particle association in freshwater solution by counteracting the van der Waals attraction, but in salt solutions, they are no longer powerful enough to prevent aggregation. Salt is expected to screen the electrostatic repulsive forces between the charged particles in solution and thus via short-range van der Waals interaction to promote the rate of particle flocculation.

There was no visible clay-coat trend observed in HA/quartz-clay mixtures as a function of pH and salinity (Figs. S2–S3). An increase in pH for both saline and non-saline solutions show a minor increase in the extent of clay-coat coverage in all HA-containing experiments (Figs. S2–S3). Even though the solution chemistry varied, in general it appeared that any small variations in the extent of clay-coat coverage are to be considered negligible (Figs. S2–S3). But the clay-coat coverage appeared slightly higher in the alkaline pH range compared with acidic and neutral pH values. Increasing the pH of the solution increases the concentration of hydroxide ions in aqueous phase facilitating the adsorption of these ions on solid phases such as HA. This interaction results in a large diffuse electrical double layer, resulting in an elevated zeta potential. This interaction can to some extent have increased instability of a suspension of clay particles resulting in settling and then attachment.

The ripidolite-HA interactions give an excellent insight into the factors influencing the clay-coat formation on the surface of quartz grains. HA substantially alters clay minerals dispersion-aggregation behavior. This interaction clearly indicates that the mechanism of clay-coat formation can be constrained by processes that can change the interfacial electrochemistry of clay minerals. In natural settings, it has been proposed that the flocs form in highly turbulent areas, such as tidal inlets and narrow straits, and near the bottom in the regions of muddy sediment. Such complexes were suggested to settle on sand bars during high tides and low tide slack water conditions. The presence of organic matter and clay-organic matter complexes in the water column was suggested to enhance the flocculation of suspended particles and thus settling (Eisma et al., 1991a). However, results of this study reveal that we need to be cautious when inferring organic matter-mineral or sediment interactions in the natural setting, resulting in the flocculation of clay particles and thus settling.

Understanding HA-clay minerals interactions in the soil and sediment is significantly important. Because such a process can shape the fate and mobility of contaminants in the natural environment. Ripidolite was adsorbed on the surface of HA irrespective of ionic strength and pH variations of the aqueous media, indicating HA was acting dynamically over a range of different solution chemistries and thus modify local

electrokinetic behavior of the media. HA-mineral interactions can be electrostatic between hydrophilic organic moieties and molecular between its hydrophobic portions. The aqueous complexation of HA due to its functional groups including carboxyl and hydroxyl can result in the dissolution of ripidolite to form colloidal particles hindering the formation of flocculated material. Yet, the mechanism(s) of interactions between most organic matter and most minerals in sediment and soil is incompletely understood (Mayer, 1994).

3.4. Implications

This study demonstrates that solid phases and solution chemistry can constrain chlorite-coat formation on the surface of quartz grains. The formation of chlorite-coats in simple quartz-chlorite batch experiments could indicate that chlorite-coats have the potential to form in many natural subaqueous settings where quartz grains and clay minerals (particles?) coexist. Quartz is a unique archive of chemical-mechanical processes that have affected sedimentary environments at and below the Earth's surface. Therefore, the use of quartz as a model represents interesting environmental applications, but there will be a potential to overlook clay-coats on the surface of sediment and soil particles in numerous environmental systems. This overlooking of clay-coats is highly possible, as it has been mainly studied only from the context of petroleum reservoir quality.

Therefore, the presence of thin clay-coats (~2–3 μm) on sediment surfaces should be carefully checked in various environments. The presence of clay-coats on the surface of sediment can significantly influence the physicochemical behavior of the sediment. Understanding how and where clay-coats form on quartz and other mineral particles can therefore be crucial during modeling a spectrum of biogeochemical processes in sediment and soil. Some examples include predicting the pore network distribution in deeply buried sediments, sediment wettability (e.g., crucial for predicting CO_2 storage capacity) and determining the fate and transport of contaminants in aquifer and soil column matrix. According to their sorption affinities, clay-coats can serve as either permanent or temporary sink for contaminants. These realities signify the importance of paying attention to the factors controlling the clay-coat formation in sediment and soil systems.

Based on our investigation of the effect of binding agents on the formation of chlorite-coats, we propose that the presence of binding agents do not necessarily enhance clay-coat formation on the surface of quartz grains in opposition to the prevalent consensus. This implies that the interactions between Fe-bearing clay minerals and the binding agents as a model explanation of how clay-coats form on the surface of quartz grains were overly simplistic. Rather the solution chemistry influences the process of the clay-coat formation, which is exclusively overlooked in previous studies. This study suggests the importance of investigating the solution chemistry of diverse natural environments that host clay-coat formation. Solution chemistry is indispensable to understand various interfacial reactions and their combined impacts on the fate and transport of contaminants, cycling of nutrients and trace elements in abiotic and biotic systems.

HA remained in suspension complexed with the clay particles and metal oxides and charged ions, which suggests that HA does not necessarily result in clay-coat formation on the surface of quartz grains. Similar properties apply to other types of continentally derived organic matter carried by rivers that are entering the oceans. This result implies that complexed organic matter particles cannot settle in a relatively small area close to the mouth of the river. Therefore, such particles can travel far into the ocean. This result has implications resulting in refining our thinking regarding biogeochemical cycling of Fe in the ocean, the fate of emerging pollutants such as microplastics and heavy toxic metal distribution in the ocean.

In addition to essential nutrients (e.g., N, P, Si), rivers delivering 300–380 Tg of organic matter per year to the coastal zone (Seitzinger et al., 2010). Therefore, the observed property of HA can also have

implications for the transfer of essential nutrients from the coastal sea to the open ocean i.e., obscuring what proportion of riverine nutrients reaches the open ocean. Therefore, the behavior of HA in aqueous medium should be scrutinized to be incorporated into ocean biogeochemistry models. Considering this property allows a realistic picture of the effects of riverine nutrients and organic carbon on ocean biogeochemical cycling of nutrients.

4. Conclusion

Chlorite-quartz batch mixing experiments were conducted to study detrital clay-coat formation on the surface of quartz grains. In contrast to the prevailing hypothesis that considers binding agents and salinity as a crucial part of clay-coat formation, we show for the first time detrital clay-coats can form in the absence of the common binding agents such as Al- and Fe oxide and non-saline solution. Also, clay-coats scarcely formed in the presence of organic matter, which is the commonly proposed binding agent. Therefore, salinity and binding agents cannot be prerequisites to dictate clay-coat formation under conditions relevant in natural environments. Rather the experimental results reveal that the clay-coat formation is controlled by electrokinetic properties of the multicomponent mixtures. This indicates that the precursor chlorite coating formed at the redox boundary attach to quartz grains when dispersion of such iron rich clay minerals takes place during sediment reworking.

Clay-coats on the surface of quartz grains, one of the most abundant primary rock-forming minerals on the surface of the earth, can predominantly influence several geochemical processes at liquid-solid interfaces including contaminant mobilization, mineral dissolution kinetics, wettability and subsurface CO₂ storage. Failure to understand how clay-coats form on the surface of quartz grains can have serious consequences for deciphering various geochemical reactions, where reservoir quality prediction, contaminant mobilization in sediments, sediment and groundwater remediation methods can be compromised. These results add to our knowledge and understanding of the clay-coat formation in complex sediment surface-aquatic ecosystems.

Data statement

The data that support the findings of this study are available in the article and supplementary Information files.

Author contributions

Beyene G. Haile: conceptualization; methodology; validation; investigation; data curation; writing original draft; writing review and editing; visualization. **Henrik N. Hansen:** conceptualization; methodology; validation; investigation; data curation; writing review and editing; formal analysis; visualization. **Per Aagaard:** conceptualization; writing review and editing; supervision. **Jens Jahren:** conceptualization; supervision; funding acquisition; project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.petrol.2022.110682>.

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