EVIDENCE OF OSTWALD RIPENING RELATED RECRYSTALLIZATION OF DIAGENETIC CHLORITES FROM RESERVOIR ROCKS OFFSHORE NORWAY

J. S. JAHREN

Department of Geology, University of Oslo, PO Box 1047 Blindern, 0316 Oslo 3, Norway

(Received 6 August 1990; revised 21 September 1990)

ABSTRACT: Chemical variations in individual chlorite crystals of diagenetic origin delineated by energy dispersive X-ray spectroscopy (EDS) in a transmission electron microscope (TEM) indicate a temperature dependent chemical zonation in each grain. Silicon decreases and Al increases with higher temperature resulting in a decreasing Si/Al ratio away from the crystal core reflecting the time and rate of the crystal growth. Chlorite particle-size distributions obtained by scanning electron microscopy (SEM) give steady state profiles which suggests that the chlorite growth is controlled by a grain coarsening process related to Ostwald ripening.

In chemically closed systems, it is often observed that some crystals are growing while other and smaller crystals of the same crystal population are dissolving. This process, known as Ostwald ripening (Ostwald, 1900), is driven by a decrease in surface energy and is a well established process in solution chemistry and metallurgy (Bigelow & Trimble, 1927; Greenwood, 1956; Lifshits & Slyozov, 1961; Wagner, 1961; Speight, 1968; Kirchner, 1971; and others).

In geology, Chai (1974) used Ostwald ripening kinetics to explain recrystallization of calcite in an experimental hydrothermal system, and also gave a brief summary of the theory behind the Ostwald ripening process. Other important papers describing Ostwald ripening kinetics in geologic systems have been presented by Baronnet (1982) on the coarsening of calcite and synthetic phlogopite mica and the relation to growth kinetics, and by Morse & Casey (1988) who summarized the thermodynamic behaviour of many sedimentary minerals in relation to Ostwald ripening kinetics.

There has not been any extensive study of whether or not clay minerals in complex sedimentary environments undergo Ostwald ripening, but recently some evidence presented by Eberl & Srodon (1988) on sericites, Eberl et al. (1990) on both clays and metamorphic minerals, and Inoue et al. (1988) on illite-smectite indicates that Ostwald ripening might be an important process in clay mineral growth. Their work, which is based on the Warren-Averbach X-ray particle size analysis technique (Warren & Averbach, 1950), SEM and TEM measurements, and expandability calculations, showed that clay mineral size distributions are consistent with the distributions predicted by Ostwald ripening kinetics.

Jahren & Aagaard (1989) argued that tetrahedral Al increases as a function of formation temperature and that the number of octahedral vacancies decreases with increasing formation temperature in Fe-rich diagenetic chlorites, based on EDS of grain edges. The increase in tetrahedral Al results in a substantial decrease in the Si/Al ratio in the structure. This
TABLE 1. Sample details.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>Location</th>
<th>Formation</th>
<th>Stage</th>
<th>Porewater P(b)/T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS1</td>
<td>3080</td>
<td>Viking Graben</td>
<td>Intra Dunlin Sand</td>
<td>Pliensbachian</td>
<td>350/120</td>
</tr>
<tr>
<td>HB1</td>
<td>3800</td>
<td>Haltenbanken</td>
<td>Garn</td>
<td>Bajocian</td>
<td>680/140</td>
</tr>
<tr>
<td>HB2</td>
<td>3840</td>
<td>Haltenbanken</td>
<td>Garn</td>
<td>Bajocian</td>
<td>680/140</td>
</tr>
<tr>
<td>HB3</td>
<td>4360</td>
<td>Haltenbanken</td>
<td>Tilje</td>
<td>Sinemurian</td>
<td>445/145</td>
</tr>
<tr>
<td>HB4</td>
<td>4464</td>
<td>Haltenbanken</td>
<td>Tofte</td>
<td>Pliensbach/Toarch</td>
<td>480/155</td>
</tr>
<tr>
<td>HB5</td>
<td>4470</td>
<td>Haltenbanken</td>
<td>Tofte</td>
<td>Pliensbach/Toarch</td>
<td>480/155</td>
</tr>
<tr>
<td>NS2</td>
<td>4900</td>
<td>Central Graben (1)</td>
<td>—</td>
<td>Triassic</td>
<td>—/170</td>
</tr>
</tbody>
</table>

A decrease should be recorded in the chlorite structure as a Si/Al gradient from the core to the edge of a grain if the grain has undergone Ostwald ripening, and if the crystal has been ripened over a temperature interval large enough to reveal the temperature dependent compositional change in the chlorite structure.

The samples studied were chosen to document eventual closed-system kinetics in overpressured multicomponent diagenetic environments, and to delineate eventual internal mass transfer processes in the chlorite system and/or chlorite grain growth from other dissolving Mg/Fe minerals. Effects of different chlorite residence time in the sandstones studied both as changes in crystal chemistry and in the particle-size distribution and relations to Ostwald ripening processes will also be discussed.

If Ostwald ripening or other grain coarsening processes are operative in multicomponent sedimentary systems, detailed chemical, structural and morphological studies of chlorite or other Ostwald ripened minerals with a temperature dependent composition, will be very useful as these minerals, when present, will record the diagenetic evolution in the sediment.

METHODS AND MATERIALS

After screening of several thin sections by optical microscopy and SEM, chlorite samples of the grain coating type were selected for further study. The samples chosen were from medium to deeply buried (3100–4900 m) Jurassic sandstones from the North Sea area and the Haltenbanken area off the Norwegian coast (Table 1, Fig. 1).

Core samples were gently crushed in an ethanol filled mortar in order to bring the chlorite content into suspension (see Fig. 2a for morphology of in situ chlorite). A drop of suspension in alcohol was transferred on to a Cu grid covered with a holey carbon film. After evaporation of the alcohol, the samples were investigated in a Jeol 2000 Fx 200 kV TEM equipped with a Tracor Northern TN2000 EDS X-ray analyser to determine chemical variations in individual grains.

Size distribution profiles were obtained by SEM using a Jeol 840 JSM instrument equipped with a Link analysis system and a Digiscan analysis package. Both backscatter intensity and chemical windows (Fe and Mg) were applied to distinguish between the chlorite population and all other phases present. Some abraded chlorite grains were noticed, but crushing of chlorite grains did not appear to be a problem in the grain size measurements. To minimize the problem of crushing, grains <0.7 μm in size were not considered in the size-distribution plots. An average of 560 particles were measured in each
Recrystallization of diagenetic chlorites

sample and the mean diameter normal to the [001] direction in each grain was used in the size-distribution profile. The sample preparation was similar to that for the TEM, except that the crystals were sedimented on to a polished graphite slab.

RESULTS

Both core and rim areas of authigenic euhedral crystals were analysed in order to indicate systematic compositional variations, and additional line-scan analyses were performed on selected crystals (Fig. 2b). The spacing chosen between analyses points was a function of the actual grain size (i.e. large spacings for large crystals) so that eventual compositional trends reflect the temperature dependence in each chlorite population. The results indicate an increase in the X-ray Al/Si intensity ratio from the core towards the rim of individual chlorite crystals (Fig. 3) in agreement with earlier findings (Jahren & Aagaard, 1989). No Fe/Fe + Mg variations were observed in any of the samples investigated as shown in Fig. 4 where Fe/Fe + Mg concentration ratios are plotted for the different samples studied.

Small amounts of K were nearly always present in the euhedral chlorite crystals,

Fig. 1. Well location map. Samples HB1-HB5 are from the Haltenbanken area, and samples NS1 and NS2 are from the Viking Graben and Central Graben in the North Sea area, respectively.
decreasing in concentration away from the crystal cores towards the neoformed rims where it was almost always not detectable. The concentration of K in the chlorite matrix was usually <1% of the total cations present, and as K was eventually lost due to volatilization, quantitative or semiquantitative EDS measurements of K/Al ratios from core to rim were not possible. However, some of the smallest crystals interpreted petrographically from their morphology (small crystals with rounded edges) as dissolving chlorite crystals were found from EDS analysis in the TEM to have a substantial illitic component (>10% illite), indicating that at least some chlorite crystals originate as a mixed-layer illite-chlorite phase. The reason for this is not known but chlorite seem to pre-date illite formation (Bjørlykke et al., 1986), indicating that the illite component in the chlorite phase originates from the rapid early stage chlorite precipitation as a result of illite supersaturation in the porewater, and that illite is unable to precipitate on its own for some kinetic reason. The K content is believed to decrease from core to rim partly due to purification of the chlorite crystals.
Recrystallization of diagenetic chlorites during growth, and partly as a consequence of illite formation acting as a sink for potassium. Illite was found in all the samples studied, but in the shallowest well (NS1), only incipient illitization, detectable only in the TEM, was found, supporting earlier findings by Björlykke et al. (1986).

Size distribution patterns plotted as \( f(r)/f(r)_{\text{max}} \) vs. \( r/r_{\text{mean}} \) diagrams (Fig. 5) to reveal the eventual steady state properties of the distributions (Exner & Lukas, 1971) show that the distributions fit between the ideal theoretical distribution calculated from second-order grain growth kinetics in a closed system (Baronnet, 1982), and a log-normal distribution (Eberl et al., 1990). Second-order grain growth, also known as BFC type of crystal growth (Burton et al., 1951) is typical of low saturation growth (e.g. Sunagawa, 1984) where the growth rate is controlled by outcropping screw-dislocations on the crystal faces. The rate law responsible for the log-normal distribution is still not understood (Eberl et al., 1990), but second-order grain growth would be the expected grain growth process in the conditions prevailing in the rocks investigated.

The distribution profile is, in addition to the growth process, also a function of (i) the amount of the ripened phase present in the system and the interaction between the diffusion fields between the individual crystals, and (ii) minor stress/strain effects if sufficiently rigid interfaces exists (Ardell, 1972). The result of these factors always yields a broadening of the size distribution profile compared to the theoretical distribution.

The fact that even the chlorite size distribution profile for the shallowest sample NS1 fits the steady state profile and that the sample show signs of a temperature related Al/Si gradient indicates that the internal mass transfer process resulting in grain coarsening in

![Fig. 3. Compositional variations in chlorites plotted as Al/Si X-ray intensity vs. analysis position in individual chlorite crystals. The uncertainties in the ratios average 4%.](image-url)
chlorite is operative in sandstones from at least around 120°C, based on bottom hole temperatures.

**DISCUSSION**

The Al/Si ratios determined are related both to the shape of the growing chlorite crystals and the eventual illite-chlorite mixed-layer composition of the original core of the crystal. A three-dimensional growth pattern will decrease the Al/Si ratio difference between the core and rim of individual chlorite crystals because growth in the c-direction is expected to decrease relative to the a and b directions when supersaturation is lowered during growth, whereas an illite component in the crystal core will increase the difference between core and rim. This is due to the different Al/Si ratios in illite and chlorite. To evaluate the effect of crystal growth, information about the behaviour of the c-dimension during growth must be known. The c-dimension information can be obtained in the TEM using shadowing techniques, or if the crystals are not infinitely thick (<1000 Å), by using the Warren-Averbach XRD technique (Warren & Averbach, 1950). These methods were not available during this work, but because the illite component can be back calculated from the concentration of K in the crystal core, a qualitative evaluation of the relative importance of the two processes could be made. The calculations showed that the chlorite growth pattern is the dominating process if three-dimensional chlorite growth based on ab plane growth
Recrystallization of diagenetic chlorites

175

rates is assumed, resulting in only a slight underestimation of the Al/Si ratio in the core area (Al/Si > 1 in chlorites, Al/Si < 1 in illites).

The absence of Fe/Mg trends (Fig. 4) in the chlorites investigated indicates that the chlorite crystals initially had a more or less uniform composition, and that no measurable partitioning of Fe and Mg between the porewater and the chlorite phase has occurred during the particle coarsening process. This result supports earlier observations and calculations made by Cathelineau (1988) and Jahren & Aagaard (1989) which indicated that the Fe/Mg ratio of diagenetic chlorites reflects the local Fe/Mg ratio in the sediment only.

The mean diameter of the different chlorite populations investigated is shown in Fig. 6, and, as expected, there is a correlation between size and temperature, indicating the time-temperature dependent crystal coarsening. There is no reason to expect a simple relationship between mean size and temperature because the rate of the grain coarsening is also a function of the total amount of the ripened phase in the system (Ardell, 1972).

Although the temperature dependent Al/Si zonation curves (Fig. 3) are comparable to earlier results (McDowell & Elders, 1980; Cathelineau, 1988; Jahren & Aagaard, 1989), they show that factors other than temperature are important for the actual Al/Si ratio. This is because if the Al/Si ratio was a function of temperature only, one would expect that the sample taken from the formation with the highest present day temperature would also have the highest Al/Si ratio. This is not the case, and precludes the use of the slope of the Al/Si curve directly as a measure of, for example, ripening time and chlorite nucleation temperature.

Fig. 5. Size-distribution profile plotted in a normalized coordinate system (frequency/max frequency vs. radius/average radius) to reveal the eventual “steady state” properties in the different chlorite populations. An average of 560 particles were analysed in each sample, and the plot is based on all the samples studied.
The information inherent in the absolute Al/Si ratio measured at the crystal rim can be utilized in an evaluation of the non-temperature dependent effects governing Al for Si substitution in the crystal structure. The steep NS2 curve is an example of this, and can be explained as a combination of ripening time and the effect of a more Fe-rich chlorite composition with an initial high Fe³⁺/Fe²⁺ ratio at the time of formation partly excluding Al in the early stages of the grain coarsening process. Variation in Fe³⁺/Fe²⁺ is frequent in hydrothermal chlorites (Walshe, 1986) but it is not possible to check this in individual chlorite grains. If this could be done in the future, for example by electron energy loss spectroscopy (EELS), ferrous iron residence time in the porewater could be determined by Fe³⁺/Fe²⁺ line-scan measurements. This would give an approximate growth rate for chlorite during ripening, and also indicate the possible starting material (e.g. iron oxides) and chemical environment (e.g. early or late).

Another important aspect related to Ostwald ripening is the change in isotope signature expected for the ripened phase as a result of re-equilibration with the porewater before material from dissolving sub-critical grains are reprecipitated on to super-critical grains (Eberl & Šrodon, 1988). For example, the result of an increase in the mean diameter by a factor of three is that ~85% of the original solid phase will have taken part in the grain coarsening process (Chai, 1974). This should result in an isotope vs. temperature pattern similar to the pattern found for mean size vs. temperature (Fig. 6) for ripened chlorites.

CONCLUSIONS

Temperature dependent compositional variations in chlorites formed in low-temperature environments (Cathelineau & Nivea, 1985; Jahren & Aagaard, 1989) have been documented in individual crystals. The chlorite size-distribution profiles indicate that closed
Recrystallization of diagenetic chlorites

system second-order related kinetics could be the growth mechanism responsible for the coarsening of chlorite crystals with increasing burial, although the experimental distribution is intermediate between second-order and log-normal distributions. Minor temperature dependent compositional variations question true Ostwald ripening grain coarsening kinetics because the chlorite system is not entirely closed chemically. The steady state crystal size distributions indicate that most of the material involved in the grain coarsening process is derived from dissolving sub-critical chlorite grains. The restricted porewater flow suggested by the closed system kinetics indicates that one or more of the initial chlorite components are restricted to the chlorite system and are not removed by eventual porewater flow or diffusion when unstable chlorite crystals are dissolving, but are rapidly reprecipitated on to bigger stable chlorite crystals. Good candidates for conservative cations in the chlorite system are Fe and Mg because they are unaffected by the grain coarsening process. Restricted porewater flow is also indicated by regional studies of the Norwegian shelf areas, theoretical considerations (Bjørlykke et al., 1988), and the fact that all the samples studied are from overpressured reservoirs.

ACKNOWLEDGMENTS
This research was supported by the Norwegian Research Council for Science and the Humanities (NAVF). Samples were provided by Statoil, Norsk Hydro, and the Norwegian Petroleum Directorate. The TEM work was carried out at the EM laboratory in the Department of Physics, and the SEM work was carried out in the Department of Geology at the University of Oslo where technical assistance from B. L. Berg and T. Winje is acknowledged. I am especially grateful to Arne Olsen and Per Aagaard for their comments on the manuscript and general interest. D. D. Eberl and an anonymous referee are thanked for their constructive reviews of the original manuscript.

REFERENCES


