SOME COMMENTS ON THE CHEMISTRY AND STABILITY OF INTERSTRATIFIED ILLITE–SMECTITE AND THE ROLE OF OSTWALD-TYPE PROCESSES

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ABSTRACT: Much emphasis has been placed recently on the role of Ostwald-type processes (both ripening and the step rule) in the formation of interstratified illite–smectite clay minerals during diagenesis. Closer investigation of the relationships between illite particle thickness (as defined in terms of the fundamental particle theory) and particle chemistry show that simple Ostwald ripening is too simplistic a mechanism to describe observed changes in illite thickness and composition. In addition, available thermodynamic data on clay minerals suggest that the conventional notion of metastability associated with Ostwald’s step rule is an inaccurate description of the relationship between illitic clay minerals and their macroscopic 2:1 phyllosilicate analogues.

Interstratified illite–smectite (I–S) has long been considered an enigmatic mineral species. Notwithstanding the attempts of numerous authors to develop a singular, self-consistent mineralogical description of the species (compare the ‘MacEwan crystallite’ approach of Altaner et al., 1988 with the fundamental particle model devised by Nadeau et al., 1985a), considerable effort has also been made to define the stability of I–S in terms of equilibrium thermodynamics (Aagaard & Helgeson, 1983; Garrels, 1984; Sass et al., 1987; Aja et al., 1991). In summarizing the work of Sass et al. (1987) and Aja et al. (1991), Rosenberg et al. (1990) have shown that the interpretation of solubility experiments on I–S becomes a more rational process if the solubility controlling phases are considered as a series of four discrete thermodynamic entities of different (illitic) chemical composition. This they termed the multiphase model, where I–S was considered a mixture of two or more of each discrete phase. By alloying their observations with the mineralogical model of Nadeau et al. (1985b) and the range in chemical composition of some natural hydrothermal illites reported by Inoue et al. (1988), Rosenberg et al. (1990) suggested that each discrete illitic phase, of a specific thickness, has a well constrained chemistry (in terms of interlayer $K^+ / O_{10}(OH)_2$) and exists as a singular thermodynamic entity. Hence, according to their model, the diagenetic conversion of smectite to illite is facilitated via each discrete phase (which correspond to the ordered interstratification types R0, R1 and R3) where thickness and interlayer $K^+ / O_{10}(OH)_2$ increase progressively.

To this extent, the multiphase model appears totally self-consistent. However, Rosenberg et al. (1990) also extended their discussion to include Ostwald-type processes and their application to clay mineral diagenesis. These include the mechanism governing particle thickening (Ostwald ripening) and the extent to which each discrete illitic phase in the conversion of smectite to illite is metastable with respect to muscovite (an illustration of Ostwald’s step rule). Evidence to support the view that Ostwald-type processes are important in clay mineral transformations comes from an increasing variety of sources. Eberl & Środoń (1988) have described the hydrothermal alteration of illite to sericite as an example of Ostwald ripening. Similarly, Jahren (1991) has described the diagenetic recrystallization of chlorite in much the same way. On the other hand, Freed & Peacor (1992) have described the combined process of dissolution of smectite and precipitation of illite (as distinct from illite particle growth itself) in Gulf Coast mudrocks in terms of Ostwald’s step rule. Similar use of the step rule principle has been made by Baxter Grubb et al. (1991) to explain the 1M to 2M$_i$ illite
polytype transition and by Jiang & Peacor (1991) to explain the kaolinitization of muscovite via illitic intermediates.

Both Ostwald-type processes are claimed to be consistent with the proposed multiphase model of Rosenberg et al. (1990) but closer examination of the relationship between particle chemistry and particle thickness actually shows that a simple Ostwald ripening model is inappropriate to describe particle thickening. Similarly, the conventional notion of metastability for Ostwald-type processes (Morse & Casey, 1988) may also be an inaccurate description of the relationship between sub-microscopic illitic clays and macroscopic micas.

RELATIONSHIPS BETWEEN PARTICLE CHEMISTRY AND PARTICLE THICKNESS

Instead of comparing data from two independent sources as did Rosenberg et al. (1985b) and Inoue et al. (1988), a more consistent analysis of the relationships between particle chemistry and particle thickness can be achieved by combining the chemical composition of the same mineral size-fractions obtained by Nadeau & Bain (1986) with the particle thickness data measured by Nadeau (1985). If the convention adopted by Nadeau & Bain (1986) is followed, an ideal 2:1 mica structure can be considered to contain \((n-1)\) layers of non-exchangeable cations sandwiched between \(n\) 2:1 aluminosilicate layers. As the repeat spacing of each aluminosilicate layer is 10 Å (1 nm) thick, measurements of mean particle thickness \(T_m\) (in nm) by transmission electron microscopy (TEM) enables the ratio of the number of non-exchangeable cation interlayers to the number of aluminosilicate layers to be calculated for each sample (i.e. \((T_m - 1)/T_m\)). By analogy to calculated structural formula for micas, this ratio should be equal to the number of fixed interlayer cations calculated on a half unit-cell basis (designated here \(M^+\)) divided by the magnitude of the net negative charge as a result of isomorphous substitution in the 2:1 aluminosilicate layers \((L^-)\). In an ideal mica therefore, the ratio \(M^+/L^-\) should be equal to 1. As an ideal mica is also infinitely thick, the ratio \((T_m - 1)/T_m\) would similarly be equal to 1.

The same is not so for thinner illitic particles. Structural formulae recalculated from chemical compositional data that also take into account exchangeable cations show that the ratio \(M^+/L^-\) is never equal to 1. In fact the data of Nadeau & Bain (1986) show that values of \(M^+/L^-\) for ordered mixed-layer I-S are often significantly <1. Calculation of \((T_m - 1)/T_m\) for particle thickness measurements on the same samples (Table 1) also shows this ratio to be significantly <1. If the ratios are plotted against each other they appear to co-vary in a linear fashion (Fig. 1a). This is not surprising as similar relationships have already been established between thickness and % expandable “smectite” layers determined by X-ray diffraction (XRD) (Nadeau et al., 1985b) and % expandable layers determined by both XRD and from particle thickness measurements and fixed interlayer cations (Srodolf et al., 1986; 1992). Further, in addition to an increase in the ratio \(M^+/L^-\) with \((T_m - 1)/T_m\) there is also a

Table 1. Particle thickness, layer charge and fixed interlayer cation contents for illite-smectites studied by Nadeau & Bain (1986)

<table>
<thead>
<tr>
<th>Illite-smectite</th>
<th>Thickness (T_m) (nm)</th>
<th>((T_m - 1)/T_m)</th>
<th>Layer charge ((L^-))</th>
<th>Fixed interlayer cations ((M^+))</th>
<th>(M^+/L^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMS</td>
<td>2.93</td>
<td>0.650</td>
<td>0.57</td>
<td>0.35</td>
<td>0.614</td>
</tr>
<tr>
<td>C1B</td>
<td>2.51</td>
<td>0.600</td>
<td>0.59</td>
<td>0.37</td>
<td>0.627</td>
</tr>
<tr>
<td>ORB</td>
<td>2.95</td>
<td>0.600</td>
<td>0.69</td>
<td>0.51</td>
<td>0.739</td>
</tr>
<tr>
<td>DIB</td>
<td>3.82</td>
<td>0.738</td>
<td>0.70</td>
<td>0.53</td>
<td>0.757</td>
</tr>
<tr>
<td>LBP</td>
<td>3.52</td>
<td>0.716</td>
<td>0.70</td>
<td>0.51</td>
<td>0.729</td>
</tr>
<tr>
<td>SFB</td>
<td>2.57</td>
<td>0.611</td>
<td>0.74</td>
<td>0.54</td>
<td>0.730</td>
</tr>
<tr>
<td>RAN</td>
<td>3.70</td>
<td>0.730</td>
<td>0.71</td>
<td>0.57</td>
<td>0.803</td>
</tr>
<tr>
<td>TGB</td>
<td>4.94</td>
<td>0.789</td>
<td>0.87</td>
<td>0.70</td>
<td>0.805</td>
</tr>
<tr>
<td>ROT</td>
<td>9.22</td>
<td>0.892</td>
<td>0.88</td>
<td>0.78</td>
<td>0.886</td>
</tr>
</tbody>
</table>
corresponding linear increase in the magnitude of layer charge itself (Fig. 1b). This constrains the possible chemical relationships in a very specific manner. Not only does fixed interlayer cation content increase as particles get thicker but layer charge itself increases as particles get thicker.

This has important ramifications concerning Ostwald ripening. Clearly the observed trends in Fig. 1 cannot be accomplished by simply adding on extra 2:1 aluminosilicate layers with a constant layer charge \( L^- \) as would be the case if a simple ripening process were invoked. All this would allow is an increase in the fixed interlayer cation content in the structural formula at the expense of the exchangeable cation content. The net result therefore would be to change the ratio of fixed interlayer cations to exchangeable cations at a constant layer charge as the particles get thicker. Although the ratio \( M^+/L^- \) may change as particle thickness increases (and \( T_m = 1/T_m \) tends to one), the magnitude of \( L^- \) will not change under these circumstances.

The multiphase model for illite particles proposed by Rosenberg et al. (1990) suggests that particles of a given thickness, specific layer charge, interlayer and exchangeable cation content (Fig. 2) have a discrete thermodynamic entity. It is implicit that each of these thermodynamic entities must nucleate as well as grow at each successive stage in the evolution of illite towards a mica-type composition. Successive nucleation of each discrete illitic phase fundamentally contradicts one of the basic tenets of Ostwald ripening; that following initial nucleation, no further nucleation of grains occurs during ripening (Morse & Casey, 1988). Other factors in the multiphase model further militate against simple Ostwald ripening as a process to produce thicker particles. As the chemistry of successively thicker particles is different, equilibrium thermodynamics demands that the compositions of solutions in equilibrium with particles of different thickness and chemistry must also be different (e.g. the activity ratio \( a_{K+}/a_{H^+} \), see Fig. 3). By changing components in the system like this, another two conditions governing Ostwald ripening are broken (Morse & Casey, 1988); these being that the system does not remain closed and mass is not conserved between solvent and growing crystals. An alternative view of the layer charge distribution in I–S (Fig. 2) is given by Šrodón et al. (1992). They proposed that the external ‘smectitic’ surfaces of the particles have a lower layer charge (~0.4/O\(_{10}(OH)_2\)) than in the internal ‘illitic’ portions of the particles (fixed at 0.89/O\(_{10}(OH)_2\)). The average layer charge for any thin illite particles (equivalent to \( L^- \) in Fig. 1) then varies according to thickness in a similar manner to that described above.

Although Šrodón et al. (1992) have not addressed the aspect of I–S stability in the same thermodynamic terms as Rosenberg et al. (1990), their analysis seems to be fully consistent with all the available chemical and physical data and is just as compatible with the original concepts of fundamental particle theory proposed by Nadeau.
et al. (1985a) as the multiphase model of Rosenberg et al. (1990). Unfortunately, it is still difficult to reconcile the model of Srodon et al. (1992) for mixed-layer I-S with proposals for Ostwald ripening as a mechanism for the growth of the I-S during diagenesis. For simple Ostwald ripening to occur, layer charge on the external surfaces of illite particles would have to increase by more than a factor of two as a new layer is accreted with the new layer also accommodating a strongly asymmetrical charge distribution (the equivalent of 0.4/\text{O}_{10}(\text{OH})_2 on the outer surface of the layer and 0.89/\text{O}_{10}(\text{OH})_2 on the internal surface of the layer). Achieving and maintaining such extremes in the chemical environment close to the surface of such thin particles seems to be both energetically unfavourable and too complex a mechanism to be explained by simple Ostwald ripening.

IMPLICATIONS FOR ILLITE STABILITY

Although reasonable grounds for rejecting Ostwald ripening as a mechanism to produce thicker illite particles can be demonstrated, the multiphase model of Rosenberg et al. (1990) also requires that consideration should also be given to the view that increasing particle thickness represents a progressive move toward increased thermodynamic stability and is an example of Ostwald’s step rule. As the chemical composition of each discrete phase is non-stoichiometric with respect to the standard mica formula, efforts have been made to model such compositions as solid-solutions (Stoessell, 1979; 1981; Tardy & Fritz, 1981; Aagaard & Helgeson, 1983). In the simplified K_2O-Al_2O_3-SiO_2-H_2O system investigated by Rosenberg et al. (1990), each discrete phase can be defined in terms of the apparent solid-solution between muscovite and pyrophyllite. From recent experimental work on neoformed clay minerals, Primmer et al. (1993) have determined the equilibrium solubility products for both muscovite and pyrophyllite end-members using the ideal solid-solution of Tardy & Fritz (1981). They have shown that the experimentally determined values of log K at 150°C and 200°C for the muscovite end-member are the equivalent of 5–6 kcal mol\(^{-1}\) less stable in free energy terms than the values given for muscovite by the internally consistent SUPCRT data of Helgeson et al. (1978) extrapolated to the same temperature. Values for pyrophyllite on the other hand are identical within experimental error. In accordance with Ostwald’s step rule, therefore, it seems that progression towards an ideal mica composition through a series of sequential reactions producing higher energy, metastable illitic phases is correct.

The extent of apparent solid-solution, however, is defined by crystal thickness. This concept

![Fig. 2. An interpretation of two models for the chemical constitution of thin illite particles with a thickness of 4 nm (which correspond to R3 ordered I-S) where M+/L-, L-, (T_m - 1)/T_m are all approximately equal to 0.75](image-url)
is unprecedented in classical equilibrium thermodynamics where no limits are placed on the physical dimensions of the phases concerned. It should also be noted that the thermodynamic data for muscovite given by Helgeson et al. (1978) are for the 2M₁ polytype, whereas all available data suggest that illites are 1M₅ or 1M₆ mica polytypes (Bailey, 1980). Baxter Grubb et al. (1991) have already suggested that polytype transitions in illite are expressions of Ostwald's step rule. However, it is important to account for both the combined energy difference between different polytypes, estimated to be in the order of 2 kcal mol⁻¹, between the disordered 1M₅ and the more stable 2M₁ polytype (Aagaard & Helgeson, 1983), and the energy contribution of very thin particles represented by an indeterminant surface energy term. These two factors combine to exclude thin illites from being representative of a thermodynamic continuum from low-temperature metastable discrete illitic phases to macroscopic dioctahedral muscovite.

The multiphase model of Rosenberg et al. (1990) demonstrates the utility of regarding interstratified I-S in terms of a family of discrete illitic phases of constrained composition and structure. It provides an entirely self-consistent analysis of their mineralogical and petrological behaviour. Closer investigation of the chemical compositional data and particle thickness measurements, however, show that Ostwald ripening as a process to produce thicker particles cannot be supported. In addition, careful appraisal of the available data shows that the difference in energy between polytypes as well as changes in surface energy combine to form a more complex expression of Ostwald's step rule than that considered by Rosenberg et al. (1990).

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**REFERENCES**


Jahren J.S. (1991) Evidence of Ostwald Ripening related...


