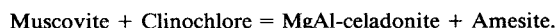


## DIAGENETIC ILLITE-CHLORITE ASSEMBLAGES IN ARENITES. II. THERMODYNAMIC RELATIONS

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**Abstract**—The internal equilibrium status among chlorite-illite pairs has been evaluated through coupled substitution reactions. Compositional data of chlorites and illites from arenites at present burial temperatures between 90° and 180°C have been used to calculate end member activities and reaction quotients of the combined Tschermak reaction:



The reaction quotient data in the 90° to 180°C temperature range have then been compared with the equilibrium curve for the same reaction, and found to be in reasonable agreement. This indicates that chlorites and illites in these arenites grow at near equilibrium conditions.

The data set has also been compared with chlorite-illite pairs from hydrothermally altered arenites of the Salton Sea area. For chlorite-illite containing assemblages, these data agree well with the diagenetic ones. The introduction of biotite at higher temperatures alters with the iron-magnesium distribution and breaks down the substitution relationship between chlorite and illite.

The model predicts an increasing stability of muscovite and clinochlore components with increasing temperature, while celadonite and amesite would be stabilized with increasing pressure. This is consistent with high pressure occurrences of phengite. However, at the low pressure region of diagenesis and hydrothermal alteration, the temperature effect is dominant.

**Key Words**—Arenites, Diagenesis, Illite/Chlorite, Tschermak reaction.

### INTRODUCTION

The chlorite-illite assemblage is a characteristic pair in the upper diagenetic and lower metamorphic regimes. A number of recent studies have attempted to establish the compositional variations found in these minerals as a function of pressure and temperature (McDowell and Elders, 1980; Curtis *et al.*, 1985; Cathelineau and Neiva, 1985; Bishop and Bird, 1987; Cathelineau and Izquierdo, 1988; Cathelineau, 1988; Velde and Medhioub, 1988; Jahren and Aagaard, 1989; Jahren, 1991; Hillier and Velde, 1991). This large accumulation of compositional data offers a new base from which to examine chlorite-illite equilibrium relations in this temperature-pressure range. In the first part of this study (Jahren and Aagaard, 1992), we reported chemical compositions of coexisting chlorite-illite from 16 sandstone petroleum reservoirs from the Norwegian shelf. The purpose of the present contribution is to evaluate the equilibrium status for chlorite-illite pairs on the basis of this data set and corresponding ones from hydrothermally altered arenites. This thermodynamic analysis is carried out by coupled end member substitution reactions between chlorite and illite.

In complementary studies of the same arenites (Egeberg and Aagaard, 1992; Aagaard *et al.*, 1992), we have explored the stability of late diagenetic minerals relative to formation water chemistry and found that the waters were generally saturated with respect to these phases. The minerals appear to have grown under close

to equilibrium conditions. The chemical composition of the authigenic phases thus records the geochemical environment at the time of formation. By applying appropriate solid solution models for the minerals in question, the aqueous phase composition can be calculated. Chlorite is, therefore, a key phase for estimating the activity of ferrous/ferric iron as well as magnesium ions (Stoessel, 1984; Walshe, 1986; Jahren and Aagaard, 1989). Walshe (1986) has specifically demonstrated how the oxygen fugacity can be calculated from the chemical composition of hydrothermal chlorites. The approach employed in this paper is quite different, as an evaluation of internal equilibrium in chlorite-illite pairs requires no information about the pore water chemistry, and offers an independent test of equilibrium formation.

### COMPOSITIONAL VARIATIONS

The compositional temperature trends found in diagenetic chlorite and illite pairs from arenites offshore Norway are described in detail in Jahren and Aagaard (Part I, this issue), but will also be briefly summarized here. They are all based on the assumption that present day burial temperatures are equal to the conditions of formation. Supportive evidence for this is found in the dynamic dissolution/reprecipitation behavior of these minerals in clastic arenites offshore Norway (Jahren, 1991).

The chemical composition of coexisting late diage-

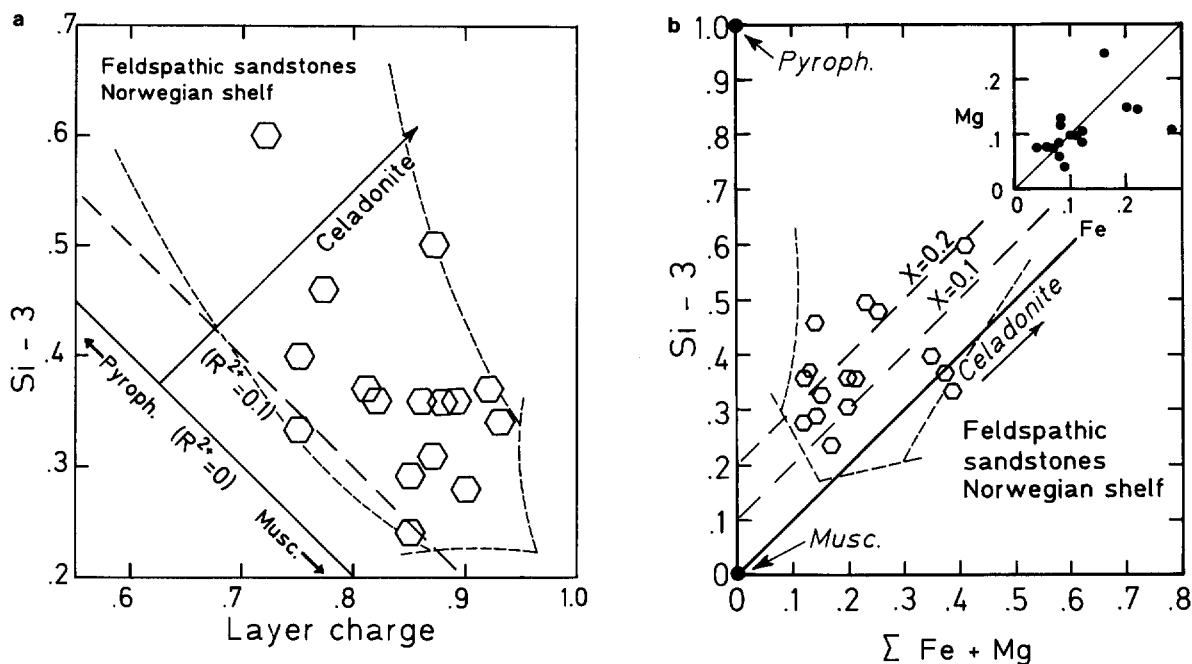


Figure 1. Compositional trends in authigenic illites from deeply buried arenites offshore Norway. Large arrow indicates average trends with increasing temperatures. (a) The ordinate displays tetrahedral silica in excess of that in muscovite, while the abscissa depicts layer charge in the 2:1 backbone layer. (b) Tetrahedral silica in excess of that in muscovite vs total iron and magnesium content. Magnesium vs iron shown in insert.

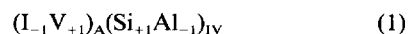
netic chlorites and illites in arenites of 2400 to 5000 m burial depth is reported in Part I (Table 2, Jahren and Aagaard, this issue), where also the analytical methods and uncertainties are discussed. All iron was taken to be ferrous, as no separate  $\text{Fe}^{2+}/\text{Fe}^{3+}$  determinations were carried out. This assumption is not critical for our solid solution model and thermodynamic calculations, but may be justified, as Curtis *et al.* (1985) found only minor amounts of ferric iron in diagenetic chlorite.

#### Illites

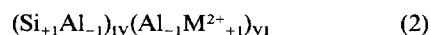
In an earlier study on diagenetic illites and chlorites in clastic petroleum reservoirs offshore Norway (Jahren and Aagaard, 1989), we were not able to delineate any compositional temperature dependence of illite. However, the present study by Jahren and Aagaard (Part I, this issue) has clearly demonstrated that temperature-compositional trends exist.

Most distinctly, the potassium content increases regularly with increasing temperatures. This can be partly accounted for by an increase in the thickness of illite particles, but it is also followed by a corresponding increase in tetrahedral aluminum (Jahren and Aagaard, Part I, this issue: Figure 6c), reflecting an increase in the muscovite component. The celadonite substitution exhibits a somewhat more irregular pattern, but there is a general trend of decreasing celadonite component with increasing temperature. These compositional

variations are depicted in Figures 1a and 1b. It thus appears that the chemical behavior of diagenetic illites in arenites can be described by two main substitution vectors from the muscovite reference:



and



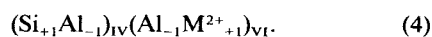
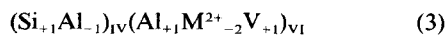
where I, V, and  $\text{M}^{2+}$  represent interlayer cation (mainly  $\text{K}^+$ ), vacancy, and divalent cation, respectively, while subscripts A, IV and VI denote interlayer, tetrahedral and octahedral sites.

The first vector corresponds to the muscovite-pyrophyllite substitution, while the second is the Tschermak substitution between muscovite and celadonite. Both substitutions lead toward the muscovite composition with increasing temperatures, and closely parallel trends of hydrothermal systems seen elsewhere (McDowell and Elders, 1980; Bishop and Bird, 1987; Cathelineau and Izquierdo, 1988; Cathelineau, 1988).

#### Chlorite

The compositional data (Jahren and Aagaard, 1992) do show some scatter, but there is a definite temperature dependence of both the octahedral vacancy as well as tetrahedral aluminum. This is illustrated in the classification diagram of Wiewiora and Weiss (1990) shown in Figure 2. The main feature is that the octa-

hedral vacancy decreases with temperature, moving towards the amesite/chamosite-serpentine join. This substitution is, however, accompanied by a tetrahedral aluminum increase. This chemical temperature trend can be described by two substitution vectors from the amesite/chamosite reference:



The main substitution vector corresponds to the amesite/chamosite-sudoite substitution, while the second is the Tschermak substitution between amesite and clinochlore (or the iron analogues: chamosite and daphnite). This temperature-compositional behavior is the same as the one favored by Cathelineau (1988) for hydrothermal systems.

The iron magnesium substitution is not described by the classification scheme shown in Figure 2. There is, however, a marked tendency toward increase in iron content of these chlorites with increasing temperatures (Jahren and Aagaard, 1992). This was also noted by Cathelineau (1988). Consequently, an additional substitution vector is necessary to treat the solid solution of diagenetic chlorites, going out from the amesite reference:



In summary, five substitution vectors can be employed to describe the compositional variations among diagenetic chlorite-illite pairs in arenites. In illite, the muscovite-pyrophyllite and Tschermak substitution, and in chlorite, the amesite-sudoite, amesite-chamosite and Tschermak substitution.

#### SOLID SOLUTION MODELS, REACTION QUOTIENTS, AND EQUILIBRIUM CALCULATIONS

Do the compositional temperature trends found in chlorite-illite pairs reflect a mineral formation/crystallization at or close to equilibrium, and how can we test this hypothesis? We have previously argued (Jahren and Aagaard, 1989), by comparing ion activity ratios in formation water with corresponding equilibrium constants, that these minerals grow from saturated to only slightly supersaturated solutions.

The internal equilibrium between chlorite and illite can also be expressed through combined end member substitutions. Because thermodynamic data are missing for many end members, we have focused on substitutions where data are available or can be estimated with some confidence. The most suitable substitution appears to be the Tschermak reaction:



which has been shown to take place in both illite and

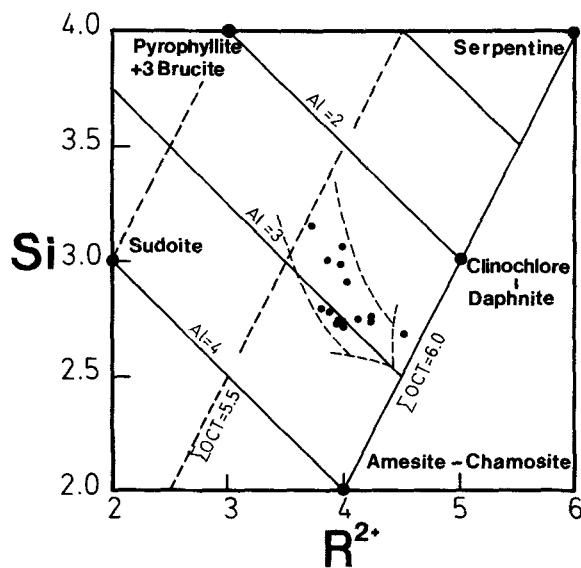
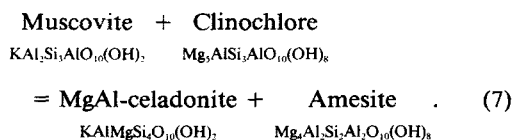


Figure 2. Composition of authigenic chlorites from deeply buried arenites offshore Norway plotted in the classification diagram of Wiewiura and Weiss (1990). Si denotes tetrahedral silica, while  $R^{2+}$  stands for divalent octahedral cations. The compositional temperature trend, indicated by the large arrow, is described by the two substitution vectors from the amesite/chamosite corner (see text).

chlorite (substitution vectors 2 and 4), and can be expressed through the end member reaction:



The corresponding equilibrium expression is then given by:

$$K = \frac{a_{\text{illite}}^{\text{KAlMgSi}_4\text{O}_{10}(\text{OH})_2} a_{\text{chlorite}}^{\text{Mg}_6\text{Al}_2\text{Si}_2\text{Al}_2\text{O}_{10}(\text{OH})_8}}{a_{\text{illite}}^{\text{KAl}_2\text{Si}_4\text{AlO}_{10}(\text{OH})_2} a_{\text{chlorite}}^{\text{Mg}_3\text{AlSi}_3\text{AlO}_{10}(\text{OH})_8}} \quad (8)$$

The equilibrium constant,  $K$ , for the specified  $P, T$  condition, is calculated directly from thermodynamic data. The right hand side of Eq. (8) denoted the reaction quotient,  $Q$ , can also be calculated, given chemical analyses and appropriate activity-composition relations of illites and chlorite. This offers a test of equilibrium, where the reaction quotient of Eq. (8), calculated from the activity of end member components in analyzed illite-chlorite pairs, is compared with the corresponding equilibrium constant. If they agree within the uncertainties of the thermodynamic data and solution model, it can be concluded that the observed chlorites and illites formed close to equilibrium.

#### End member activities and reaction quotient

Several solid solution models have been put forward for the clay minerals, from the simple ideal mixing on

Table 1. Activity of end member components and reaction quotient, *Q*, of Eq. (7), calculated from Eqs. (9a–d) and (10) (see text). Sources of compositional data: McDowell and Elders (1980), Jahren and Aagaard (this issue).

| Depth (m) | T (°C) | a (muscovite) | a (celadonite) | a (clinochlore) | a (amesite) | log <i>Q</i> |
|-----------|--------|---------------|----------------|-----------------|-------------|--------------|
| 2393      | 90     | 0.319         | 0.189          | 0.005817        | 0.01056     | 0.03         |
| 2852      | 110    | 0.601         | 0.054          | 0.000640        | 0.00158     | -0.65        |
| 3077      | 120    | 0.479         | 0.100          | 0.000334        | 0.00153     | -0.02        |
| 3463      | 130    | 0.688         | 0.043          | 0.001568        | 0.00410     | -0.78        |
| 3803      | 140    | 0.534         | 0.063          | 0.000324        | 0.00154     | -0.25        |
| 3838      | 142    | 0.604         | 0.089          | 0.000147        | 0.00080     | -0.10        |
| 4182      | 150    | 0.627         | 0.101          | 0.009547        | 0.01940     | -0.48        |
| 4258      | 150    | 0.619         | 0.030          | 0.000052        | 0.00025     | -0.63        |
| 4357      | 155    | 0.634         | 0.079          | 0.000064        | 0.00042     | -0.09        |
| 4370      | 155    | 0.748         | 0.061          | 0.000391        | 0.00103     | -0.67        |
| 4464      | 160    | 0.613         | 0.069          | 0.000098        | 0.00057     | -0.18        |
| 4470      | 160    | 0.660         | 0.074          | 0.000289        | 0.00121     | -0.33        |
| 4504      | 162    | 0.505         | 0.096          | 0.000356        | 0.00149     | -0.10        |
| 4505      | 162    | 0.559         | 0.115          | 0.000179        | 0.00094     | 0.03         |
| 4900      | 175    | 0.568         | 0.082          | 0.000011        | 0.00010     | 0.13         |
| 4967      | 180    | 0.712         | 0.062          | 0.000004        | 0.00004     | -0.08        |
| 439       | 190    |               |                | 0.000662        | 0.00210     |              |
| 439       | 190    | 0.224         | 0.173          | 0.005405        | 0.00732     | 0.02         |
| 622       | 251    | 0.396         | 0.176          | 0.042967        | 0.03786     | -0.41        |
| 675       | 264    | 0.466         | 0.121          | 0.021023        | 0.02336     | -0.54        |
| 759       | 280    |               |                | 0.010367        | 0.01442     |              |
| 844.5     | 295    | 0.670         | 0.046          | 0.033844        | 0.03437     | -1.16        |
| 923.5     | 306    | 0.712         | 0.047          |                 |             |              |
| 990.5     | 315    | 0.696         | 0.024          | 0.017291        | 0.02230     | -1.36        |
| 1064      | 322    | 0.672         | 0.027          | 0.051085        | 0.04759     | -1.43        |

homological sites (Tardy and Fritz, 1981; Aagaard and Helgeson, 1983; Helgeson and Aagaard, 1985; Walshe, 1986) to more “non ideal” models (Stoessel, 1979, 1981, 1984). The actual solid solution behavior of illites and chlorites is far from known in any detail, and by realizing the uncertainties in the thermodynamic data of several of the end member components, as well, we feel that any advanced solution model is not warranted at our present stage of knowledge.

The assumption of ideal mixing of atoms on homological sites offers a simple way to express the component activities ( $a_i$ ) based only on the knowledge of the site occupancy given by the structural formula (Helgeson and Aagaard, 1985):

$$a_i = k_i \prod_j \prod_s (x_{j,s})^{\nu_{j,s,i}} \quad (9)$$

where  $x_{j,s}$  is the mole fraction of the  $j$ th atom on site  $s$ ;  $\nu_{j,s,i}$  is the number of the  $j$ th atom on site  $s$  in the  $i$ th component; and  $k_i$  is a standard state constant determined by the stoichiometry of the  $i$ th component (see Helgeson and Aagaard, 1985).

For the end member components of concern in reaction (7): muscovite, celadonite, clinochlore, and amesite, Eq. (9) is expressed as:

$$a_{\text{musc}}^{\text{illite}} = 9.4815 \cdot X_{\text{K,A}} \cdot (X_{\text{Al,O}})^2 \cdot X_{\text{Al,T}} \cdot (X_{\text{Si,T}})^3 \quad (9a)$$

$$a_{\text{cela}}^{\text{illite}} = 4 \cdot X_{\text{K,A}} \cdot X_{\text{Mg,O}} \cdot X_{\text{Al,O}} \cdot (X_{\text{Si,T}})^4 \quad (9b)$$

$$a_{\text{clino}}^{\text{chlorite}} = 141.6 \cdot (X_{\text{Mg,O}})^5 \cdot X_{\text{Al,O}} \cdot X_{\text{Al,T}} \cdot (X_{\text{Si,T}})^3 \quad (9c)$$

$$a_{\text{ames}}^{\text{chlorite}} = 729 \cdot (X_{\text{Mg,O}})^4 \cdot (X_{\text{Al,O}})^2 \cdot (X_{\text{Al,T}})^2 \cdot (X_{\text{Si,T}})^2 \quad (9d)$$

where A, O, T denote the interlayer, octahedral, and tetrahedral sites, respectively. An implicit assumption is that there is no tetrahedral ordering, the illite is purely dioctahedral, the two octahedral units in chlorite are equivalent, and there is no ordering on octahedral sites.

End member activities were calculated from chemical composition of chlorite-illite pairs reported by Jahren and Aagaard (this issue) and McDowell and Elders (1980). The results are both given in Table 1 and depicted in Figure 3. The calculated activities exhibit a temperature dependence, but the two data sets define separate trends. The activity of the chlorite components do show opposing temperature dependence, caused mainly by the decreasing octahedral Mg occupancy with increasing temperature.

Knowing the end member activities, the reaction quotient,  $Q$ , for reaction (7) can now be calculated from the right hand side of Eq. (8), or from a more direct expression by combining Eqs. (8) and (9a–d) to:

$$Q = \left( \prod_i n_i k_i \right) \cdot \left( \frac{(X_{\text{Mg,O}} X_{\text{Si,T}})}{(X_{\text{Al,O}} X_{\text{Al,T}})} \right)_{\text{illite}} \cdot \left( \frac{(X_{\text{Al,O}} X_{\text{Al,T}})}{X_{\text{Mg,O}} X_{\text{Si,T}}} \right)_{\text{chlorite}} \quad (10)$$

where  $n_i$  denotes the stoichiometric coefficient of component  $i$  in reaction (7).

The calculated reaction quotients for the illite-chlorite pairs are given in Table 1 and plotted in Figure 4. It should be noted that, despite the separate and discontinuous variation observed in the component activity, the reaction quotients exhibit a uniform and continuous trend.

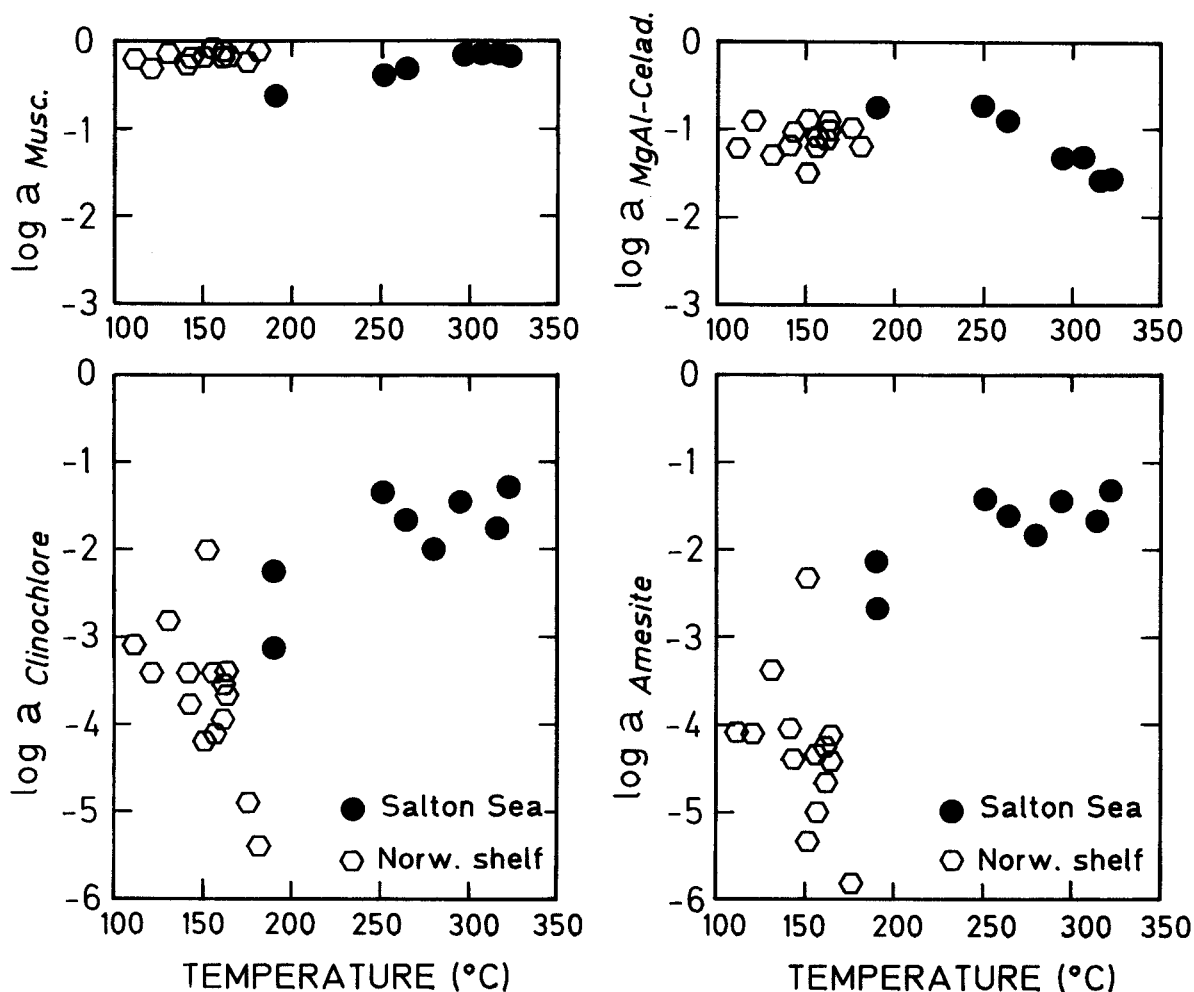


Figure 3. Activities of end members of chlorite and illite calculated by assuming ideal mixing on homological sites. Source of chemical data: Jahren and Aagaard (this issue) and McDowell and Elders (1980).

#### Equilibrium calculations

The thermodynamic data of Helgeson *et al.* (1978), with its latest update given by Johnson *et al.* (1992), was used as a basis for the calculations. The enthalpy and Gibbs free energy for 14-Å amesite and MgAl-celadonite are not given in Helgeson's data base, and some of the molar volumes also had to be revised in accordance with recent unit cell determinations. Before going into the equilibrium calculations, we will briefly discuss our selection of thermodynamic data, which is summarized in Table 2.

**Muscovite and MgAl-celadonite.** All the thermodynamic properties of the muscovite component are taken to be those of the SUPCRT data base. These data relate to the 2M<sub>1</sub> polytype, while the illites studied in this paper are of the 1M polytype. We expect the 1M to be less stable than the 2M<sub>1</sub> polytype, but, given the uncertainties in the thermodynamic data of the celadonite

end member (see below), we consider these data acceptable. The molar volume of MgAl-celadonite listed in the SUPCRT data file appears to be far too large, which will also lead to an unreasonably large third law entropy estimate. We have calculated the molar volume of MgAl-celadonite to be 141.0 cm<sup>3</sup>, based on cell dimension algorithms given by Weiss (Research Coal Institute, Ostrava-Radvanice, Czechoslovakia, personal communication). We used the structural algorithm approach (Helgeson *et al.*, 1978) for the corresponding entropy, building MgAl-celadonite from muscovite, and found a third law entropy of 71.0 e.u. The heat capacity coefficients were estimated by the same structural algorithm approach. These values are expected to be quite reliable, but the reference enthalpy of MgAl-celadonite is harder to determine. We have followed the estimation procedures of Helgeson *et al.* (1978), where the enthalpy of the Tschermak substitution reaction in various mineral groups is assumed



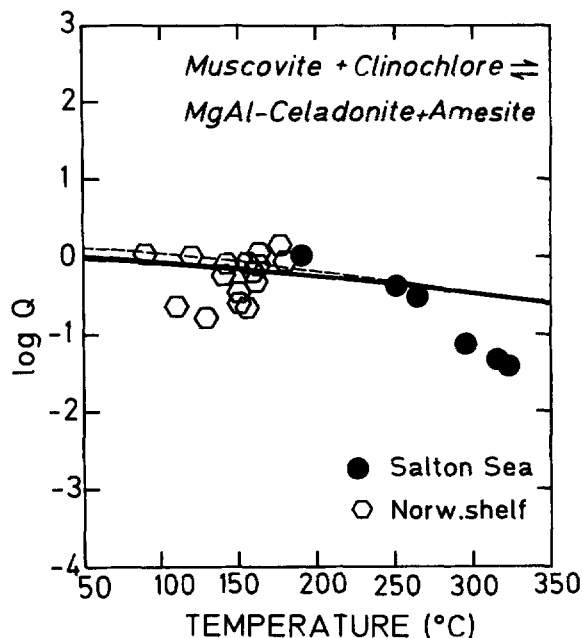


Figure 4. Coupled Tschermak substitution in chlorite-illite pairs from arenites (Jahren and Aagaard, this issue) and hydrothermally-altered feldspathic sandstones from the Salton Sea area (McDowell and Elders, 1980). The symbols correspond to calculated reaction quotients of reaction (7) while the heavy line denotes the equilibrium constant for the same reaction along an average North Sea gradient. The isobars corresponding to 500 and 5000 bars, respectively, were also calculated and are plotted in the figure. The thin dashed line represents the 5000 isobar, while the 500 isobar coincides with the equilibrium line for the North Sea gradient.

the number of moles of oxygen in the structural formula.

*Clinocllore and amesite.* Jenkins and Chernosky (1986) reported the molar volume of clinocllore and amesite to be 211.0 and 209.3 cm<sup>3</sup>/mol, respectively (recent determinations by Roots (1991) give 210.9 and 209.2), while the SUPCRT data base gives 207.11 and 205.4. The volume difference remains the same and the relative change in third law entropies are also minor. However, we have accepted the new volume data, and

estimated a corresponding third law entropy. The SUPCRT reference free enthalpy value of clinocllore has been kept, and the reference Gibbs free energy has only changed by 340 cal. For amesite, the estimated reference enthalpy is based on the Tschermak substitution from clinocllore, and the resulting reference Gibbs free energy is close to the value reported by Stoessel (1984; data set no. 4).

The equilibrium constant for reaction (7) has been calculated for pressure/temperature conditions along an average North Sea gradient (Smith and Ehrenberg, 1989). The pressure dependence is rather small, so the same calculations can also be applied for the Salton Sea P,T conditions. Figure 4 offers a comparison between the reaction quotients and the equilibrium curve of Eq. (7). The agreement is reasonably good, despite some scatter in the reaction quotient data. It should be kept in mind, however, that an uncertainty of only 600 cal in  $\Delta G^\circ$  will account for most of the reaction quotient data. The high temperature data from the Salton Sea hydrothermal system are notable exceptions. The low reaction quotient values are caused by the very low Mg content in the illites above 290°C (McDowell and Elders, 1980), which leads to the low activity of MgAl-celadonite (compare Figure 3). The reason for the low Mg-content in these illites may be the appearance of other ferro-magnesium phases, especially a Mg-rich biotite (McDowell and Elders, 1980). There are also textural differences between the Salton Sea low and high temperature illites. The low temperature illites occurred as fine-grained aggregates in a matrix, while the high T illites were coarse-grained and recrystallized from detrital white mica (McDowell and Elders, 1980).

The combined Tschermak reaction between muscovite and chlorite [Eq. (7)] has also been of special interest in metamorphic petrology, as it relates to the high pressure occurrences of phengitic mica. Fawcett and Yoder (1966), Kotov (1974), and Guidotti (1984) have all considered the chlorite-muscovite equilibrium to account for the high celadonite content in white mica at low T/high P. The thermodynamic data applied here give a negative volume of reaction, as is required to explain the stabilization of the celadonite and amesite

Table 2. Summary of thermodynamic data used to calculate the equilibrium constant of the coupled Tschermak reaction (7).  $\Delta G^\circ_f$  and  $\Delta H^\circ_f$  represent standard molal Gibbs free energy and enthalpy of formation at 25°C and 1 bar, and  $S^\circ$  and  $V^\circ$  standard molal entropy and volume also at reference conditions. The standard molal heat capacity coefficients in the Maier-Kelley power functions are a, b, and c. Reaction properties calculated according to Eq. (7).

| End member          | $\Delta G^\circ_f$ | $\Delta H^\circ_f$ | $S^\circ$ | $V^\circ$ | a     | b     | c      |
|---------------------|--------------------|--------------------|-----------|-----------|-------|-------|--------|
| Muscovite           | -1,336,301         | -1,427,408         | 68.8      | 140.71    | 97.56 | 26.38 | -25.44 |
| MgAl-celad          | -1,322,336         | -1,412,449         | 71        | 141       | 91.5  | 33.5  | -21.24 |
| Clinocllore         | -1,962,045         | -2,116,964         | 112.3     | 210.9     | 166.5 | 42.1  | -37.47 |
| Amesite             | -1,976,002         | -2,132,000         | 109.9     | 209.2     | 169.4 | 41.24 | -44.37 |
| Reaction properties | 8                  | -77                | -0.2      | -1.41     | -3.16 | 6.26  | -2.7   |

components with high pressure as well as the opposing favoring of muscovite and clinocllore with increasing temperature.

### CONCLUSIONS

Despite the fact that the Tschermak substitution is not the main temperature dependent substitution in diagenetic chlorites and illites, it is a substitution vector in both minerals which can be coupled in one solid-solid reaction. It is thus well-suited to express internal equilibrium in chlorite-illite pairs, and it requires no information about the pore water chemistry.

Our analyses, based on chemical compositions of coexisting chlorites and illites and thermodynamic calculations, show that these minerals presently are in or close to equilibrium with each other. This study further supports the hypothesis that chlorites and illites adjust their chemical composition during burial diagenesis, through a dynamic grain coarsening mechanism, and that they grow from saturated or slightly supersaturated pore waters.

The model predicts an increasing stability of muscovite and clinocllore components with increasing temperature, while celadonite and amesite would be stabilized with increasing pressure. This is consistent with high pressure occurrences of phengite. However, at the low pressure region of diagenesis and hydrothermal alteration, the temperature effect is dominant.

### ACKNOWLEDGMENTS

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