

# Reaction pathways and reaction progress for the smectite-to-chlorite transformation: evidence from hydrothermally altered metabasites

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**ABSTRACT** The transformation from smectite to chlorite has been interpreted as involving either a disequilibrium chlorite/smectite mixed-layering sequence, or an equilibrated discontinuous sequence involving smectite–corrensite–chlorite. Here, analysis of the smectite to chlorite transition in different geothermal systems leads us to propose that the transformation proceeds via three contrasting reaction pathways involving (i) a continuous mixed-layer chlorite/smectite series; (ii) a discontinuous smectite–corrensite–chlorite series and (iii) a direct smectite to chlorite transition. Such contrasting pathways are not in accord with an equilibrium mineral reaction series, suggesting that these pathways record kinetically controlled reaction progress. In the geothermal systems reviewed the style of reaction pathway and degree of reaction progress is closely correlated with intensity of recrystallization, and not to differences in thermal gradients or clay grain size. This suggests a kinetic effect linked to variation in fluid/rock ratios and/or a contrast between advective or diffusive fluid transport. The mode of fluid transport provides a means by which the rates of dissolution/nucleation/growth can control the reaction style and the reaction progress of the smectite to chlorite transition. Slow rates of growth are linked to the first reaction pathway involving mixed-layering, while increasing rates of growth, relative to nucleation, promote the generation of more ordered structures and ultimately lead to the direct smectite to chlorite transition, representative of the third pathway.

**Key words:** chlorite, chlorite/smectite, mixed-layer, reaction progress, smectite.

## INTRODUCTION

The conversion of trioctahedral smectite into chlorite is a widespread feature of very low-grade metamorphism and it is a ubiquitous feature of meta-igneous rocks of basic and intermediate composition. As a common feature of hydrothermal metamorphism of the ocean crust this transition represents one of the most widespread of any mineralogical transformation in the Earth's crust (Schiffman, 1995; Alt, 1999). However, there are many points about the mineralogical character of the phases involved, and of the conversion process that are the subject of active debate. Some have regarded the reaction style of the smectite to chlorite transition as involving a continuous sequence of chlorite/smectite mixed-layering (Liou *et al.*, 1985; Bettison-Varga *et al.*, 1991; Schiffman & Fridleifsson, 1991; Robinson *et al.*, 1993), with random and ordered interstratification types. Others regard the reaction style as being of a discontinuous nature, involving steps from smectite to corrensite and then to chlorite, without a continuous sequence of mixed-layering (Tribble, 1991; Shau & Peacor, 1992; Schmidt & Robinson, 1997). In this second model, corrensite is taken as a discrete phase, rather than a mixed-layer phase of

50 : 50 chlorite/smectite composition. If mixed-layering is present at all, then it is suggested to be between corrensite and smectite, or corrensite and chlorite (Reynolds, 1988; Shau *et al.*, 1990; Shau & Peacor, 1992).

Linked to these points of debate, there is also the more general consideration as to whether changes in clay mineral characters and assemblages, such as those in the smectite to chlorite transition, represent equilibrium or nonequilibrium progression. Clay mineral assemblages and the various clay mineralogical progressions have been found to be widely repeated in time and space, supporting the argument that they represent equilibrated systems (Velde, 1992). On this basis, many studies have utilised clay mineral assemblages, reactions or clay mineral parameters, such as illite and chlorite crystallinities, Al<sup>IV</sup> content in chlorite, and changes in layer ratios (illite/smectite; chlorite/smectite) as geothermometers (Frey & Robinson, 1999).

However, there is also evidence that clay systems are not equilibrated, and Essene & Peacor (1995) have given a comprehensive review of the features involved in the opposing nonequilibrium model of clay mineral evolution. With respect to this model, clay mineral parameters cannot be utilised as geothermometers as

they are linked to kinetic controls and thus variable from setting to setting. In recent years there has been an increasing trend to assess clay mineral parameters in terms of measuring reaction progress, rather than being used as specific geothermometers (Merriman & Peacor, 1999; Arkai *et al.*, 2000). With particular reference to the smectite-chlorite transition, a main point of interest is which of the opposing evolution models is valid, and if the progression of different phases can be used as a general measure of variation in grade or to define specific temperatures.

Here we have utilised previously published data on the smectite to chlorite transition, but they are critically analysed in a different fashion to the original publications to provide new insight to contribute to the debate on the smectite to chlorite transition by providing:

- i a new assessment of the reaction style of this mineralogical transition from which we propose three contrasting reaction pathways for the transition.
- ii evidence for the relative control of a number of potential kinetic effects on the reaction style and reaction progress.
- iii a new model that can accommodate the varied types of reaction styles and pathways that have been reported for the smectite to chlorite transition.

#### HOW DOES THE SMECTITE TO CHLORITE TRANSITION PROCEED?

The present two main interpretations of a continuous sequence of chlorite/smectite mixed-layering, vs. a discontinuous progression are first briefly reviewed below.

The continuous smectite to chlorite progression has been supported by X-ray diffraction (XRD), electron microprobe and transmission electron microscopy (TEM) data. For example, Schiffman & Fridleifsson (1991) identified a well-developed continuous sequence of 10–90% chlorite/smectite mixed-layering in metabasites from the Icelandic, Nesjavellir geothermal system. Similar progressions have also been reported from regional low grade metabasite sequences in Greenland (Robinson *et al.*, 1993) and Californian Coast Range ophiolite complexes (Bettison & Schiffman, 1988; Bettison-Varga *et al.*, 1991). Most work has relied on XRD data, but there is direct, high resolution TEM evidence of chlorite/smectite mixed layering, that includes random mixed-layering examples (Shau & Peacor, 1992; Bettison-Varga *et al.*, 1991; Bettison-Varga & Mackinnon, 1997).

The discontinuous pathway of smectite, corrensite and chlorite has also been supported by XRD, electron microprobe and TEM data. Inoue *et al.* (1984) identified that in the smectite to chlorite transition, three phases were dominant, namely (i) a smectitic phase with <20% chlorite mixed-layers (ii) corrensite and (iii) a chloritic phase with <20% smectite mixed layers. This discontinuous pattern has been supported

by TEM work (e.g. Shau *et al.*, 1990; Shau & Peacor, 1992). One example is from the La Palma complex of the Canary Islands, where Schiffman & Staudigel (1995) reported abundant discrete smectite, corrensite and chlorite, without chlorite/smectite mixed-layering. In particular, well-crystallized corrensite with well-developed rational series of XRD peaks, was recorded rather than diminutive superlattice peaks as in many previous examples.

To account for the two different pathways of the continuous mixed-layering, and discontinuous smectite–corrensite–chlorite models, it has been suggested that the latter transition represents an equilibrium series in response to increasing temperature, and develops in areas of high fluid-rock ratios. In contrast, the continuous chlorite/smectite mixed-layer series is proposed to represent nonequilibrium, metastable mixtures formed in response to incomplete reaction or low integrated fluid/rock ratios (Schiffman, 1995). In support of this proposal are accounts of low amounts of recrystallization in the Nesjavellir geothermal system with the continuous mixed-layer chlorite/smectite series (Schiffman & Fridleifsson, 1991), while the discontinuous series is reported from rocks that had higher integrated fluid fluxes and show more intensive recrystallization (Shau & Peacor, 1992; Laverne *et al.*, 1995). Schmidt & Robinson (1997) reported a well-documented account of contrasting mafic phyllosilicate development in response to differences in rock porosity and permeability from low grade metabasite lavas of the Keweenaw sequence in Minnesota. There, smectite dominates in areas of low permeability/porosity such as in massive flow centres, while on the scale of a few metres in the same flow, corrensite and chlorite were dominant in zones of high permeability/porosity such as flow tops.

#### A NEW ASSESSMENT OF THE SMECTITE TO CHLORITE TRANSITION

Recent debate about the smectite to chlorite transition has concentrated on interpreting the evidence in terms of either the continuous or discontinuous models of the transition. However, evidence from a hydrothermally altered volcanic sequence in the Chipilapa geothermal system of El Salvador provides a new insight into this mineralogical transition. In this system, the main phyllosilicate assemblage for the <2  $\mu\text{m}$  size fraction consists of either smectite or chlorite end-members that in each case have <15% of mixed-layers. Intermediary chlorite/smectite or corrensite was rarely recorded (Robinson & Santana de Zamora, 1999). Similar results for <2  $\mu\text{m}$  fractions were also presented by Beaufort *et al.* (1995) who analysed material from the same wells. They recorded end-member smectite and chlorite, both having <5% mixed-layers, and although they recorded corrensite more frequently (in 8% of samples) than Robinson & Santana de Zamora (1999), the occurrences were, in all but three samples, of minor abundance.

From these records of the smectite to chlorite transition in hydrothermal settings, we propose that there is greater variation than just two pathways. Overall, three basic pathways can be recognised, namely (i) continuous chlorite/smectite mixed-layering (ii) discontinuous smectite, corrensite and chlorite, and (iii) smectite direct to chlorite. Such contrasting pathways are not in accord with a model involving a mineralogical reaction under the constraints of equilibrium thermodynamics, whose character should be controlled by composition, temperature and pressure. We thus consider that the different pathways for this same mineralogical series provide strong evidence of a nonequilibrium progression for the smectite to chlorite transition. Accordingly, these pathways are better interpreted in terms of irreversible, episodic reactions that proceed in one or more steps with a minimization of free energy (Peacor, 1992; Essene & Peacor, 1995). Thus, interpreting the smectite to chlorite series in terms of a reaction progress sequence as suggested in general for clay minerals by Essene & Peacor (1995) might offer the best means for understanding the controls on this mineralogical progression. Accordingly, this proposal involving variable pathways means that the debate on the smectite to chlorite transition should not simply be between an equilibrium pathway and a nonequilibrium pathway.

A principal feature of the concept of the nonequilibrium irreversible stepped approach to clay mineralogy is that it reflects kinetic processes dependent on variables that have greater influence than temperature (Peacor, 1992; Essene & Peacor, 1995). In these circumstances, the main question is what are the controls on reaction mechanisms that lead to the development

of the different pathways and reaction progress in the smectite to chlorite transition?

#### KINETIC CONTROLS ON REACTION PATHWAYS AND REACTION PROGRESS

In the geothermal settings being examined, there are data available that allow the influence of temperature and whole rock composition on the smectite to chlorite transition to be considered. There are also additional data that allow the role of some potential kinetic factors, including thermal gradient, surface energy differences and fluid/rock ratios, to be considered. Tectonic stress is a further potential kinetic factor, and while it could be an important variable in settings where chlorite and illite crystallinity measurements are utilised (Merriman & Peacor, 1999), its role in the geothermal settings examined here is likely to be of no significance.

#### Temperature

Specific data on temperatures related to the smectite to chlorite transition, rather than estimated values are relatively few. Data are available for Icelandic (Kristmannsdottir, 1979; Schiffman & Fridleifsson, 1991), Newberry Caldera, Oregon (Keith & Bargar, 1988) and Chipilapa, El Salvador (Robinson & Santana, 1999) systems, for which the data are taken as representative of equilibrium conditions for the reported mafic phyllosilicate distributions. In all of these systems, the upper temperature limit of smectite stability is similar at 180–210 °C (Fig. 1). In the Nesjavellir (Icelandic), Newberry Caldera and Chipilapa systems, for which most detailed data are

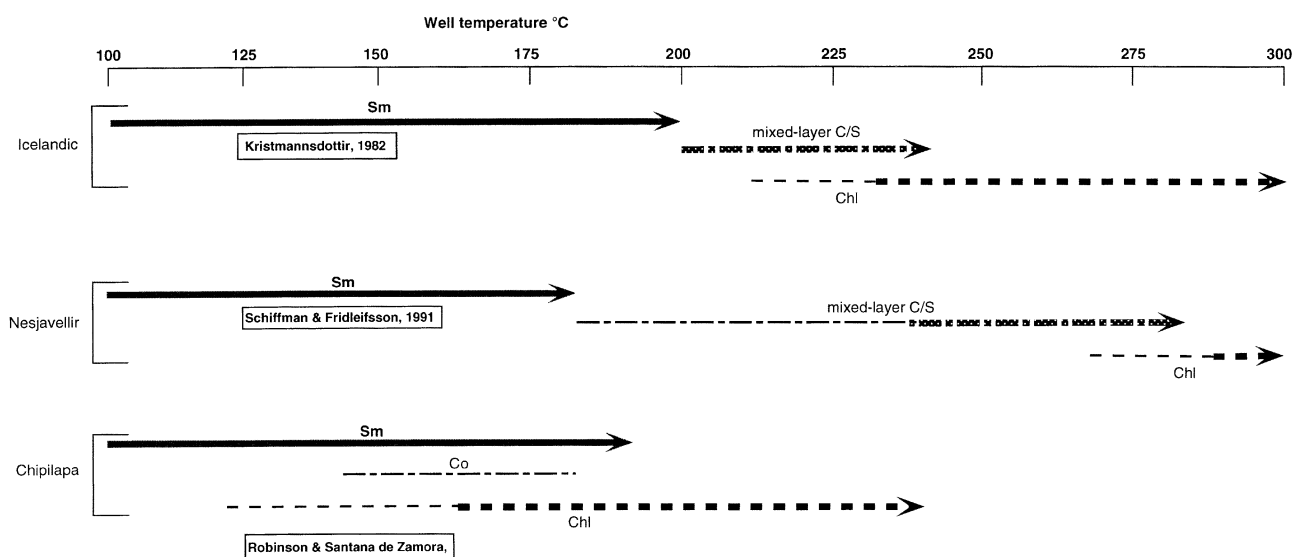


Fig. 1. Comparison of temperature ranges for which mafic phyllosilicate minerals are recorded in the Icelandic (Schiffman & Staudigel, 1995; Kristmannsdottir, 1979) and Chipilapa (Robinson & Santana de Zamora, 1999; Patrier *et al.*, 1996) geothermal systems. Thick lines represent that mineral is present in abundance, and thin lines indicate mineral is of minor occurrence.

available, the initiation of the smectite to chlorite transition occurs over the range 150–200 °C. Following initiation of the transition, the subsequent pathway followed by the mineralogical series, and the temperature at which discrete chlorite first appears, differs in these different geothermal systems. In the Icelandic systems, there is a transitional zone with mixed-layer chlorite/smectite and corrensite before chlorite appears. The temperature at which chlorite appears varies from *c.* 210 °C (Kristmansdottir, 1979) to *c.* 270 °C (Schiffman & Staudigel, 1995). In marked contrast in the Chipilapa system, corrensite is rare and is recorded as a minor phase in only three samples over the range 140–180 °C, while chlorite occurs as a minor phase at temperatures as low as *c.* 120 °C, and becomes the main phase at *c.* 160 °C (Fig. 1) (Robinson & Santana de Zamora, 1999). In the case of the Newberry Caldera, mixed-layer smectite/chlorite and chlorite occur over a similar temperature range from *c.* 150 °C to the base of the well at *c.* 265 °C. The temperature for chlorite occurrence at *c.* 150 °C is in fact similar to that seen in the Chipilapa system.

The marked similarity in the temperature range at which smectite begins to convert to chlorite-rich phases (chlorite/smectite, corrensite and chlorite) in these different settings suggests that the primary control on the initiation of this transition point is thermal. Support for this point is also forthcoming from regional low grade metamorphism of Keweenawan metabasites, where different mafic phyllosilicate assemblages developed in response to contrasting flow morphologies, only once grade had exceeded an estimated threshold of *c.* 150 °C (Schmidt & Robinson, 1997).

The data records reviewed here indicate that the conversion of smectite is initiated from *c.* 150 up to *c.* 200 °C, then different reaction pathways are followed over broad and different temperature ranges. Thus, according to the nature of the reaction step, the appearance of mixed-layer chlorite/smectite, corrensite or chlorite is not diagnostic of a specific temperature or even temperature range, but relates to the process(es) driving the reaction step. This scenario differs to a previously proposed model for the smectite to chlorite transition that involves just two pathways namely, a mixed-layer chlorite/smectite metastable series associated with incomplete reaction, and an equilibrium series of smectite-corrensite-chlorite, both driven by increasing temperature (Schiffman & Staudigel, 1995).

### Whole rock chemistry

Differences in whole rock chemistry between the basaltic and calc-alkaline systems for which the main reports of the smectite to chlorite transition are presently documented, may be a relevant factor. However analysis of the data from the Chipilapa system found no link between whole rock type and mafic phyllosilicate type (Patrier *et al.*, 1996; Robinson & Santana de Zamora, 1999). Also, comparisons of mafic

phyllosilicate distributions and mineral chemistry between the calc-alkaline Chipilapa and Newberry Caldera and the basaltic Icelandic systems suggested that this primary difference was not a major control on mafic phyllosilicate development (Robinson & Santana de Zamora, 1999).

### Thermal gradient

Variable thermal gradients may play a role in the initiation of geothermal systems by promoting reaction overstepping. This may especially apply in cases, such as here, of a nonequilibrium sequence of irreversible reaction steps, each involving a small reduction in free energy, and so high gradients promote overstepping and favour the direct transition pathway. The continuous, mixed-layer pathway developed at Nesjavellir is linked with a generalised gradient over the well depth of *c.* 150 °C km<sup>-1</sup>, contrasting with the development of a discontinuous pathway of Chipilapa where the thermal gradient is markedly lower at *c.* 50 °C km<sup>-1</sup>. This implies that there is another variable with a more immediate effect than that of the thermal gradient.

### Grain size

In the case of clay minerals, there is potential for significant contrasts in surface energy as a result of differences in crystal sizes, which may be an influence on the reaction steps and pathways developed. In a situation where smallest crystal sizes are dominant, the surface energy would represent a greater proportion of the overall free energy, and could drive recrystallization influencing reaction progress, compared to a setting dominated by coarser crystals. For the Chipilapa system, published data are available for mafic phyllosilicate distributions of the <2 µm (Robinson & Santana de Zamora, 1999) and <0.2 µm (Patrier *et al.*, 1996) fractions, and if these size fractions represent true crystal size differences, it is equivalent to surface area contrasts of some two orders of magnitude. However, as shown in Table 1, there is a remarkable

**Table 1.** Temperature–depth ranges for occurrences of <2.0 µm (Robinson & Santana de Zamora, 1999) and <0.2 µm (Patrier *et al.*, 1996) clay fractions from samples taken from CH7, CH7B and CH9 wells of Chipilapa geothermal system. Columns labelled Chl (°C) and Sm (°C) record, respectively, the lowest temperature at which chlorite is first documented, and the highest temperature at which smectite is found. The range (°C) documents the temperature range between these two temperatures. The second three columns record the same features for the depth intervals in metres.

		Chl (°C)	Sm (°C)	range (°C)	Chl (m)	Sm (m)	range (m)
CH7	<0.2 µm	132	183	51	485	631	146
	<2.0 µm	122	180	58	284	550	266
CH7B	<0.2 µm	150	196	46	318	565	247
CH9	<0.2 µm	172	198	26	429	874	445
	<2.0 µm	144	195	51	300	950	650



correspondence between the distributions of minerals in these two datasets. Accordingly, this suggests that surface energy effects have not in this case been a relevant factor in the distributions of these mafic phyllosilicates.

#### Fluid/rock ratios

A prominent difference between the Chipilapa (El Salvador) and Icelandic geothermal systems is that extensive recrystallization is characteristic of the Chipilapa system, with secondary minerals commonly totalling some 40–55% of the bulk rock (Santana de Zamora, 1991; Robinson & Santana de Zamora, 1999). Also, the immediately adjacent Ahuachafan field shows pervasive recrystallization, with clay mineral abundances of up to 30% (plus additional chlorite), and total secondary minerals commonly in excess of 50% (Aumento *et al.*, 1982). The extensive recrystallization, from a largely anhydrous primary character indicates high fluid-rock ratios and it may thus represent a critical effect that has influenced the development of the discontinuous one-step smectite to chlorite transition in this system. Differing intensities of fluid-rock interaction have been cited by various workers as a controlling factor in the smectite to chlorite conversion (Shau *et al.*, 1990; Shau & Peacor, 1992; Schiffman & Staudigel, 1995; Alt, 1999). For example, clear evidence for the interrelationship between intensity of albitisation, morphological character and mafic phyllosilicate parageneses is available in low-grade metabasite flows of the Keweenaw sequence. Within individual flows, there is a high concentration (*c.* 30%) of amygdales in flow tops, with primary feldspar totally albitised and mafic phyllosilicates of corrensite and chlorite. In contrast, within a few metres (<10) in the massive flow centres there is a near zero amygdale content, the feldspar is dominantly primary andesine/labradorite and the mafic phyllosilicate is restricted to smectite (Schmidt, 1990, 1993; fig. 1(c, d); Schmidt & Robinson, 1997).

Schiffman & Staudigel (1995) explained the contrast between the continuous mixed-layer chlorite/smectite sequence in the Nesjallevir field, and the discontinuous smectite–corrensite–chlorite series from La Palma as the result of differing degrees of recrystallization linked, respectively, to low and high fluid-rock ratios, giving rise to, respectively, a nonequilibrium and equilibrium progression. However, Schmidt & Robinson (1997) suggested that the concept, rather than be based simply on differing fluid/rock ratios, might be better considered in relation to the mode of fluid transport. It was suggested that areas with high permeability and porosity would permit advective fluid movement, whereas in areas with very low permeability and porosity, transport might be restricted to a diffusive mode.

In most very low grade metamorphic settings, partial and restricted recrystallization is a clear pointer to low

integrated fluid/rock ratios and linking this to restricted nutrient supply, it is clear that this would act as a kinetic constraint on the smectite to chlorite conversion.

## DISCUSSION

The evidence accumulating is of the importance of protolith morphological contrasts in porosity and permeability exerting a major control on the style of reaction pathway, and on the extent of reaction progress in the smectite to chlorite transition. The variability of these features for the smectite to chlorite transition can be linked to the reaction mechanisms for the formation of clay minerals and the generation of mixed-layered structures. The two end-members involve (i) solid state transformation and (ii) dissolution and crystallization processes (Srodon, 1999).

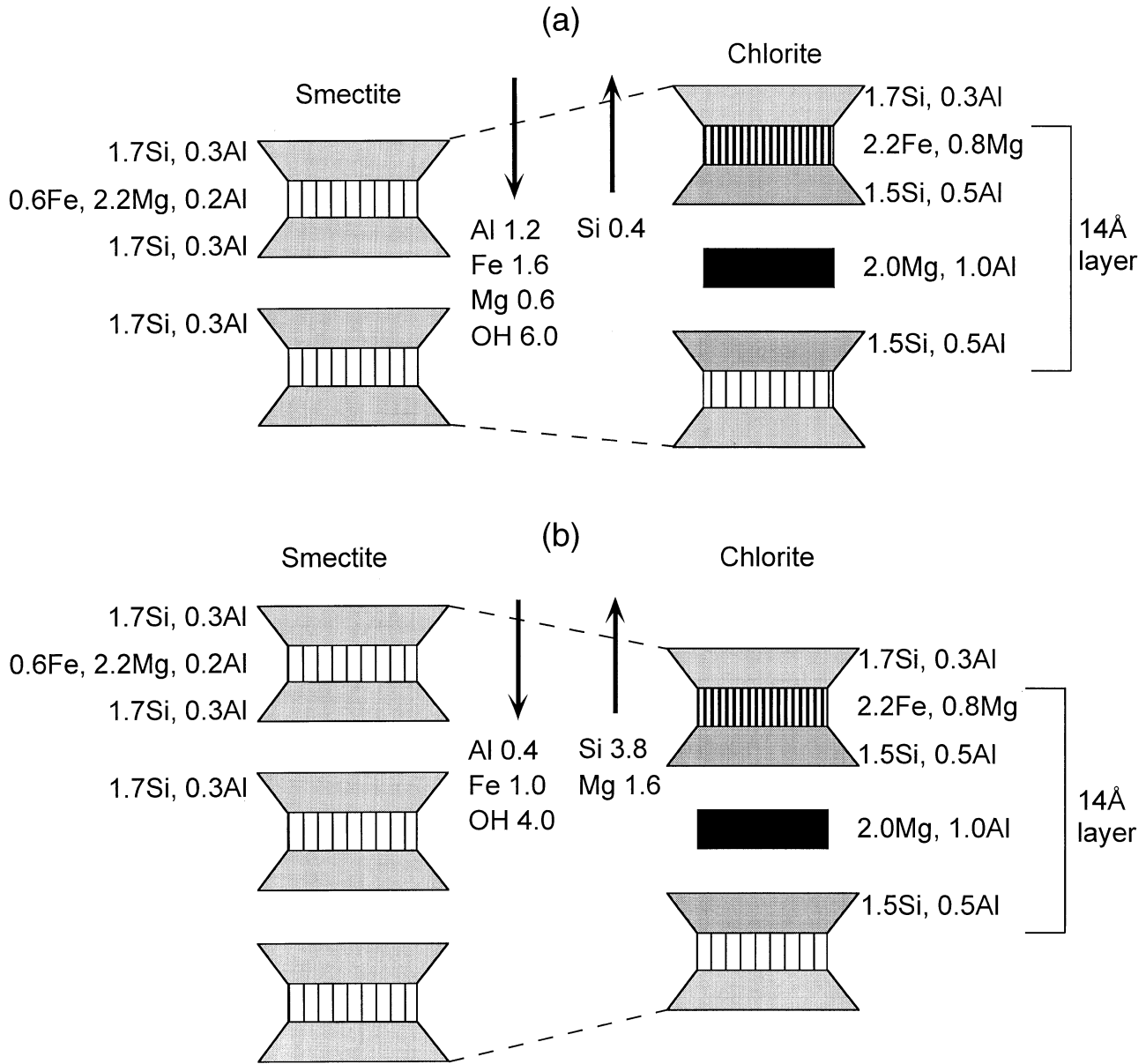
### Reactions mechanisms for the smectite to chlorite transformation

#### *Solid state transformation*

A main mechanism envisaged for the formation of mixed-layer clay minerals is via a solid-state transformation process, with the typical postulated change being of a smectitic interlayer transformed into a new sheet structure thereby giving rise to a mixed-layer mineral. With respect to the smectite to chlorite transition, the reaction pathway involving continuous mixed-layering is typically found in settings where recrystallization was restricted and in which fluid/rock ratios were low, such as in massive metabasites. However, examples of the continuous mixed-layering pathway can be juxtaposed closely with examples of the discontinuous smectite–corrensite–chlorite pathway (Bettison-Varga & Mackinnon, 1997; Schmidt & Robinson, 1997). This suggests that there has been a kinetic constraint on the development of the reaction pathway and reaction progress in those areas of a massive character. The most obvious effect that could restrict recrystallization is supply of nutrients necessary to effect the change from smectite to chlorite. In the massive areas of metabasites the porosity and permeability are extremely limited and so it can be envisaged that the nutrient transport is dominated by processes of diffusion, thus providing the kinetic constraint as a rate limiting step.

#### *Dissolution/crystallization transformation*

The second mechanism for the formation of clay minerals is a process whereby the original mineral is dissolved and a new phase nucleates and grows in response to the prevailing conditions and fluid chemistry. Srodon (1999) has postulated that the character of clay minerals arising from the dissolution/crystallization mechanism will differ according to whether crystallization takes place within a pre-existing smectite crystal,



**Fig. 2.** Schematic diagram to show chemical and structural changes involved in the transformation of smectite to chlorite. (a) Formation of brucite layer between two smectite layers and chemical adjustment of adjacent tetrahedral sheets in neighbouring smectite layers to form a chlorite layer (Bettison-Varga & MacKinnon, 1997). (b) Formation of brucite layer by loss of central of three smectite layers, involving dissolution of the two tetrahedral sheets and conversion of octahedral sheet into brucite layer and chemical adjustment of adjacent tetrahedral sheets in neighbouring smectite layers to form a chlorite layer (Bettison-Varga & MacKinnon, 1997). Chemical data for tetrahedral and octahedral sheets of smectite and chlorite layers taken from AEM data of Shau *et al.* (1990). Chemical input and losses needed as a result of these different conversion methods are shown, respectively, by the downward and upward pointing arrows in the centre of the figure.

or outside to form a completely new phase. Where it takes place within a smectite, then a high nucleation/growth ratio of a new layer structure would likely give rise to a random to regular mixed-layered sequence, while a low ratio gives rise to ordered mixed-layers. Nucleation and growth outside an existing smectite would give rise to discrete corrensite or chlorite depending, respectively, on a high or low nucleation/growth

ratio. Thus the three reaction pathways identified here are predicted by this model of Srodon (1999).

A close correlation exists between occurrences of the discontinuous and the direct reaction pathways with rocks having high initial porosities/permeabilities (as in highly brecciated/vesiculated flow tops, or pyroclastic sequences (e.g. Shau *et al.*, 1990; Schiffman & Staudigel, 1995; Schmidt & Robinson, 1997). Such rocks in which

the porosity is infilled with a fluid, provide a setting in which there are not only void areas in which direct crystallization from fluid could occur, but a medium in which nutrient transport would be enhanced in comparison to rocks having a massive morphology. Furthermore in geothermal settings with strong thermal gradients the conditions are favourable for advective transport of fluid and nutrients to occur. This would provide a kinetic enhancement of the reaction progress by promoting dissolution of protolith minerals releasing and transporting nutrients to promote rapid growth giving rise to the direct smectite to chlorite transition.

#### Variability of the smectite to chlorite reaction pathways

The record of the smectite to chlorite transition is one of variability on the megascopic scale (metres, Schmidt & Robinson, 1997) to a within-sample scale between a rock groundmass and a vesicle infill (Bettison-Varga & MacKinnon, 1997). Such variability can be related to variability in the rates of nutrient diffusion and processes of dissolution/nucleation/crystallization, each of which could vary as a continuum in response to the changing character of the protolith rock. Consideration of postulated reaction mechanisms involved in the solid state transformation process of smectite to chlorite, coupled with AEM chemical data of end member compositions of smectite, corrensite and chlorite (Shau *et al.*, 1990; Bettison-Varga & MacKinnon, 1997) can be used demonstrate one aspect of the variability in this transition.

Bettison-Varga & MacKinnon (1997), from analysis of layer transition boundaries in TEM images of chlorite/smectite, suggested two main mechanisms for the solid state transformation of smectite to chlorite. The first mechanism involves conversion of an inter-layer region between two smectite layers into a brucite sheet, and accompanying chemical modification of the tetrahedral sheets of the immediately adjacent smectite layers, to form a chlorite layer (Fig. 2a). The second mechanism involves three smectite layers, with dissolution of the two tetrahedral sheets in the central smectite layer, conversion of the remnant octahedral sheet into a brucite layer and chemical modification of the tetrahedral sheets of the immediately adjacent smectite layers to form a chlorite layer (Fig. 2b). The broad compositional changes involved in these two transformations styles can be considered using compositions of the tetrahedral and octahedral sheets, and brucite layer taken from AEM data of Shau *et al.* (1990). For the first mechanism, input of Al, Fe, Mg and OH is required, and release of Si (Fig. 2a), with a similar change for the second mechanism, apart from release, rather than input of Mg (Fig. 2b).

The process of albitisation of primary igneous feldspar in low grade metamorphism has been identified as the mechanism providing the Al for the smectite to chlorite transition. However, this process requires an input of Si to albite that could be sourced

by the release of Si from smectite undergoing chloritization (Fig. 2). Thus, the role of albitisation in the process should be seen not as a one-way Al supply to the smectite site, but involving reciprocal Si supply to the plagioclase site. The input of Fe needed for both reaction mechanisms can be linked to the breakdown of ilmenite to form titanite and releasing Fe, that is a common feature of metabasites at these low grades of metamorphism.

Finally, the input of OH required for the smectite to chlorite transformation varies between the two modes, with 50% more needed in the case of the first reaction (Fig. 2a), compared to the second (Fig. 2b). Thus, which of these two mechanisms might operate could also be controlled by features such as fluid pH, or availability of fluid necessary to convert the primary anhydrous assemblage into the hydrous low grade assemblage.

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