Chlorite-smectite clay minerals and fault behavior: New evidence from the San Andreas Fault Observatory at Depth (SAFOD) core

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ABSTRACT

Segments of the modern San Andreas fault experience creep behavior, which is attributed to various factors, including (1) low values of effective normal stress, (2) elevated pore-fluid pressure, and (3) low frictional strength. The San Andreas Fault Observatory at Depth (SAFOD) drill hole in Parkfield, California, provides new insights into the importance of smectite clay minerals, as demonstrated by analysis of mudrock and fault gouge samples from zones between 3186 and 3199 m and 3295 and 3313 m measured depths. X-ray diffraction (XRD) results show illite, chlorite, and mixed-layered illite-smectite and chlorite-smectite minerals in the faulted mudrock, whereas serpentine, Mg-rich smectite, and chlorite-smectite minerals are concentrated in the southwest deformation zone and the central deformation zone of the two actively creeping sections in the San Andreas fault. These rocks are abundantly coated by shiny clay mineral layers in some cases, reflecting mineral formation during creep. Secondary- and transmission-electron microscopy (SEM/TEM) and XRD studies of these slip surface coatings reveal thin films of neoformed chlorite-smectite phases, similar to previously described illite-smectite microscale precipitations. The abundance of chlorite-smectite minerals within fault rock of the SAFOD borehole significantly extends the potential role of mineralogic processes to depths up to 10 km, with cataclasis and fluid infiltration creating nucleation sites for neomineralization on displacement surfaces. We propose that localization of illitic to chloritic smectite clay minerals on slip surfaces from near the surface to the brittle-ductile transition promotes creep behavior of faults.

INTRODUCTION

The slip behavior of faults has been variably attributed to different mineralogical and fluid processes (Evans and Chester, 1995; Vrolijk and van der Pluijm, 1999; Sibson, 2005; Wibberley et al., 2008). While fluid pressure has the capability to reduce the effective stress state and promote slip, mineralogic properties of fault-related rocks can similarly affect fault behavior by introducing weak mineral phases at interfaces. Increasingly, the presence of smectitic clay minerals has been advanced as evidence for mineralogic weakening in cores collected from the SAFOD project in Parkfield, California (Schleicher et al., 2006, 2010; Holdsworth et al., 2011; Bradbury et al., 2011), reflecting the widespread occurrence of phyllosilicates and their localization in fault-rock samples. Indeed, recent laboratory results support the mechanical role and stability of smectitic clays by showing low friction coefficients in experiments on SAFOD core (Tembe et al., 2006; Morrow et al., 2007; Carpenter et al., 2011; Lockner et al., 2011) and in other natural settings (e.g., Saffer et al., 2001; Bos and Spiers, 2002; Mizoguchi et al., 2006; Smith and Faulkner, 2010; Ikari et al., 2011). More extensive work on a variety of materials has been an important part of evaluating the role of clays in controlling friction (Lupini et al., 1981; Brown et al., 2003; Saffer and Marone, 2003).

In order to determine the change in shear strength and stability of clay minerals with depth, temperature, and time must be considered in addition to the influence of fluid and mineral chemistry. There are two keys in establishing such reaction parameters: (1) Different clay mineral phases change under low temperatures, particularly between ~75 °C and 250 °C, and (2) different phases occur in different chemical environments (Veale, 1992). Numerous attempts have been made to characterize the low-temperature mineral stability fields of clay minerals, which are notably difficult to study because of their small size, variable structural composition, and relatively slow rate of formation and alteration (e.g., Ransom and Helgeson, 1993, 1994; Blanc et al., 1997). Despite these difficulties, reliable information about stability, formation mechanisms, and structural features of smectitic clays has been gained from the study of single-phase specimens (Kloprogge et al., 1999). Whereas the correlation between experimentally determined stability fields and thermodynamic predictions is generally good, many natural phases formed are metastable and depend on chemical parameters such as pH, element activity, and the fluid-rock ratio (Essene and Peacor, 1995). The stability of pure smectite minerals is typically restricted to the uppermost 3–4 km of the upper crust (Huang et al., 1993). In this paper, we will explore the role of mixed-layer chlorite-smectite minerals, including 50:50 chlorite-smectite varieties like corrensite, which have been reported to appear at ~120 °C and persist to temperatures as high as 260 °C with decreasing smectite content (Hiller, 1993). The occurrence of localized, variably ordered chlorite-smectite phases in SAFOD fault-related rock would extend the role of fault weakening from clay neomineralization to a greater range of depth and host-rock compositions, influencing fault behavior down to the brittle-ductile transition of continental rocks. Whereas weak fault behavior in the deeper crust has been mostly attributed to elevated fluid pressure (Cox, 2002; Becken et al., 2008; Kurz et al., 2008) or the occurrence of serpentinizing phases (Moore and Rymer, 2007; Wibberley, 2007; Jung et
al., 2009; Viti and Collettini, 2009), chlorite-smectite phases offer an alternative explanation for these scenarios, because of their probable low frictional strength and stabilities across a broader range of upper-crustal conditions. Chloritic clay commonly forms in areas where mafic lithologies are present, forming Mg/Fe-bearing chlorite-smectite instead of K-bearing illite-smectite in felsic lithologies. In both cases the hydrous smectitic interlayers affect the fault-slip behavior, but the apparent higher pressure-temperature stability of chlorite-smectite phases described in this paper extends the stability of mixed-layer smectitic clay mineralization to 8–10 km depth. Chlorite-smectite is important here because it is one of the minerals growing together with Mg-rich smectite (including saponite) in the fault gouge of the San Andreas fault (Solum et al., 2006; Lockner et al., 2011), and together with illite-smectite in adjacent fault rocks of the deformation zone (Schleicher et al., 2006, 2010). In this study, we used X-ray diffraction (XRD) combined with NEWMOD modeling (Reynolds and Reynolds, 1996), as well as scanning electron microscopy (SEM) and high-resolution transmission-electron microscopy (HRTEM), combined with analytical elemental microscopy (AEM), to determine microstructures and mineral compositions of chlorite-smectite within phase III fault rocks from SAFOD drilling, including samples from recently active segments of the fault.

San Andreas Fault Observatory at Depth (SAFOD)

The SAFOD drill site is situated on the Pacific plate near Parkfield, California, ~1.8 km west of the surface trace of the San Andreas fault. It penetrates a segment of the fault that accommodates displacement between the North American plate in the northeast and the Pacific plate in the southwest through a combination of aseismic creep and repeating earthquakes (Nadeau et al., 2004; Ellsworth et al., 2007). The SAFOD project drilled a pilot hole and a main hole with the goal to sample and instrument the San Andreas fault at depth in the creeping section, the transition zone, and the locked section (Hickman et al., 2004, 2005, 2008; Fig. 1). In 2002, the vertical pilot hole was drilled to 2.2 km through Cenozoic sediments into Salinian granite at an intersection with the Valley granite at ~760 m (Solum and van der Pluijm, 2004). During phase 1 and 2, in the years 2004–2005, the main hole was drilled, first vertically and then deviated by 55°, through Mesozoic Salinian granitoids into arkosic sedimentary rocks and alternating layers of sand-, silt-, and mudstone to a final depth of 3987 m measured depth (Draper-Springer et al., 2009; Bradbury et al., 2007; Holdsworth et al., 2011). Depths are reported here in meters measured depth (m MD), which were measured along the borehole, and they represent the distance below the drill-rig floor (http://www.earthscope.org/data/safod). Based on rock texture, composition, and the presence of fossils at ~3360 m MD, these rocks have been identified as the Cretaceous Great Valley Group (K. Mc Dougall, 2006, written commun., in Draper-Springer et al., 2009). Two different localities drilled during phase 2 show pronounced casing deformation, identified through low Vp, Vs, resistivity, and natural gamma signatures in geophysical logs. Those two regions of fault creep are referred to as the southwest deformation zone, located at 3192 m MD, and the central deformation zone, located at 3302 m MD (Zoback et al., 2010; Bradbury et al., 2011). Whereas the central deformation zone is actively creeping, as documented by casing surveys (Zoback et al., 2010), repeating micro-earthquakes are thought to occur on the southwest deformation zone below its intersection with the SAFOD hole (Thurber et al., 2010). During phase III in summer 2007, three boreholes were sidetracked off the main hole at a relatively high angle. Drilling included both deforming zones (central and southwest deformation zones) and a third zone that cuts the boundary between sedimentary rocks of Mesozoic Salinian granitoids and the Great Valley Group. In total, a 41 m section of whole-rock core was retrieved between 3141.4 and 3153 m MD (hole E, runs 1–3), between 3186 and 3198 m MD (hole G, runs 1–3), and 3294–3312.7 m MD (hole G, runs 4–6).

Sampling and Analytical Methods

Sampling took place on-site during drilling phase III in summer 2007. Core chips, averaging ~3–5 cm in size, were collected directly after arrival at the surface, and carefully cleaned by removing surface drilling mud. About 20 rock samples from different depths were taken from hole G, runs 1–6 (Fig. 2). In the laboratory, the rock chips were hand-crushed to powder for bulk-rock XRD analysis. Additionally, the <2 µm fraction was separated for clay XRD analysis. The XRD preparation followed the analytical methods described by Moore and Reynolds (1997). All samples were studied as random and oriented powders under air-dried and ethylene glycol conditions using a Scintag X1 theta-theta powder diffractometer operating at 40 kV and 30 mA (Cu-Kα radiation). Random
oriented samples were used for analyzing whole-rock mineralogy. Oriented samples were used to enhance the intensities of (001) peaks, aiding the identification of clay mineral phases. Air-dried and glycolated mounts were scanned from 2° to 15°, respectively, at 0.02° 2 dots show the location of the studied samples. (modified after Bradbury et al., 2011). Rock compositions are determined from the core atlas. The black dots show the location of the studied samples.

RESULTS

Sample Description

The location of the samples investigated across the damage zone of the San Andreas fault is shown in Figure 2. Based on the basic lithologic/structural units described in Bradbury et al. (2011), two samples belong to an area of black ultrafine-grained cataclase (3193.9–3196.4 m MD), five samples come from pronounced zones of foliated fault gouge associated with the central and southwest deformation zones (3196.4–3198 m MD and 3296.6–3299.1 m MD), and the other samples were taken from foliated phyllosilicate-rich fine-grained rock with heterogeneous clasts between 3186.7 and 3193.9 m, 3198.4 and 3199.5 m, 3294.9 and 3296.6 m, and 3299.1 and 3122.7 m MD. Images and analyses of core samples from phase III core are available in the phase III Core Photo Atlas (www.Earthscope.org/safod), and other recent publications (e.g., Chester et al., 2010; Hadizadeh et al., 2010; Schleicher et al., 2010; Bradbury et al., 2011; Holdsworth et al., 2011; Janssen et al., 2011; Mittempergher et al., 2011).

The small-sized rock chips from hole G, runs 1–3 (3186.7–3197.5 m MD), and hole G, runs 4–6 (3294.9–3311.8 m MD), were investigated in particular detail. The rock chips between 3186.7 m and 3193.9 m MD (hole G, runs 1–3) belong to the foliated phyllosilicate-rich fine-grained unit with heterogeneous clasts and/or interlayers. The samples are mostly dark gray and finely foliated, with some massive grayish-black shale lithologies. The foliated fault gouge samples between 3196.4 and 3197.9 m MD are associated with the southwest deformation zone, and they exhibit a pervasive foliation wrapping around isolated centimeter-scale clasts that have a strong preferred orientation (Sill, 2010). We also investigated grayish-black rock chips with an incohesive matrix and a micro-scaly fabric. The fault-related rocks from hole G, runs 4–6, at 3294.9–3296.6 m MD, are dark gray,
Mineral Assemblages

The powder XRD analysis shows primary mineral components of quartz, feldspar (both plagioclase and K-feldspar), mica (both biotite and muscovite), and occasional serpentine. Secondary minerals are calcite, oxides, and sulfides, especially pyrite. The <2 µm size fraction is dominated by illite, chlorite, mixed-layered illite-smectite and chlorite-smectite, and accessory amounts of serpentine and discrete smectite (Figs. 3A–3D). The bulk mineralogy and clay mineralogy of the shaly mudrock samples do not significantly differ from both runs, except for slightly more chlorite in core runs 1–3 and discrete smectite in core runs 4–6, and more illite-smectite in core runs 1–3, based on qualitative XRD intensity data.

The mixed-layered illite-smectite and chlorite-smectite minerals in the rocks outside the southwest deformation zone occur together with discrete illite and chlorite (Fig. 3A). Chlorite-smectite 001 reflections range from 1.42 to 1.45 nm in all samples investigated, which expand to 1.45–1.50 nm after ethylene glycolation. The broader peaks and the changes in d-values show the occurrence of chlorite-smectite or chlorite-vermiculite minerals. The diffraction patterns of illite and illite-smectite also show broader peaks, caused by the combined contribution of two illitic phases (see also Schleicher et al., 2009b).

The diffraction pattern of the shaly mudrocks from the rocks outside the central deformation zone also show, in addition to illite and illite-smectite, mixtures of chlorite and chlorite-smectite (Fig. 3C), with the latter containing small quantities of expandable phases (smectite or vermiculite) and air-dried peaks ranging between 1.41 and 1.46 nm. The NEWMOD calculations and matching of measured and modeled patterns indicate typical average percent smectite contents in chlorite-smectites to be ~10%–20%, with poor degrees of ordering (“reichweite 0”; Reynolds and Reynolds, 1996). After glycol treatment, the 1.4 nm peak shifts to ~1.5 nm and becomes asymmetrically broader with a hump on its low-angle side.

The dominant mineral in the clay fraction of the gouge samples from the southwest and central deformation zones at ~3297 m and ~3197 m is chlorite-smectite (Figs. 3B and 3D). This mixed-layered clay mineral occurs both as randomly and as regularly interstratified phases, with different amounts of smectitic and chloritic components. NEWMOD calculations indicate average smectite contents of between 20% and 50% interlayered with both Fe- and Mg-rich chlorites showing varying degrees of ordering (reichweite 0 and 1). The crystallite sizes of these clay mineral packs are notably thin (<14 layers), with an average defect-free distance of just 4 layers. When present, corrensite, a 1:1 regularly interstratified (mixed-layer) trioctahedral chlorite with either 50% trioctahedral smectite or vermiculite, is characterized by a distinct superlattice reflection at ~2.9 nm.

Figure 3. X-ray diffraction patterns of some representative samples taken from hole G runs 1–3 and hole G runs 4–6. (A–B) Clay mineralogy from rock samples adjacent to and within the southwest deformation zone (SDZ). (C–D) Samples adjacent to and within the central deformation zone (CDZ). Chl—chlorite, C-S—chlorite-smectite, I-S—illite-smectite, I—illite, Cor—corrensite, Srp—serpentinite.
(Figs. 3B and 3D); this peak shifts to ~3.1 nm after ethylene glycolation (Chen, 1977). The superlattice is weakly defined or nonexistent in a few samples containing the phase, indicating the presence of a poorly ordered form with higher proportions of randomly interstratified layers. Other expandable chloritic phases show 1.4 nm reflections that broaden to 1.45–1.5 nm after ethylene glycolation. The ~0.7 nm peak is separated into 0.72 nm and 0.74 nm peaks, corresponding to 002 chlorite serpentinite and 004 of corrensite, respectively.

**Microstructures**

Representative SEM and HRTEM images in Figures 4, 5, and 6 show characteristic clay mineral assemblages and microstructural characteristics of the fault gouge and adjacent rocks. Confirming the XRD patterns (Figs. 3A–3D), the dominant clay minerals in the shaly mudrocks adjacent to the central deformation zone and southwest deformation zone are illite-smectite and chlorite-smectite, as well as illite and chlorite. The backscattered SEM image in Figure 4 reveals notably angular quartz and feldspar clasts in a clay mineral matrix with a scaly microfabric together comprising >50% of the sample. Representative TEM images show that this matrix contains aligned packets of well-developed, 10–50-nm-thick illite crystallites forming adjacent to illite-smectite crystallites (Figs. 5A–5D). The illite edges are often altered into illite-smectite by dissolution-precipitation reactions (Fig. 5A), possibly resulting in lower concentrations of deformation-induced lattice distortions. The contacts are characterized by low-angle crystallite boundaries <30°. Other areas show well-oriented illite and illite-smectite
packages that are 10–30 nm in average thickness (Fig. 5B). Many illite-smectite packets display a long-range ordering, mostly R1–R3, characterized by the reoccurrence of single smectite layers stacked optically parallel between 2–5 illite layers. Deformation features like bending and areas of lattice distortion are abundant, and the distribution of these features indicates that slip occurred along packet boundaries. Chlorite minerals tend to cluster together with chlorite-smectite, forming packets of 10–50 nm thickness (Fig. 5C). Chlorite-smectite also occurs as wavy layers with particle thicknesses of less than 30 nm and variable spacing between 2.7 and 2.9 nm and short-range ordering (Fig. 5D). Lenticular micropores are common in this area and are typical of those observed in smectite-rich materials (Alcover et al., 2000).

TEM study of the fault gouge with scaly fabrics investigated from and near the central and southwest deformation zones showed chlorite and chlorite-smectite packets that are clustered together (Figs. 6A–6D). The packages are in general >30 nm thick, with characteristically straight margins (Fig. 6A). Corrensite commonly occurs in aggregates coexisting with discrete chlorite crystals (Fig. 6A). The thickness of the corrensite packages varies from 30 to 50 nm, with ~2.4 nm single layers that are interstratified with chlorite and other chlorite-smectite. The relatively smooth transition between some particle surfaces reflects direct alteration, likely by dissolution and re-precipitation mechanisms (Peacor, 1992; Lynch et al., 1997; Srodon, 1999; Abad et al., 2003). In Figure 6B, thin and curvilinear particles of varying thickness are interleaved with lenticular-shaped pores. The total particle thickness ranges between 10 and 30 nm. The thickness of a chlorite and smectite layer together is typically ~2.9 nm, whereas the chlorite lattices are ~1.4 nm thick. Some areas in the fault gouge show characteristic wavy chlorite-smectite particles of 10–30 nm average thickness, surrounding and partly replacing small chlorite minerals (Fig. 6C). Higher-contrast areas of the crystal structure indicate lattice distortion of the chrysotile due to rock deformation. The clay mineral packets that surround the chrysotile tubes are >30 nm in average thickness and show deformation and strong alteration into chlorite-smectite minerals (Figs. 6C and 6D). In some instances, deformed and kinked chlorite grains were fragmented before thin neocrystallized chlorite-smectite particles grew in the adjacent pore space (Fig. 6D). Such relationships clearly indicate that multiple generations of clay mineral growth occurred in these fault-related rocks.

Chemical Composition of Chlorite-Smectite

Quantitative microchemical analyses, plotted in Figure 7A (as wt% oxides), show the composition of MgO/(MgO + FeO) relative to SiO$_2$ wt% of chlorite-smectite minerals for...
two representative fault-rock samples from the southwest deformation zone and the central deformation zone (see also Table 1). For comparison, the compositional fields of chlorite, chlorite-smectite (corrensite), and Mg-smectite are shown from the well-studied hydrothermally altered mafic rocks of La Palma, Canary Islands (Schiffman and Staudigel, 1995). The 3191 m MD sample from the southwest deformation zone contains chlorite-smectite minerals that are more Fe-rich than the La Palma rock suite, with a narrow range of MgO/(MgO + FeO) values lying between 0.19 and 0.45. In contrast, the 3295 m MD fault-rock sample, positioned close to the central deformation zone, shows a broader range of MgO/(MgO + FeO) values, between 0.26 and 0.62, reflecting high Mg content. Based on these variations, together with the broad range of SiO₂ contents for both samples (~29–54 wt% SiO₂), the chlorite-smectites show a continuous span from chlorite-rich to smectite-rich end members. Such compositional variations in the samples could indicate a lack of equilibrium due to heterogeneous precipitation-dissolution mechanisms with transport of materials within the fault zone, or diversely rich Mg- and Fe-rich fluids that circulated through the faulted rocks.

The large variety of chlorite-smectites in these samples is also seen by plotting the compositionally modeled percentage of chlorite against its octahedrally coordinated metal content (Fig. 7B). The lowest abundances of chlorite layers, and hence the most smectite-rich varieties, are present in the 3295 m MD fault-rock sample. Over half of the chlorite-smectite particles measured in this sample contain ~30% or less of di, diotahedrally or di, triotahedrally coordinated chlorite. The other mixed-layered particles contain 40% or more of the triotahedrally chlorite variety, and these are the most chlorite-rich minerals (90% chlorite, 10% smectite). A similar mixture of chlorite-smectite types was detected in the 3191 m MD sample. However, the chlorite-poor, di, diotahedrally coordinated variety appears to be less abundant. These analyses also indicate a lower content of smectite (average ~48%, n = 22) for the chlorite-smectite minerals for this sample, compared to the 3191 m MD fault rock (average ~61%, n = 12).

DISCUSSION

There is now a general consensus on the importance of weak clay minerals in the intensely foliated fault gouge of the two active creeping sections, southwest deformation zone and central deformation zone, of the San Andreas fault zone at Parkfield. However, the precise mechanisms of deformation resulting in fault creep remain a topic of continuing debate. Based on microstructural observations, Schleicher et al. (2006, 2010) and Holdsworth et al. (2011) suggested that the clay mineral fabric and localized stress-induced dissolution-precipitation contribute to the mechanical weakness of the intensely foliated fault rock. Schleicher et al. (2010) documented in their high-resolution microscopic study the occurrence of smectitic nanocoatings on closely spaced and interconnected slip surfaces in isolated samples. Holdsworth et al. (2011) described similar interconnected clay networks at the micron to centimeter scale of observation across the active fault segments. Lockner et al. (2011) considered the presence of metasomatically formed triotahedral Mg-smectite (saponite) in the serpentine gouge to explain the creep behavior, with suitably low frictional strength (µ ≤ 0.2) and a close to zero healing rate (Carpenter et al., 2011; Lockner et al., 2011), which could explain the inferred low absolute shear strength of the San Andreas fault (Lachenbruch and Sass, 1980; Zoback et al., 1987). Similar to prior work, the weakness of the material is attributed directly to the abundance of smectite in the bulk rock, but they estimated >60% content based by petrographic analysis (Lockner et al., 2011).

A significant problem with the proposal that pure (Mg-)smectite is responsible for creep behavior of the San Andreas fault is that these
mineral phases are generally unstable at temperatures >150 °C (Inoue and Utada, 1991) and are therefore expected not to occur at depths >4 km (assuming the present geothermal gradient). Within this context, fault weakness below ~4 km remains a question of debate. Consequently, additional mechanisms are invoked to explain fault weakness at these depths, such as the presence of other weak mineral phases like talc (Moore and Rymer, 2007; Wibberley, 2007), pore-fluid pressures (Rice, 1992; Faulkner and Rutter, 2001; Jefferies et al., 2006a, 2006b; Fulton and Saffer, 2009; Wu, 2011), or stress-induced solution-precipitation creep (Holdsworth et al., 2011). Here, we propose the potential role of other clay mineral phases in the fault zone in terms of their formation conditions and stability at depth, and in particular highlight the implications of the chlorite-smectite mixed-layer minerals for understanding faulting mechanisms down to the brittle-ductile transition zone.

Fault Zone Clay Mineralogy and Conditions at Depth

All mudrock samples collected during phase III drilling in the SAFOD borehole and investigated in this study contain mixed-layer clay minerals of illite-smectite and/or chlorite-smectite (Fig. 3). The samples investigated in the southwest deformation zone and the central deformation zone (the area of recent casing deformation) contain, in addition to saponite (Lockner et al., 2011) and serpentine minerals, a characteristic assemblage of Mg-rich chlorite and chlorite-smectite. The overall mineralogy in samples taken during phase III is similar to spot-core samples and cuttings taken during drilling phases 1 and 2, as well as to the rocks in the pilot hole. The cuttings from the pilot hole taken between 488 and 914 m and between 1585 and 2012 m MD show chlorite and chlorite-smectite. The overall mineralogy in the sedimentary rock, but they are absent in granite (Solum and van der Pluijm, 2004).

On the other hand, the washed cuttings from the SAFOD main hole exhibit a variety of mineral assemblages, including highly variable amounts of smectite occurring as illite-smectite and chlorite-smectite mixed-layer phases (Solum et al., 1986; Bradbury et al., 2007; Draper-Springer et al., 2009; Schleicher et al., 2009a, 2009b). The spot-cores taken from the main hole during phase II (3066 m, 3426 m, ~3300 m, ~3200 m MD) show on average similar amounts of mixed-layer illite-smectite minerals but with varying degrees of ordering and smectite abundance, whereas the deepest samples at 3992 m have the lowest amount of smectite in their mixed-layered illite-smectite phases (2%–5%; Schleicher et al., 2009b).

Temperature Conditions

Many studies have been conducted on the occurrence and stability of illite-smectite (e.g., Wu et al., 1975; Junfeng et al., 1997; Agard et al., 1999; Day-Stirrat et al., 2010), but only a few investigations have been done on the stability of chlorite-smectite and/or chlorite minerals (e.g., Schiffman and Staudigel, 1995). The average temperature for smectite-dominated, poorly ordered, illite-smectite minerals in burial environments is ~80–150 °C (Velde et al., 1986; Srodon et al., 1986; Srodon et al., 1986; Huang et al., 1993; Pollastro, 1993; Blanc et al., 1997) and up to ~220 °C for illite-smectite in hydrothermal environments (Day-Stirrat et al., 2010). With a normal geothermal gradient of 25–30 °C/km, this would reflect stability at depth down to ~5.5 km (Fig. 8). R3 type illite-smectite minerals with lower quantities of well-ordered interlayered smectite are,

### Table 1. Quantitative Microchemical Analyses of Chlorite and Chlorite-Smectite Using Weight Percent Oxides, Calculated Based on 14 Oxygens

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The conversion of smectite to chlorite, as advocated through randomly (chlorite-smectite) or regularly ordered (corrensite) interlayers, has been reported from prograde metasalts (Bettison and Schifffman, 1988; Bevins et al., 1991) and sedimentary sequences (Helmhold and van der Kamp, 1984; Chang et al., 1991). With increasing temperature, chlorite-smectite can form at temperatures as high as 250 °C (Suchecki et al., 1977; Kristmannsdottir, 1979). Fluid-dominated systems can produce significant amounts of mixed-layered clays by dissolution of higher-temperature crystalline phases, such as the deformed and fragmented chlorite and chrysotile grains shown in Figure 6C. Importantly, in such systems, there are typically higher proportions of smectite interlayers developed at these temperatures in metabasite lithologies than found in equivalent illite-smectite minerals within mudrock sequences (Velde et al., 1986).

The 2.2-km-deep pilot hole in the San Andreas fault shows a variable, relatively high geothermal gradient that ranges from 27 °C/km up to 40 °C/km, with major transitions at the sediment-basement interface (770 m) and the intersection of a major shear zone at 1380 m (T1 in Fig. 8; Williams et al., 2004; Draper-Springer et al., 2009). The temperature near the bottom of the pilot hole at 2160 m (T2 in Fig. 8) is 92.5 °C. The SAFOD main hole shows very similar temperatures of 93.3 °C at ~2200 m depth (Williams et al., 2005). The average modern geothermal gradient may thus be as high as 38 °C/km in the uppermost crust (C. Williams, 2006, written commun., in Draper-Springer et al., 2009). Blythe et al. (2003) usedapatite fission track and (U/Th)/He analysis in the pilot hole to evaluate the geothermal gradient and exhumation history of the drill-hole site. They suggested a geothermal gradient of 35 °C/km and little or no evidence of recent exhumation. D’Alessio and Williams (2007) explored the exhumation history at the SAFOD site using thermochronometry and concluded that the area has experienced less than 1 km of exhumation or burial since the onset of the San Andreas fault activity at ca. 30 Ma. Using this geothermal gradient and limited exhumation, the temperatures that occur in the SAFOD borehole are suitable for the formation of smectite-containing clay minerals. Indeed, secondary illite-smectite and chlorite-smectite mixed layers occur at least down to a depth of 3311 m (Schleicher et al., 2009b, 2010) where a temperature of ~115 °C is to be expected. With a representative geothermal gradient of 35 °C/km, it is probable that chlorite-smectite minerals containing significant quantities of smectite will form within the fault zone down to 8–10 km depths, whereas the lower content of expandable components of illite-smectite minerals is expected to have less influence (Fig. 8). These depths are considerably greater than the stability depth for smectite suggested by Holdsworth et al. (2011), who only considered the thermal stability of pure smectites, such as saponite, and not that of the mixed-layer chlorite-smectite composition in this study.

### Fluid-Rock Interaction Processes

The presence of Mg is essential for the formation of the type of chlorite-smectite present in the SAFOD borehole. The reason why chlorite-smectite forms rather than chlorite is related not only to temperature, but also to the activity of Mg within the reactive fluid and the mechanism of formation (e.g., Bettison-Varga and Mackinnon, 1997). Chlorite can form directly from solutions or as a replacement product of minerals, whereas chlorite-smectite forms primarily by replacing preexisting clay minerals or other mineral phases (Murakami et al., 1999; Leoni et al., 2010). The proportion of smectite to chlorite in mixed-layered minerals is considered to decrease with increasing temperature. Corrensite (ordered 50:50 chlorite-smectite), which occurs within the fault zone at Parkfield, is considered to be stable between 100 and 200 °C (Velde et al., 1986) and, thus, would be present down to depths of ~5–6 km. Cheshire and Gueven (2005) investigated the conversion of chrysotile to Mg smectite and concluded that fibrous chrysotile is converted in mild organic acids at 200 °C to smectite with a thin foil morphology, reflecting our observations described earlier. The Mg-rich chrysotile tubes in Figure 6C show deformation and dissolution features along their surfaces. We surmise that the surrounding packages of 30–50-nm-thick chlorite-smectite precipitated as a lower-temperature reaction product from chrysotile. Similarly, chlorite alters to chlorite-smectite (including corrensite) at these depths.

Although the average amount of smectite present in chlorite-smectite close to or within the creep zones typically varies between 20% and 50%, as determined by XRD, there is very strong heterogeneity in the smectite content of individual chlorite-smectite particles within any one given sample (Fig. 7A). Variations between 10% and 90% smectite (90%–10% chlorite) can occur, together with differences in the octahedrally occupied metal content of chlorite (Fig. 7B). Such a broad range of chlorite-smectite types occurring within single fault-related rock samples indicates a complex alteration history that most likely resulted from the repeated influx of fault-related fluids of varying temperature and chemistry. It is considered unlikely that the complex assemblages resulted from the exhumation history. As the maximum

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**Figure 8.** A temperature (°C) versus depth (km) profile extrapolated down to 10 km depth showing the clay mineral stability fields that are to be expected within the fault zone taking into consideration a range of possible geothermal gradients for the San Andreas Fault Observatory at Depth (SAFOD) borehole (25–40 °C/km span). Increasing geothermal gradients indicate different mineral formation at different depths. T1, T2, and T3 are the temperatures measured in the SAFOD borehole. The dotted line shows the depth where the cores were drilled during phase III in 2007. R—reichenweite, I—illite, C—chlorite, S—smectite.
temperature attained in SAFOD rocks is not considered to have been significantly higher than current borehole temperatures, with mean vitrinite reflectance values not exceeding 0.93% (Kirschner et al., 2006), we suggest a strong chemical control on the formation of the clay mineral phases. The diverse assemblages may result as nonequilibrium assemblages formed under conditions of localized and restricted fluid flow, whereby the transport of Mg formed the limiting factor as to how much interlayered fluid flow, whereby the transport of Mg formed.

**Implications for Fault Behavior**

It is increasingly recognized that clay minerals play an important role in fault weakening behavior, which increases with the number of water layers stored in interlayer sheets of smectite (e.g., Wu et al., 1975; Saffer and Marone, 2003; Ikari et al., 2007; Morrow et al., 2007; Collettini et al., 2009). In earlier contributions (e.g., Schleicher et al., 2006, 2010), we demonstrated the role of newly grown illite-smectite on displacement surfaces close to the actively creeping segment of the San Andreas fault that was cored down to ~3 km vertical depth (~3.9 km MD). Instead, samples described in this paper contain chlorite-smectite coatings on displacement surfaces, which imply that a range of clay mineral coatings can be formed that are stable down to greater depths than R0 and R1 illite-smectite coatings. Based on today’s geothermal gradient of 25–35 °C/km and the stability of chlorite-smectite, we predict that the formation of clay coatings can occur as deep as 8–10 km where the activity of Mg is appropriately high (Fig. 8). We propose, therefore, that smectite-bearing clay coating, and in particular the chlorite-smectite minerals formed by the dissolution of mafic lithologies, governs brittle fault behavior down to the brittle-plastic transition.

The frictional behavior of smectite-chlorite phases has not been extensively studied yet, especially at depths where illite-smectite is not expected to be stable (cf. Fig. 8). Published work on smectite-rich fault rocks shows that they are very weak but leaves open questions about the frictional strength of chlorite-smectite phases, such coronites, at greater depths. The stability of Mg-rich chloritic clays at higher-temperature conditions offers a possible explanation for fault weakness at depth, pointing the way forward for important experimental and analytical studies. However, laboratory experiments conducted at appropriate temperatures and pressures on hydrated chlorite-smectite phases will be needed to test this hypothesis, which would require artificial samples rather than naturally exhumed (or shallowly drilled) samples, which have typically been altered since their initial formation.

**ACKNOWLEDGMENTS**

The National Science Foundation (EAR-0345985 and EAR-0738435) and the Deutsche Forschungsgemeinschaft (SCHL 1821/1-1 and 1-2) provided financial support for our SAFOD research. We thank our SAFOD colleagues for many stimulating and challenging discussions, especially on the importance of clay in fault behavior. Jafer Hadizadeh, Bob Holdsworth, Diane Moore, and Demian Saffer are thanked for constructive reviews that significantly improved the paper, although we remain solely responsible for the interpretations.

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