

Origin and significance of clay-coated fractures in mudrock fragments of the SAFOD borehole (Parkfield, California)

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[1] The clay mineralogy and texture of rock fragments from the SAFOD borehole at 3067 m and 3436 m measured depth (MD) was investigated by electron microscopy (SEM, TEM) and X-ray-diffraction (XRD). The washed and ultrasonically cleaned samples show slickensite striations and thin films of Ca-K bearing smectite that are formed on polished fault surfaces, along freshly opened fractures and within adjacent mineralized veins. The cation composition and hydration behavior of these films differ from the Namontmorillonite of the fresh bentonite drilling mud, although there is more similarity with circulated mud recovered from 3479 m MD. We propose that these thin film smectite precipitates formed by natural nucleation and crystal growth during fault creep, probably associated with the shallow circulation of low temperature aqueous fluids along this shallow portion of the San Andreas Fault. **Citation:** Schleicher, A. M., B. A. van der Pluijm, J. G. Solum, and L. N. Warr (2006), Origin and significance of clay-coated fractures in mudrock fragments of the SAFOD borehole (Parkfield, California), *Geophys. Res. Lett.*, 33, L16313, doi:10.1029/2006GL026505.

1. Introduction

[2] The San Andreas Fault Observatory at Depth (SAFOD) provides an ideal opportunity to investigate the nature of fault-related clay mineral assemblages along an active portion of a plate boundary [Wintsch *et al.*, 1995; Scholz, 1999; Zoback, 2000; Hickman *et al.*, 2004]. The occurrence of low layer charged smectitic clays are particularly important because of their ability to swell, exchange cations, and transform at low temperatures [Ahn and Peacor, 1986; Cuadros and Altaner, 1998]. In addition to their reactive behavior, the combination of a high water content and very low permeability gives the swelling clays their lubricating properties. The occurrence of smectite-bearing fault rock has, therefore, been suggested to contribute to the weakening of faults and is possibly a controlling factor in governing seismic stick-slip versus creep mechanisms [Wu *et al.*, 1975; Chester *et al.*, 1993; Morrow *et al.*, 2000; Warr and Cox, 2001; Bedrosian *et al.*, 2004]. Although swelling clay mineral assemblages have been described along the surface

trace of the San Andreas Fault [e.g., Wu *et al.*, 1975] and along exhumed portions of the fault system [e.g., Solum *et al.*, 2003], our knowledge on the depth distribution of these minerals along the fault zone is limited.

[3] In this contribution we report the first occurrence of natural smectite-coatings at ca. 3 km depth along polished fractures and mineralized veins within mudrock fragments recovered from the SAFOD drill hole (stars in Figure 1a). Based on a detailed microscopy, microchemical and diffraction study of the well-washed rock fragments, we have been able to distinguish between the natural smectite and that introduced via the drilling mud.

2. Samples and Methods

[4] Rock fragments were collected from a spot-core of a clay-rich shear zone at 3067 m MD (Figure 1a). This part of the bore hole represents a potentially active section of the fault zone, although it is not considered to contain the main fault trace [Zoback *et al.*, 2005; Ellsworth *et al.*, 2005]. The grayish-black, fine-grained fragments are up to 10 mm in average length and show distinct polished surfaces with visible striations. Other rock samples with similar polished surfaces were collected at 3436 m MD from inside a core catcher after a failed coring attempt. The rock fragments were carefully washed and ultrasonically cleaned to remove the bentonite drill-mud from the rock surfaces. Bentonite was used as a drilling fluid during rotary drilling and during the failed coring attempt, whereas a KCl-brine was used during the coring run at 3067 m MD. The nature of rock surfaces and freshly opened fractures were then investigated using scanning electron microscopy after carbon coating.

[5] The fracture-coating and vein filling minerals were investigated by high-resolution transmission electron microscopy (HRTEM) and analytical electron microscopy (AEM) following the analytical procedure outlined in Warr and Nieto [1998]. Representative rock chip samples were vacuum impregnated with L.R. White resin to prevent a collapse of the smectite interlayers following the procedure of Kim *et al.* [1995]. Small copper washers (1 mm diameter) were glued onto the prepared thin section, then ion milled and carbon coated. HRTEM-AEM work was undertaken using a Philips CM12 scanning-transmission electron microscope (STEM) with a Kevex Quantum solid-state detector (120 kV/20 mA). This was combined with lattice-fringe imaging and selected area electron diffraction pattern (SAED) study. Qualitative AEM analyses of fixed octahedral and exchangeable cations were obtained using the intensity of dispersed X-rays obtained under consistent measurement conditions.

[6] X-ray diffraction (XRD) study was undertaken on minerals sequentially extracted from polished and striated

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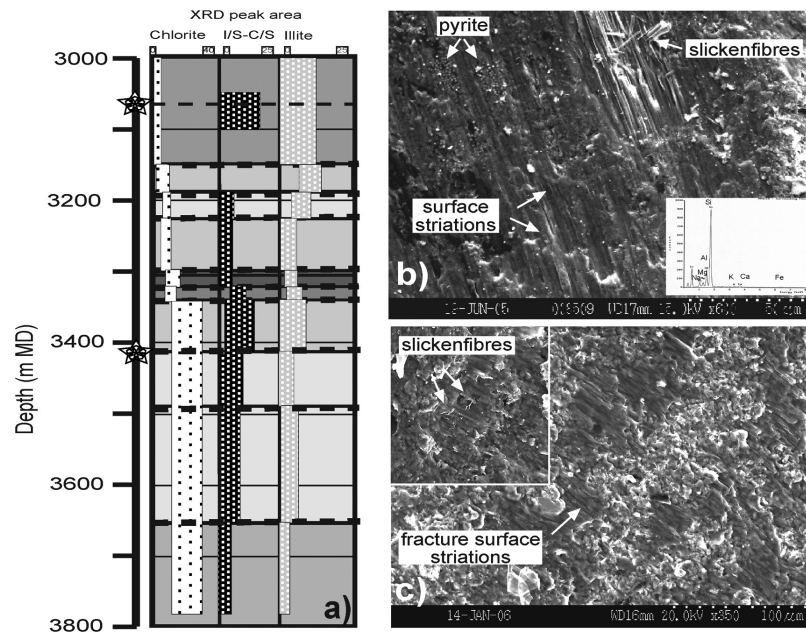


Figure 1. (a) Mineralogical characteristics of the SAFOD main hole obtained from XRD powder patterns. Main minerals are chlorite (chl), illite (ill), mixed-layer illite-smectite and chlorite-smectite (i-s/c-s). Major boundaries are shown by dashed lines and bands correspond to lithologic units (see Solum et al., submitted manuscript, 2006). (b) SEM image of well developed polished slip surfaces on sedimentary mudrock chips. (c) Note the distinct slickenfibres indicating authigenic growth of clays along the sheared surface striations occur as well in closed fractures with tiny developed slickenfibres.

fracture surfaces by ultrasonic dispersion in a solution bath. The extracted fraction was dried and analyzed using a Siemens-Bruker D5000 theta-theta diffractometer operating at 40 kV and 30 mA (Cu-K α radiation). Other material was scratched directly from the fracture surface and prepared as oriented smear mounts. All samples were studied under air-dried, ethylene glycol and water saturated conditions, using the same analytical settings and procedures.

[7] For comparison, two drill-mud samples were investigated. A fresh Na-montmorillonite used for drilling (MI-Gel) and a used drill-mud sample from 3679 m MD. These samples were prepared and analyzed by the same methods used for the fracture coatings.

3. Results

3.1. Scanning and Transmission Electron Microscopy

[8] The SEM images in Figures 1b and 1c show surface slickenfibres and an ultra thin film mineral coating that characterizes the polished fracture surfaces. The energy dispersive spectroscopy (EDS) patterns of these surface coatings reveal alumino-silicate minerals with a diverse cation content of Na, K, Ca, Mg, and Fe (Figure 1b). Pore spaces beneath the fracture surface are partly filled with neocrystallized pyrite that shows well developed cubic crystal forms and no signs of crystal damage. Large irregular grains of detrital illite and chlorite with curved and damaged particle shapes are surrounded by a compactional fabric. These minerals lie perpendicular to the polished fractures and contain notably higher concentrations of K, Mg and Fe. Authigenic fibrous to columnar Ca-alumino-silicate minerals were detected in the pores of some rock-chip fractures that are likely zeolite minerals (laumontite) [see Solum and

van der Pluijm, 2004; J. G. Solum et al., Mineralogical characterization of protolith and fault rocks from the SAFOD main hole, submitted to *Geophysical Research Letters*, 2006, hereinafter referred to as Solum et al., submitted manuscript, 2006]. Similar cations can be observed in all SEM and TEM analyses by EDS (see inset in Figure 2a) when comparing the elemental composition of the smectitic coatings with the fresh and used drilling mud. However, the drilling muds are best recognized by the occurrence of Na, Cl and S. Distinct differences also occur in the Si-Al ratio of the natural and contaminating smectite phases whereby the fracture surface clays are characterized by lower ratios than the Si enriched drill mud.

[9] A smectite phase with a similar elemental composition as the fracture coatings was also detected by TEM analysis of a mineralized vein in a sample recovered from 3436 m MD (Figure 2c). The wavy smectite particles are about 4 nm in thickness and have average d-values of ca. 13 Å. The particle flakes are randomly oriented, with characteristic curved shapes and coat the margins of the veins. Here, they lie parallel to thin packets of illite (ca. 100 Å in thickness) and illite-smectite (mixed-layer) phases.

[10] HRTEM imaging of the smectite within the drill mud also shows ~13 Å lattice spacing (Figure 2a), but here the packets are notably thin and wavy in character. The small particle thickness of this material explains the rapid electron beam damage observed when imaging the mud [e.g., Peacor, 1993]. Qualitative AEM measurements of individual particles were used to characterize compositional differences between the samples (Figures 2a and 2b). The elemental composition was similar to that recorded by SEM analysis; however, the elemental content of the frac-

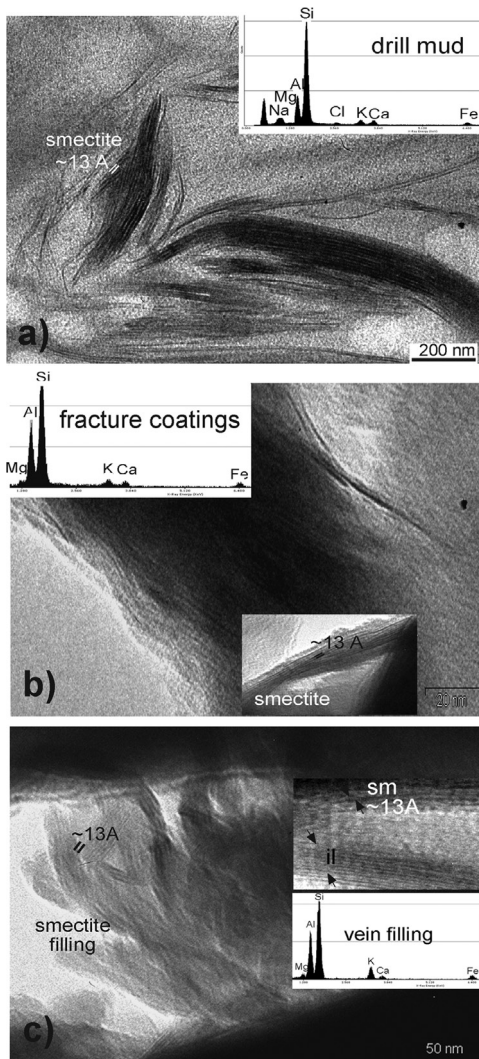


Figure 2. TEM lattice fringe images of the ultrasonically removed smectite (*sm*) particles from (a) the drill mud at 3679 m MD and (b) the fracture surface sample at 3067 m MD. (c) Vein filling of sample from 3436 m MD show smectitic phases with a similar elemental composition as the fracture coatings. The *d*-values of the randomly oriented flaky minerals have lattice fringes of ca. 13 Å in average, and occur together with thin packets of illite on the vein margins.

ture coating smectite is much less variable than the drill-mud smectite.

[11] Si-Al plots of all smectites follow linear trends with reliabilities (R^2) between 0.90–0.98 (Figure 3a). The linear trends reflect variations in measurement intensity caused by different particle thicknesses of the smectite minerals and the differences in gradient represent variations in Si-Al content. Clear differences in composition are also observed when plotting the sum of interlayer cations (Na + Ca + K) or octahedral cations (Mg + Fe) against the Si content (Figures 3b and 3c). The fracture coatings show less compositional variation in interlayer cations than the drilling muds. Whereas Ca occurs in all samples, Na is most abundant in smectite of the fresh drilling mud, and K in both the surface-coating smectite and the used drill mud.

The highest fluctuation in interlayer cation content is observed in the used drill mud from 3679 m, probably because of contamination from wall rock minerals in the borehole, the loss of fracture coatings during drilling, and some cation exchange with the circulating saline drilling fluids. A large variability also occurs in the octahedral cation content of the same sample. The Fe-Mg content of surface-coating smectite is higher than the fresh drilling mud, but does not differ significantly from that of the used drilling mud. This feature may reflect mixing with the fracture-coating smectite.

3.2. X-Ray Diffraction Analyses

[12] The X-ray diffraction patterns of the fracture-coatings and the unused drilling mud smectite show characteristic differences in behavior when saturated with ethylene glycol or water (Figures 4a and 4b). The air-dried sample of the fresh drill mud consists mainly of one water layer smectite at 12.6 Å that is characteristic of Na-montmorillonite with trace amounts of illite at 9.98 Å. After H₂O saturation, this smectite hydrated to interlayer thicknesses of

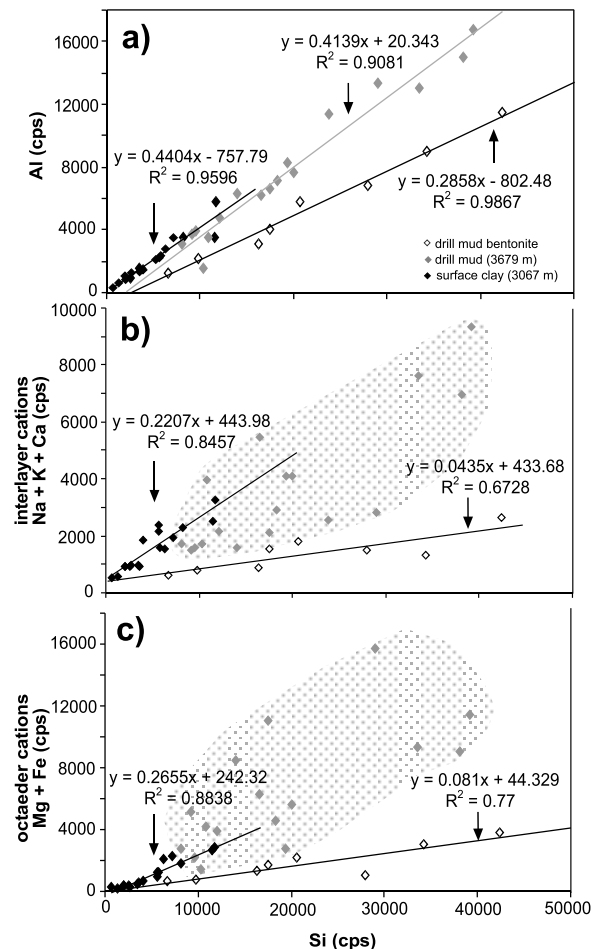


Figure 3. Qualitative microchemical analyses of the drilling mud and the smectitic surface mineralogies. The intensity of interlayer and non-interlayer cations is measured in counts per seconds (cps). Interlayer (Na, Ca, K) and octahedral (Fe, Mg) cations are summed and plotted against Si. The different smectites show a similar elemental composition, but different ratios and distributions.

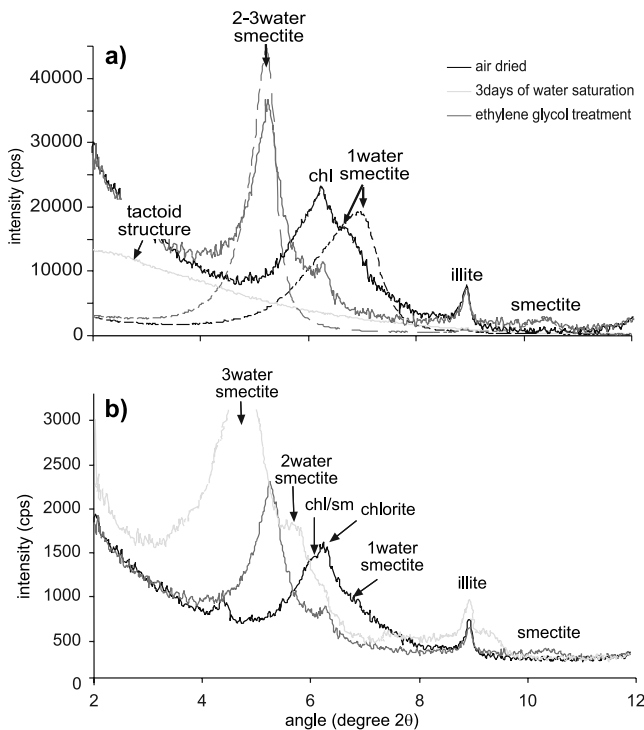


Figure 4. (a) X-ray diffraction pattern of the fresh bentonite drill mud (dashed lines) and the used drill mud from 3679 m MD (solid line). Whereas the fresh drill mud shows only little contamination with illite, (b) the used drill mud contains more chlorite and illite derived from the fracture surface clays the fracture surface smectite. Note the contamination with illite, chlorite (chl) and chlorite-smectite (chl/sm).

greater than 4 water layers and produced no distinct XRD reflections due to the formation of an incoherent particle structure (tactoid [Jasmund and Lagaly, 1993]). XRD analyses of the modified drilling mud from 3679 m depth show contamination with chlorite and illite, whereas the smectitic phases in this mud display a mixing behavior representative of both fracture-coating and Na-montmorillonite clay (Figure 4a).

[13] In comparison, the air-dried sample of the ultrasonically removed surface minerals show a smectite phase with a mixture of both 1- and 2 water layer structures (d-value of 12.6 Å and ca. 15 Å) overlapping with a chlorite peak at 14.1 Å (Figure 4b). A distinct illite peak is observed at 9.98 Å. After ethylene glycol treatment, the smectite peak expanded to ca. 17 Å, whereas the chlorite and illite peaks remained unchanged, indicating no mixed layered structures in this sample. After hydration for three days in saturated H₂O vapor, the smectite peak shifted to a typical 3-water-layer structure at 18.3 Å and coexists along with 2 and possibly 4 water-layer thicknesses at ca. 15 and 21 Å respectively. This hydration behavior is characteristic of smectites where Na is not the dominant interlayer cation [Jasmund and Lagaly, 1993].

4. Discussion

[14] One of the primary challenges of studying the swelling clay minerals of different rock fragments from

the SAFOD borehole is to distinguish between the natural mineral assemblages and clays introduced via the drilling mud. Natural clay minerals can be easily modified by cation exchange reaction, particularly when using supersaturated KCl brines to improve drilling performance in mudrock sequences. Such fluids were used for coring the bottom of the Phase 1 bore hole, where the sample at 3067 m MD originates (J. Thordsen, personal communication, 2005).

[15] Despite these difficulties, the variations in composition and hydration of smectite phases found as thin film coatings on well washed polished fractures and within mineralized veins are notably different from the fresh Na-montmorillonite based drilling muds. These smectite films show little to no contamination by Cl or S anions, and differ in both octahedral and interlayer cation concentrations with higher Al/Si, Fe-Mg/Si and Na-Ca-K/Si ratios than recorded in fresh mud or that expected to result from exchange with the drilling fluids. Furthermore the hydration behavior of these fracture-coatings is also characteristically different, with a 3 water layer structure dominating the H₂O-saturated condition with Ca and K interlayer cations, as opposed to the Na-dominated drilling mud states hydrated to form tactoid structures [Jasmund and Lagaly, 1993].

[16] Based on these differences we conclude that a natural, swelling smectite phase is present in the clay-rich fault rocks from 3067 m MD and the mudrock from 3436 m MD. This authigenic phase occurs both as oriented platy and fibrous minerals, forming thin film coatings that can be recognized in hand specimen by the occurrence of well polished surfaces. The slickensite geometries and well developed texture of these clays are interpreted as mineral coatings on microfault surfaces that formed synchronous with some increments of displacement. However, based on the described textural relationships the timing of initial fracture formation remains unclear and the clay-films could represent growth along reactivated structures.

[17] The thin-film smectite phase is recognized but difficult to characterize in the whole-rock mineralogy (Solum et al., submitted manuscript, 2006), and is best detected by electron microscopy studies after ultrasonic extraction of the surface particles. The association with illite-smectite mixed layering detected in TEM can indicate the relatively high K amount in the smectite phases was derived by partial dissolution of adjacent clay particles. Other possible sources of cations remobilised to form the surface precipitates are the breakdown of chlorite, biotite or other mafic minerals. Interestingly, the analyses of the drilling mud reveal significant contamination by natural clays of the mudrock lithologies. The broad scatter of composition reflects a mixture of the Na-montmorillonite from bentonite mud with the natural smectite phase of fracture coatings, together with chlorite and illite grains from the mudrock matrix. Whereas interlayer exchange with K and Na is possible, the different types of octahedral cations are considered to be distinctive of differences in mineral assemblage.

[18] The smectite thin films are interpreted as authigenic phases formed by dissolution-precipitation reactions during the movement of aqueous fluids along permeable fractures and veins at possible temperatures of ~130°C [Moore and Reynolds, 1997; Robinson and Santana de Zamora, 1999]. This coincides with the temperatures measured at these depths of the San Andreas Fault [Williams et al., 2005].

As no direct replacement of detrital grains was observed, precipitation from migrating fluids is the likely mechanism for deposition on slip surfaces. This is consistent with the suggestion of fluid-driven seismicity and the occurrence of microearthquakes and creep in the low resistivity zone at Parkfield [Unsworth *et al.*, 1997], although elevated fluid pressures have yet to be observed in the SAFOD hole [Zoback *et al.*, 2005].

[19] In the vicinity of SAFOD, the San Andreas Fault is moving through a combination of aseismic creep and repeating micro-earthquakes [Hickman *et al.*, 2004]. These well oriented smectite coating and slickenfibres geometries are interpreted as precipitation associated with slow creep motion in this segment of the fault zone and, thus, represent relatively long-term displacements, as nucleation and crystal growth are generally envisaged to be a slower process than the duration of seismic slip events.

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