

Sericite from the Silverton caldera, Colorado: Reply

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Is sericite from the Silverton caldera composed of a single phase (illite), as proposed by Eberl et al. (1987), or is it a mixture of phases (illite + mixed-layer illite/smectite), as proposed by Altaner and Vergo (1988)? Is mixed-layer illite/smectite (I/S) itself two phases? By definition, a phase is a state of matter that is "uniform throughout, not only in chemical composition but also in physical state." The words are Gibb's, quoted by Atkins (1978). This definition is applied readily to the interior of an illite particle, and to the particle's surrounding solution or atmosphere. But the definition is difficult to apply to the interface between particle and solution, the region that comprises Altaner and Vergo's (1988) smectite. Where does the smectite phase end, and where do the solution and illite phases begin? Effects related to the presence of surfaces are negligible for most coarse-grained minerals, but are substantial for materials like sericite. In a system that contains submicroscopic particles that have a large proportion of charged surfaces, phase definition is complex and open to interpretation.

We prefer to view sericite, and other illitic clays having expandabilities <50%, as being composed of a single phase, illite, having a range of particle thicknesses. What Altaner and Vergo (1988) call a second thermodynamic phase, smectite, we interpret as a surface effect. Thus, the charged surface is understood to affect the surface free energy of the illite particle, rather than to be present as a separate phase. This simpler interpretation also provides insight into the origin of the material if particle-size distributions are analyzed.

Particle-thickness distributions, such as the one presented for sample SG1 in Figure 1, were determined by the Warren-Averbach method (Warren and Averbach, 1950; Klug and Alexander, 1974) for many of the previously studied sericites from the Silverton caldera (Eberl and Środoń, 1988). As with TEM investigations of illites and I/S having small expandabilities, the Warren-Averbach method does not detect the presence of separate illite, smectite, and illite/smectite phases, but rather detects illite particles with a range of particle thicknesses. One could decide arbitrarily on a specific thickness di-

viding an I/S phase from an illite phase, but measured distributions indicate a continuum.

If particle-thickness histograms for the sericites are re-plotted using reduced coordinates according to the Lifshitz-Slyozov-Wagner (LSW) theory (Lifshitz and Slyozov, 1961; Wagner, 1961; Baronnnet, 1982), a steady-state shape for the profile is present from sample to sample. This profile, which is independent of apparent K-Ar age, indicates that the clays have re-crystallized by Ostwald ripening (Eberl and Środoń, 1988). Ostwald ripening also indicates that a single phase is present with a variety of particle sizes. As ripening progresses, matter is transferred from the finer illite particles to the coarser illite particles through solution. This reaction is driven by differences in surface free energies between particles of a single phase. It is difficult to understand how a multiphase model could be applied usefully to this situation. The large standard deviation associated with the thickness measurements of illite particles is that expected for particles that have undergone ripening. Size distribution for particles will spread out as ripening progresses (Baronnnet, 1982), and, therefore, large standard deviations do not necessarily support the two-phase interpretation of Altaner and Vergo (1988). In addition, if the Ostwald ripening mechanism is operating, then the reaction can progress in one direction only, toward decreasing expandability as illite particles coarsen. The reaction never can be reversed to form increasing amounts of the smectite "phase."

Altaner and Vergo (1988) have suggested that all of the $2M$, sericites resulted from the younger, hotter event, and that all of the $1M$ clays formed during the older, cooler event. They also have suggested that the $2M$, clays are illite, that the $1M$ clays are I/S, and that a mixture of these two phases gives rise to the two XRD peaks found by deconvolution of the 002 reflections. Although a relation between polytypes and temperature was determined in our study, it was not as good of a relation as that suggested by Altaner and Vergo (1988). For example, the youngest dated sample (AR1) and the oldest sample (RM8) contain both polytypes (see Tables 1 and 9 in

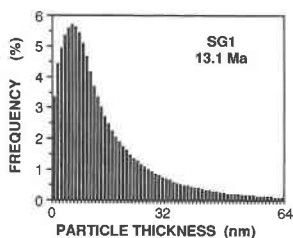


Fig. 1. Apparent particle-thickness distribution for sample SG1, determined from the 002 and 005 XRD reflections by the Warren-Averbach method.

Eberl et al., 1987). The second-order basal reflection of illite can be deconvolved into two separate peaks for samples that contain simple particle-thickness distributions, for samples that contain complex particle-thickness distributions, for old samples, and for young samples. XRD peaks for pure $1M$ (RM30) and for pure $2M_1$ (SG4) samples also yield to deconvolution. We suggest that the ability to deconvolve peaks, if not simply a mathematical artifact, results from the arrangement of fundamental illite particles on the XRD slide (i.e., both disarticulated and articulated illite particles are present), rather than from the presence of two separate phases.

The simultaneous formation of several polytypes in sericite from the Silverton caldera is in agreement with the experimental evidence of Amouric and Baronnet (1983). They determined that $1M_0$, $1M$, and $2M_1$ polytypes can nucleate side by side in the same system. Subsequently growth of these core structures during the initial layer-by-layer growth period can produce any of the three stacking structures, depending on environmental conditions such as temperature and degree of supersaturation. The type of structure propagated during the later spiral growth stage, however, depends on the structure near the surface of the particle during the creation of the screw dislocation step (Pandey et al., 1982).

The presence of disarticulated illite particles was hypothesized in the original paper in order to reconcile expandability measurements made by the conventional XRD peak position method with particle thicknesses measured by TEM. Altaner and Vergo (1988) have suggested that the smaller expandabilities measured by XRD are related to the presence of a separate illitic phase, rather than to the disarticulation of a single phase. They have stated that "If the concept of disarticulated illite particles is valid, diffracted intensities from these thin particles should be present in XRD patterns of all I/S minerals" [item 5, p. 1473]. We agree with this statement.

Data presented in Nadeau (1985) and in Eberl and Środoń (1988) indicate that a discrepancy between XRD and TEM expandability measurements is characteristic of all I/S. Expandabilities measured by the conventional XRD method for I/S from a variety of origins always are smaller for a given fixed interlayer-cation content than are expandabilities calculated from TEM measurements (Eberl and Środoń, 1988). Calculations (after Reynolds, 1980)

show that this phenomenon cannot be explained by admixture of discrete illite, as proposed by Altaner and Vergo for the Silverton sericites, nor can it be explained solely by the presence of disarticulated illite particles. The concept of disarticulated illite particles must be extended to include the concept of "short stacks" in order to explain the swelling characteristics of I/S having expandabilities greater than that determined for sericites from the Silverton caldera. The short-stack effect takes into account the concept that basal surfaces at the top and bottom of stacks of illite particles (MacEwan crystallites) are not involved in swelling (Eberl and Środoń, 1988). Expandabilities measured by XRD must be corrected for the presence of disarticulated illite particles and short stacks if expandability is to be related to the proportion of illite-particle basal surfaces.

Altaner and Vergo (1988) have cited NMR data (Altaner et al., 1988) to conclude that the charge of swelling surfaces in a sericite sample (RM30) is smaller than the charge of the illite layers in the interior of the particles. This evidence, together with the reaction of the clays during K saturation and with the structural formulae of the clays, is interpreted to indicate the presence of a separate smectite phase. We agree that the charge on the exposed basal surfaces of the illite particles is smaller than that between illite layers, but disagree that this charge difference necessitates the presence of a separate phase.

Eberl and Środoń (1988) determined a charge for the exposed surfaces [-0.48 per $O_{10}(OH)_2$], by a long extrapolation of CEC data to 100% expandable] that was identical to that determined by Altaner et al. (1988) for sample RM30 by NMR techniques, if their charge for the surface tetrahedral sheet (-0.34) is added to the octahedral charge from our chemical analysis (-0.14), thereby yielding a charge for the surface of -0.48 . Expandabilities used in our extrapolation were measured by the Warren-Averbach technique, a method that gives better correlations between expandability and other sericite properties than does the thin-sample Scherrer method used previously (Eberl et al., 1987). The charge determined for the basal surfaces of the particles is a mean charge. However, it is likely that the basal surfaces have a heterogeneous charge distribution: on K saturation and glycolation, some expanding layers collapse to 10 Å, some swell to 14 Å, and others swell to 17 Å (e.g., sample RM22 in Fig. 4 in Eberl et al., 1987). Such surface heterogeneity is expected for clays that have undergone Ostwald ripening, because some particles underwent dissolution, whereas others underwent growth. Thus, at least on a submicroscopic scale, it would be difficult to define a smectite phase based on the charge of basal surfaces.

Can a distinction between phases be made based on hydration properties? Experimental evidence indicates that the surfaces of macroscopic mica flakes are hydrated (Pashley and Israelachvili, 1984). This surface-hydration effect can be detected by XRD for illite, but not for muscovite, because the relative abundance of surfaces is so much greater for illite owing to its finer particle size. Thus,

the difference in the swelling properties of muscovite, illite, and I/S is dependent mostly on particle size. Illitic materials may appear to be heterogeneous (illite + I/S) when studied by XRD either because disarticulated illite particles are present, as with the Silverton sericites, or because illite particle-size distributions are bimodal, as with many shale samples. Thus, we consider illite (i.e., thick illite particles) and I/S (i.e., thin illite particles) to be a single phase, because particle size is not used in the definition of "phase."

To summarize, we believe that it is best to consider illitic material with a small expandability (<50%) as a single phase. Otherwise, definition of the "smectite" phase would have to be based on a material that is one-half liquid and one-half solid, the charge of which is heterogeneous and affected by the adjacent illite phase, the composition of which changes with the composition of the adjacent solution, and the structure of which is one-half of one unit cell thick. This material would be a phase that is not physically separable from the illite phase. It is difficult to reconcile these properties with the classical definition of a phase. In contrast, it may be useful to define two phases when treating the macroscopic behavior of the material (e.g., the exchange properties of bulk samples). However, such a definition would offer little insight into the crystal chemistry and origin of sericite.

Finally, applying Occam's razor, the multiphase model of Altaner and Vergo (1988) seems unnecessarily complex. Their model requires the appearance and disappearance of many phases as I/S decreases in expandability in response to diagenetic or hydrothermal alteration. With the single phase model, however, this reaction is viewed as illite crystal growth parallel to c^* , a growth that is accompanied by a changing surface term as the particles coarsen.

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