

## Sericite from the Silverton caldera, Colorado: Discussion

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Sericite is a common alteration product found in modern and fossil hydrothermal systems (McDowell and Elders, 1980; Lowell and Guilbert, 1970); it consists of mixed-layer illite/smectite (I/S) and has a high proportion of illite layers (Horton, 1985). Sericite from the Silverton caldera of the San Juan volcanic field in southwestern Colorado has recently been characterized with a variety of analytical techniques (Eberl et al., 1987). Eberl et al. (1987) should be commended for their multidimensional approach; however, we disagree with two critical interpretations made in their study. First, we think that the Silverton samples consist of two separate mineral phases, illite and illite-rich I/S. Second, we think that illitic I/S minerals contain layers with two distinct chemical compositions, layers with a smectite charge and layers with an illite charge. Thus, according to definitions in Zen (1962) and Garrels (1984), illitic I/S should be considered to be two thermodynamic phases, illite and smectite. Both issues are discussed below.

Our first difference in interpretation is that we believe there are two separate mineral phases in the Silverton samples. One phase is essentially pure illite ( $2M_1$  polytype), and the other is illite-rich I/S ( $1M$  polytype). Using X-ray powder-diffraction (XRD) data, Eberl et al. (1987) deconvolved two to three peaks in the  $17.8^\circ$   $2\theta$  region and suggested that these peaks result from a  $10\text{-\AA}$  component and an apparent I/S component in the samples. They concluded that the apparent I/S component is due to stacking of several fundamental illite particles with basal interfaces between particles that expand and accept water, glycol, and exchangeable cations. They interpreted the  $10\text{-\AA}$  component to be the result of disarticulated illite particles that are in enough misalignment to exhibit only  $10\text{-\AA}$  spacings to an X-ray beam (Fig. 7 of Eberl et al., 1987). If the model of Eberl et al. (1987) is correct, the concept of disarticulated illite particles should be considered in the XRD examination of all I/S minerals.

Eberl et al. (1987) formulated the concept of disarticulated illite particles because values of the percentage of illite layers in I/S [ $P_1(\text{XRD})$ ], measured using XRD data, were greater than values of  $P_1$  (TEM), measured using a Pt-shadowing technique and a transmission electron microscope. A deconvolution method that subtracts a discrete  $5\text{-\AA}$  peak from the XRD intensity around  $17.8^\circ$   $2\theta$  decreases the calculated  $P_1$  values and produces closer agreement between the XRD and TEM analyses. Eberl et al. also noted that correlations between physical proper-

ties (e.g., cation-exchange capacity or fixed-cation content) and  $P_1$  (deconvolved XRD) should be better than correlations between the same properties and  $P_1$  (nondeconvolved or conventional XRD). Finally, they interpreted results of the XRD examination of thin-sample preparations as supporting their model of disarticulated illite particles.

We agree that, under certain conditions, large crystallites of I/S can disarticulate. Na- and Li-exchanged smectite has been shown by XRD analysis to dissociate into single  $10\text{-\AA}$  2:1 layers by an osmotic swelling mechanism (Norris, 1954). TEM analysis subsequently showed that Na- and Li-exchanged I/S crystallites can also be disrupted at the smectite interlayer region (Nadeau et al., 1984a). Our disagreement with Eberl et al. (1987) concerns the nature of the specific  $10\text{-\AA}$  component in the Silverton samples.

Summarized below are six reasons why we suggest that the  $10\text{-\AA}$  component in the Silverton samples represents a separate mineral phase and not simply disarticulated illite particles of I/S.

1. Mineralogical and isotopic data of Eberl et al. (1987) support the existence of two illitic clay phases and two clay-forming events. An illite-rich sample consisting only of the  $2M_1$  polytype (SG4, Table 1) formed at  $322^\circ\text{C}$  during an event at 13.8 Ma. A more smectite-rich sample consisting only of the  $1M$  polytype (RM35A) formed at  $178^\circ\text{C}$  during an event at 20.3 Ma. Another sample containing both  $2M_1$  and  $1M$  polytypes (RM28) yields an intermediate K/Ar age of 17.4 Ma and has intermediate oxygen-isotope values for the I/S, interpreted by Eberl et al. (1987) to be due to the mixture of the two different sericite minerals. Moreover, nine of the sixteen analyzed samples are mixtures of  $2M_1$  and  $1M$  polytypes (Table 1 of Eberl et al., 1987). We interpret the deconvolved  $10\text{-\AA}$  component in the Silverton samples to be due to the  $2M_1$  mica phase and the  $1M$  phase as I/S.

2. Eberl et al. (1987) correctly stated that if the concept of disarticulated illite particles is valid, then correlations between physical properties and  $P_1$  (deconvolved XRD) should be better than between the same physical properties and  $P_1$  (conventional XRD). If our suggestion of two phases in the Silverton samples is correct, then physical properties should correlate better with  $P_1$  (conventional XRD). For the Silverton samples, physical properties correlate somewhat better with conventional XRD data than deconvolved XRD data. Correlations between  $P_1$  (decon-

**TABLE 1.** Isotopic temperature, K-Ar age, polytype, and mineral data for sericite samples from the Silverton caldera

Sample	Isotopic temperature (°C)	K-Ar age (Ma)	Polytype	$P_1$ (conventional) (% illite in I/S)
RM35A	178	20.3	$1M + R^*$	91.0
SG4	322	13.8	$2M_1$	97.2
RM28	62	17.4	$1M \gg 2M_1 + R^*$	96.7

Note: From Tables 1, 3, 9, and 11 of Eberl et al., 1987.

\*  $R$  = random rotations of 60° and 120°.

involved XRD) and fixed-cation content, cation-exchange capacity, and Kubler index yield  $R^2$  values of 0.27, 0.40, and 0.53, respectively, whereas correlations between  $P_1$  (conventional XRD) and the same properties have  $R^2$  values of 0.37, 0.52, and 0.53, respectively. In addition, extrapolation of fixed-cation contents versus  $P_1$  (deconvolved XRD) data to the pure illite end member yields a high layer charge of  $-1.09$ , whereas  $P_1$  (conventional XRD) data extrapolate to a more realistic layer charge of  $-0.94$ .

3. Eberl et al. noted that for samples prepared from progressively more dilute solutions,  $P_1$  (conventional XRD) varies significantly and  $P_1$  (deconvolved XRD) remains constant (Table 5 of Eberl et al., 1987), thereby supporting their model of disarticulated illite particles. However, these data are also compatible with our suggestion of two micaceous phases in the Silverton samples. Variations in sample thickness can produce different degrees of preferred orientation. If either the discrete mica or the I/S phase orients better than the other, then nondeconvolved XRD peaks (and inferred  $P_1$  values) should vary; however,  $P_1$  from deconvolved XRD peaks should remain constant. These predictions are consistent with the observations of Eberl et al. (1987).

4. Fundamental particle measurements by TEM from Eberl et al. (1987) appear to support a two-mineral assemblage. If the Silverton samples contain only one I/S phase, then the thickness of fundamental particles should be relatively uniform (e.g., samples RAN, DIB, and LPB of Nadeau et al., 1985). Presence of a discrete illite phase plus an I/S phase should produce two relatively distinct populations of fundamental particles. The extremely large standard deviations associated with size measurements of illite particles (Table 4 of Eberl et al., 1987) seem to support our interpretation; however, it would be more appropriate to make conclusions from the actual size distributions of illite particle size measured by TEM.

It is important to emphasize that the very thick particles should contribute more XRD intensity than very thin particles. For example, if a sample contains equal numbers of 50-nm-thick particles and 1-nm-thick particles, the XRD pattern should be dominated by the 50-nm component. To best address the question at hand, therefore, TEM distributions of particle size should be considered on the following axes: (frequency of particle size  $\times$  particle thickness) versus particle thickness.

5. 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. Other XRD studies of pure I/S minerals, such as those of bentonite beds, do not show the presence of discrete 10-Å components (Reynolds and Hower, 1970; Hoffman and Hower, 1979; Altaner et al., 1984).

6. Finally, a possible explanation for the discrepancy between XRD and TEM estimates of  $P_1$  is that the top and bottom tetrahedral sheets of each I/S crystallite are smectitic. The mineral composition (illite vs. smectite) of these sheets cannot be analyzed by using the XRD modeling technique. If the top and bottom tetrahedral sheets are smectitic, the additional smectite decreases the illite content estimated by XRD. This interpretation has recently been used to explain a discrepancy similar to that observed by Eberl et al. (1987) in which XRD estimates of illite content were significantly higher than those made using nuclear magnetic resonance (NMR) spectroscopy (Altaner et al., 1988).

Our second difference in interpretation is that we think illitic I/S minerals contain two types of layers with distinctive chemical compositions and, therefore, should be considered to be two thermodynamic phases, illite and smectite. We use terminology established by Zen (1962) and Garrels (1984), who define two-phase I/S as containing both illite and smectite compositions and one-phase I/S as a single composition for a given mineral. Eberl et al. (1987) and several previous investigators (Nadeau et al., 1984a, 1984b; Wilson and Nadeau, 1985; Nadeau and Bain, 1986; Inoue et al., 1987) have suggested that illitic I/S should be considered as one homogeneous phase, illite. This question is critical to thermodynamic studies of I/S minerals (Zen, 1962; Aagaard and Helgeson, 1983; Garrels, 1984).

Several lines of evidence support our interpretation that illitic I/S contains two chemically distinct types of layers and should be considered two phases.

1. NMR spectroscopy with inversion/recovery techniques permits direct analysis of the tetrahedral composition of expandable and dehydrated interlayer regions in I/S minerals. A recent NMR study of illitic I/S (Altaner et al., 1988) shows that expandable interlayers contain low-charge tetrahedral sites (layer charge =  $-0.34$ ) and that dehydrated interlayers contain high-charge tetrahedral sites (layer charge =  $-0.81$ ).

2. If illitic I/S minerals contain tetrahedral sheets having the same high-charge composition surrounding both hydrated and dehydrated interlayers, as suggested by the one-phase model of constant composition in illitic I/S, then introduction of K should irreversibly dehydrate the expanding interlayers. Introduction of K to a low-charge smectitic interlayer should not cause irreversible dehydration (MacEwan and Wilson, 1980, p. 203). K saturation of the Silverton samples does not irreversibly dehydrate the expandable layers (p. 917 in Eberl et al., 1987).

3. Values of layer charge for bulk I/S samples ( $-0.83$  to  $-0.91$ , Table 8 of Eberl et al., 1987) are significantly less than values inferred for the dehydrated layers ( $\sim -1$ ,

Fig. 16 of Eberl et al., 1987). These differences are not predicted by the one-phase model of I/S and are compatible with the two-phase model of illitic I/S.

In summary, we think that data from both the Eberl et al. (1987) study and other studies strongly support our conclusions that two mineral phases are present in the Silverton samples (a discrete illite phase and an I/S phase) and that illitic I/S contains two chemically distinct layer types, illite and smectite. The first question could be further addressed by the nature of the size distribution of fundamental particles measured by TEM. Observation by TEM of a continuum of particle sizes would support Eberl et al.'s hypothesis, whereas observation of distinct populations of particles would support our hypothesis. Regarding the second question, further work needs to be done to determine if the chemically distinct layer types in I/S actually behave as two thermodynamic phases. Garrels (1984) presented compositions of natural waters that support the two-phase model. In addition, long-term phase equilibria experiments on illitic I/S by Rosenberg et al. (1985) support the two-phase model of I/S.

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