

NOTES

AN INTERSTRATIFIED ILLITE/SMECTITE MINERAL FROM THE
HYDROTHERMAL DEPOSIT IN SIBERT, RHONE, FRANCE

Key Words—Chemical composition, Electron microprobe, Hydrothermal, Illite/smectite, Interstratification.

Since their recognition as distinct minerals (Bradley, 1950; Caillère and Henin, 1950; Caillère *et al.*, 1950), rectorite and rectorite-like minerals have been studied by many investigators. Although the X-ray powder diffraction (XRD), infrared (IR), and differential thermal analysis (DTA) data for these minerals appear to be fairly well established (Brindley, 1956; Brown and Weir, 1963a, 1963b; Farmer and Russell, 1964; Reynolds and Hower, 1970; Shimoda and Brydon, 1971), only a few chemical analyses of these natural interstratified minerals are available (e.g., see Korolev, 1960; Brown and Weir, 1963a, 1963b; Kodama, 1966; Pevear *et al.*, 1980; Matsuda *et al.*, 1981), probably because of the difficulty that exists in separating these fine-grained materials from other clay minerals that accompany them in natural assemblages. In the present investigation, electron microprobe analyses have been made on very small quantities of a purified sample of an ordered, interstratified illite/smectite from a hydrothermal porphyry deposit near Sibert (Rhône, France). The same sample has been characterized by XRD, IR, and DTA.

EXPERIMENTAL

An ordered, interstratified illite/smectite occurs in the Sibert porphyry copper-molybdenum deposit as a late stage hydrothermal alteration product. It probably formed below 200°C (Beaufort, 1981), and is commonly associated with calcite in veinlets (Figure 1) and more rarely with altered feldspars. This interstratified illite/smectite has crystallized as small flakes rimming calcite in veins or as aggregates in altered feldspars; in both occurrences the crystal size is $<10\ \mu\text{m}$. Calcite-illite/smectite veins with width between 200 and 50 μm were selected and extracted from core samples with a microdrill. The interstratified illite/smectite averages 20 to 40% of the extracted material. XRD patterns were obtained from random and oriented samples using a Philips PW 1730 apparatus operated at 40 ma and 40 kV, with $\text{CoK}\alpha$ radiation. Untreated, oriented samples were saturated with K and Li and subjected to ethylene glycol treatment to test the expandability of the interstratified mineral present. The samples were also heated to 110°, 220°, 300°, and 500°C and XRD patterns obtained.

Samples consisting of the interstratified illite/smectite phase plus calcite were purified by calcite dialysis as follows: the sample was closed in a cellophane membrane and immersed in an HCl solution at pH 3 for 8 days. The HCl solution was changed twice a day. About 10 mg of purified sample were collected by centrifugation. After verifying the absence of calcite by XRD, IR and DTA analyses were carried out to characterize the purified interstratified mineral. Approximately 0.5 mg of the purified powder was sealed in Araldite, and a thin section was made. Electron microprobe analyses were performed with a focused beam of 1- μm diameter using a Cameca MS 46 microprobe equipped with a Tractor Northern solid state detector and data-treatment system. A beam current of 1–1.5 na was used at 15-kV excitation potential. These conditions prevented the loss of alkalis and the breakdown of the clay minerals during the counting time (120 sec).

DTA were recorded on a SETARAM M4 DTA apparatus equipped with a Kipp and Zonen micrograph. About 7 mg of purified specimen was heated at a rate of 10°C/min. The IR spectrum in the 4000–300- cm^{-1} frequency region was recorded using 300-mg KBr disks containing 0.5 mg of the purified specimen and a Beckman 4120 spectrophotometer.

RESULTS

X-ray powder diffraction data

Figure 2 shows the XRD data of oriented sample. The interstratified mineral gives a series of XRD reflections at 25.5, 11.80, 5.05, and 3.28 Å. Saturation with ethylene glycol gave rise to reflections at 28, 13.5, 9.18, 5.30, 4.50, and 3.35 Å. These data show that the higher order reflections are not strictly integral, probably due to imperfect 1:1 interstratification in this mineral. After the sample was heated, the first-order reflection shifted to 21.3 Å at 300°C and 19.8 Å at 550°C. The expandability of the sample saturated with potassium persisted after ethylene glycol treatment and heating at 110°C. The Hoffmann-Klemen test (Hoffmann and Klemen, 1950) shows that the smectite layers have beidellitic substitutions because their expandability is not modified by Li saturation. A comparison of *d* values for the reflection $(001)_{10}/(003)_{27}$ and $(005)_{27}/(003)_{17}$ of the Sibert interstratified mineral by the method of Reynolds and Hower (1970) indicates that the mineral contains 35% expandable layers. The 060 value measured for randomly oriented material is 1.491 Å. The XRD data, therefore, suggest that the Sibert specimen is a partially ordered, mixed-layered illite/smectite with 35% expandable layers. Therefore, this mineral can be considered as an approach to 1:1 ordered arrangement with proportions of layers about (35% I/35% S) ordered, plus 30% more I layers added in some random manner. The smectite layers are beidellitic. Very similar XRD reflections were reported by Eberl and Hower (1977) for a synthetic, ordered, interstratified illite/smectite with about 35% expandable layers, a material that was subsequently called K-rectorite (Eberl, 1978).

Infrared spectroscopy and differential thermal analysis data

The IR spectrum of the Sibert specimen agrees with rectorite or allevardite spectra in the literature (Farmer and Russell, 1964; Van der Marel and Beutelspacher, 1976).

The DTA curve shows a double endothermic peak at 100° and 190°C due to the removal of interlayer and cation-hydrated water and a single endothermic peak at 660°C due to dehydroxylation. An S-shaped peak system including an endothermic peak between 950° and 980°C and an exothermic peak above 1000°C suggested by a rise in the base line toward 1000°C may be explained by the breakdown of structure of the mineral and recrystallization of a new mineral phase (Sudo and Shimoda, 1970). The new mineral phase have not been identified in this study.

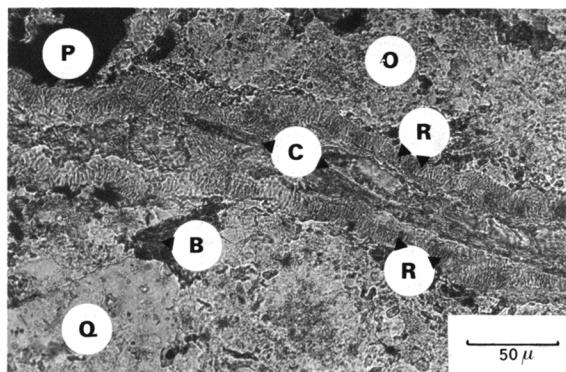


Figure 1. K-rectorite and calcite veinlet in Sibert porphyry. B = biotite; C = calcite; O = orthoclase; P = pyrite; Q = quartz; K = K-rectorite.

Electron microprobe analyses

Microprobe analyses were performed on 12 microflakes of Sibert specimen using the thin section described above. The width of the microflakes analyzed averaged 80 μm . Microprobe analyses are given in the Table 1. The sum of oxide weight percent is clearly less than 100% because (1) the H_2O content of this interstratified mineral cannot be measured with electron microprobe (Hower and Mowatt (1966) give about 10% H_2O in illite/smectite interstratified minerals) and (2) the density of clay dispersed in Araldite is less than that of the standards used. The radiations of all elements, however, were collected simultaneously using a Si(Li) detector; consequently the ratio between chemical components analyzed was not affected, and the structural formulae on the basis of 11 oxygens (dehydrated formulae) were calculated.

The composition of the mineral suggests that the octahedral sheets are very close to dioctahedral with dominant Al and minor Mg and Fe. In the structural formulae Mg has been arbitrarily assigned to octahedral sheets, although some Mg

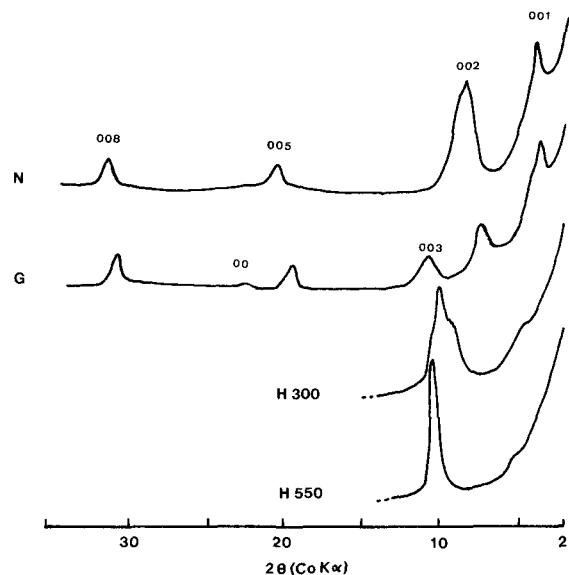


Figure 2. X-ray powder diffraction patterns of Sibert specimen. N = natural; G = ethylene glycol saturated; H 300 = heated to 330°C; H 550 = heated to 550°C.

Table 1. Microprobe analyses of Sibert illite/smectite.

| Oxide | Wt. % | | Cations per 11 O (anhydrous) | |
|--------------------------------|----------------|-----------------|------------------------------|----------------|
| | Average values | SD ¹ | Average values | Average values |
| SiO ₂ | 47.38 | 3.37 | Si | 3.65 |
| Al ₂ O ₃ | 23.95 | 1.99 | Al(IV) | 0.35 |
| FeO ² | 0.72 | 0.25 | Al(VI) | 1.83 |
| MnO | 0.10 | 0.09 | Fe ²⁺ | 0.05 |
| MgO | 0.93 | 0.58 | Mg | 0.11 |
| TiO ₂ | 0.12 | 0.04 | Ti | 0.01 |
| CaO | 0.48 | 0.09 | Mn | — |
| K ₂ O | 4.39 | 0.44 | Sum | 2.00 |
| Total ³ | 78.10 | 5.39 | Ca | 0.04 |
| | | | Na | — |
| | | | K | 0.44 |
| | | | Charge | 0.52 |

¹ Standard deviation.

² Fe total determined as FeO.

³ Total does not include water.

could exist in interlayer position. This possibility is supported by the results of potassium saturation of the Sibert specimen for XRD investigation which indicates a small amount of Mg^{2+} in the exchange solution. In spite of the fact that the amount of exchangeable Mg^{2+} was not measured with good accuracy, the presence of Mg interlayer cation not represented in structural formulae (Table 1) could explain the small excess of octahedral ions in the analyses containing the greatest amounts of Mg. Tetrahedral sheets are characterized by relatively low Al substitution which generates the main part of the layer charge. The interlayer cations are potassium and minor calcium. Sodium is not present.

DISCUSSION AND CONCLUSIONS

XRD, IR, and DTA investigations suggest that the Sibert specimen approaches an ordered interstratification of dioctahedral mica layers and smectite layers with about 35% expandable layers, which gives a superstructure reflection. Con-

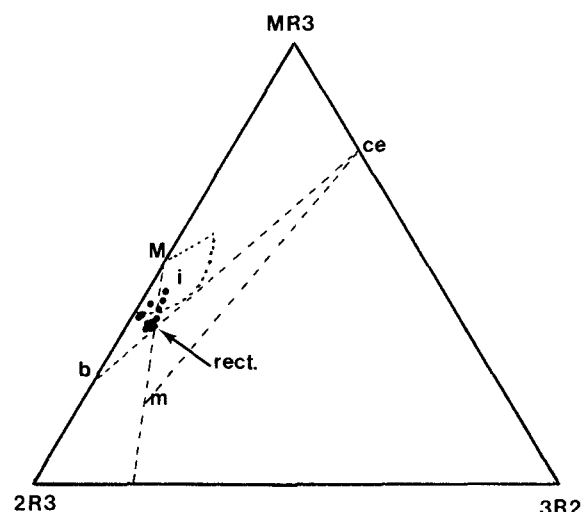
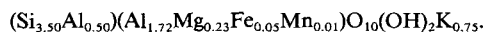


Figure 3. Compositions of the Sibert specimen plotted in $\text{Mr}^3\text{-}2\text{R}^3\text{-}3\text{R}^2$ representation (Velde, 1977). b = beidellite; ce = celadonite; i = illite; m = montmorillonite; M = muscovite; rect. = Sibert K-rectorite compositions.

cerning the expandable layers, the Sibert specimen formulae have been plotted in $MR^3 \cdot 2R^3 \cdot 3R^2$ chemiographic representation described by Velde (1972; 1977, 4–6). In this diagram, silica is in excess, MR^3 represents the feldspar composition (Na, K, 2Ca, and Al) in atoms, $2R^3$ represents trivalent ions plus Ti^{4+} , and $3R^2$ represents divalent ions (Fe^{2+} , Mg^{2+} , Mn^{2+}). This technique for plotting chemical data has been used in the present study because this diagram distinguishes among the dioctahedral silicate phases such as illite, beidellite, and montmorillonite. Consequently, the interstratified illite/smectites would give compositions intermediate between these three compositional fields, and the nature of the smectite layers could be estimated. In Figure 3, a general distribution of the chemical data is present between Mg-Fe rich illite and ideal beidellite composition fields. The Si/Al ratio of the Sibert specimen (average = 1.7) and the low Al for Si tetrahedral substitution suggest a low interlayer charge for the beidellite component. It seems reasonable to attribute the Ca^{2+} of the formulae to the beidellitic layers; but there is no evidence to indicate that they are the only interlayer cations in the beidellite layers. Concerning the nonexpandable layers, little can be deduced from these formulae except the potassic nature of the interlayer cation. A petrographic study of the Sibert porphyry alteration, however, has shown that during the lower temperature phase of the hydrothermal alteration, the ordered interstratified illite/smectite calcite episode was preceded by illite-calcite formation (Beaufort, 1981). This illite is a 1M polytype and shows a homogeneous composition giving an average structural formula:



Locally, traces of illite were detected occurring with ordered interstratified illite/smectite material during the XRD investigation, but there is no evidence that the illite component of the ordered interstratified illite/smectite mineral has the same composition as the illite reported above.

Several estimates have been made on the temperature of crystallization of K-rectorite and ordered, mixed-layered illite/smectite in diagenetic and hydrothermal systems (Pevear *et al.*, 1980; Steiner, 1968; Velde, 1977). In the present study the temperature of crystallization is probably slightly less than 200°C as found by Steiner (1968) at Wairakei, New Zealand. The geological environment during crystallization of the Sibert specimen was similar to that in which ordered interstratified illite/smectite crystallized in the Wairakei geothermal field. Crystallization occurred at low depth (<2 km) in rocks subjected to hydrothermal fluids (open thermodynamic system) which crystallized new phases along microfractures.

The above data suggest that the Sibert specimen approaches a regularly interstratified illite/beidellite mineral. This study confirms the great dispersion of composition presented by the ordered mixed-layer I/S minerals in natural occurrences, particularly in the nature of the interlayer cations and of the smectite component. It would be very interesting to have more information on the composition of ordered, interstratified illite/smectites which are commonly reported in hydrothermal systems, porphyry copper deposits particularly, where several alteration facies exist.

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