

NOTES

QUANTIFICATION OF MIXED-LAYER ILLITE-SMECTITE IN GLASS MATRICES BY FOURIER-TRANSFORM INFRARED SPECTROSCOPY

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INTRODUCTION

The Fourier-transform infrared (FTIR) technique has been used for both qualitative and quantitative determination in mineral species (McMillan *et al.*, 1988; Pandya *et al.*, 1992; Schroeder, 1992; Yanagisawa *et al.*, 1997; Zhang *et al.*, 1997). The method presents a number of important advantages: simple preparation, high sensitivity, and rapid analysis. The quantitative determination of minerals in the presence of glass is an interesting problem in mineralogy because X-ray diffraction (XRD) methods do not provide accurate results, especially for small mineral components. In this paper, we present a method for quantitative analysis of Al-rich smectite, mixed-layer illite-smectite (I-S), or illite in the presence of volcanic glass using FTIR.

MATERIALS AND METHODS

A series of hydrothermal-alteration reactions were made on volcanic tuff from the Cabo de Gata region, southeast Spain. The glass was crushed, ground, and calcined at 900°C for 2 h. After calcination, the fraction of 10–200 μm in size was selected. XRD and differential thermal and thermogravimetric analysis did not detect any phase other than glass. The glass chemical composition is: 72.89% SiO_2 , 14.47% Al_2O_3 , 1.25% Fe_2O_3 , 1.44% MgO , 0.86% CaO , 3.34% Na_2O , 4.97% K_2O . The hydrothermal reactions were made at 80, 120, and 160°C, for 60, 90, 180, and 360 d, in both deionized water and in solutions with K/Na ratios of 0.01, 0.1, 1, 10, and 100. The total ion concentrations were 1.01, 0.33, 0.20, 0.33, and 1.01 M. Five grams of glass were placed in 25 mL of solution for each reaction.

The products of reaction were separated from the solutions and washed repeatedly with deionized water by centrifugation. The fraction of $<2 \mu\text{m}$ in size was

separated also by centrifugation (further analysis refers to this fraction). The samples were Ca-exchanged with 1 M CaCl_2 and washed until no Cl^- could be detected with AgNO_3 . XRD analysis of glycolated, mineral-aggregate oriented mounts showed a crystalline phase only for the longer experiments, higher temperatures, and solutions of low total ion concentration or deionized water. The crystalline phase detected was a random mixed-layer I-S with 75% smectite, as determined by matching the experimental traces with patterns calculated using the NEWMOD program (Robert C. Reynolds, Hanover, New Hampshire, USA). The samples also were analyzed using transmission electron microscopy (TEM) and analytical electron microscopy (AEM) (Philips CM-20; AEM analyses at 200 kV, on areas of 200,000 \AA^2 , with 30-s collection time for Na and K, and 200 s for other elements), which showed the presence of flake-like particles in all samples. The chemical compositions of these particles were compatible with a random mixed-layer illite-montmorillonite, as determined by XRD. The octahedral composition of all analyzed particles was very similar (typical atom compositions are in the ranges: Al 1.3–1.6; Mg 0.3–0.6; Fe 0.07–0.3, per half formula-unit). No other minerals were detected. Since there were samples with newly formed I-S in amounts below the detection limit of XRD, FTIR was used for the quantitative determination of the experimental products, using diffuse reflectance and transmission spectra.

To use diffuse reflectance for quantitative purposes, specific conditions are required so that the Lambert-Beer law applies. These conditions are achieved in the dilution method, where the absorbing material under study is diluted in an inert matrix (Kortüm, 1969). For this, 3 mg of altered samples ($<2 \mu\text{m}$) were mixed with 100 mg of KBr. The KBr spectrum was subtract-

ed from the sample spectra. The geometry of the optical bench in the FTIR apparatus and the height of the sample in the holder were constant and thus, the different spectra are comparable. The spectra were recorded in a Nicolet 20SXB instrument, in the range of 4000–400 cm^{-1} , with 500 scans, and a resolution of 2 cm^{-1} .

The OH-stretching band at $\sim 3620 \text{ cm}^{-1}$ in Al-rich smectite, I-S, and illite (Farmer, 1974; Russell, 1987) was used for I-S quantification. This band envelops a number of components corresponding to the different cation pairs linked to an OH group. The components are two Al-OH-Mg bands at 3684 and 3602 cm^{-1} , two Al-OH-Al bands at 3635 and 3618 cm^{-1} , Al-OH-Fe at 3587 cm^{-1} , Fe-OH-Mg at 3568 cm^{-1} , and two Fe-OH-Fe bands at 3554 and 3532 cm^{-1} (Madejová *et al.*, 1994). The Fe-OH-Fe components have low intensities except in Fe-rich smectites. The position of the overall band maximum is determined by the relative area of the different components, and hence by the octahedral sheet composition, although cation ordering also affects the relative areas of the bands (Cuadros and Altaner, 1998). In any case, the position of the overall OH-stretching band for the smectite-illite series with an Al-rich octahedral sheet is near 3620 cm^{-1} , and the proportion of one or the other end-member is not relevant for the overall band position. This implies that the results from our study can be applied to the complete smectite-illite series of Al-rich composition, although this method cannot discriminate between smectite, I-S, and illite, and the three phases are quantified as one. The OH-bending bands from 920 to 840 cm^{-1} also present in smectite, I-S, and illite (Farmer, 1974) were not observable in our study owing to lower intensity and thus, those bands could not be used.

One difficulty of the analysis is that the OH-stretching band of I-S at $\sim 3620 \text{ cm}^{-1}$ superposes with the intense system of OH stretching corresponding to adsorbed water (Bishop, *et al.*, 1994) and to hydroxyls in the glass (Pandya *et al.*, 1992) at 3600–3000 cm^{-1} . The FTIR analyses in transmission mode were conducted to use conditions that permitted the removal of water. The amount of 5 mg of product was placed in 1 mL of deionized water. The suspension was sonified for complete dispersion. Then, 50 μL of the suspension were placed on an AgCl window and allowed to dry. The window is part of a cell (Willmad) for FTIR analysis in isolation from the atmosphere. The cell consists of two AgCl disks with a 0.1-mm circular depression and flat rims. The windows, placed facing their circular depression, are fit into a two-body ring which is screwed to seal the two windows together. The samples in the window were heated at 150°C for 2 h, and the cell was mounted and sealed in the heater to avoid rehydration. An empty cell was also used, and the spectrum was subtracted from the sample spectra.

The spectra were collected with an acquisition of 500 scans and 16- cm^{-1} resolution. The resolution was decreased with respect to diffuse reflectance because noise intensity was higher. Lowering the resolution produced clean spectra. This procedure does not alter the quality of the measurements because the OH-stretching band in smectite is much wider (above 100 cm^{-1}) than the resolution.

FTIR analysis of the original tuff showed the absence of the I-S 3620- cm^{-1} band. In transmission mode, there is no band in the 4000–2500- cm^{-1} region. In reflectance mode, there is a band at $\sim 3650 \text{ cm}^{-1}$ (assignment discussed below) and the 3600–3000- cm^{-1} system of molecular water and hydroxyl groups in the glass.

The calibration line for the quantification of I-S was calculated by mixing known amounts of I-S (15% illite layers, for a description of this sample see Cuadros and Linares, 1996) with the original glass used for the experiments. The mixtures were finely ground to make them homogeneous.

The spectra were analyzed in the region 4000–2500 cm^{-1} after baseline subtraction. They were simulated by curve-fitting using the I-S band at $\sim 3620 \text{ cm}^{-1}$ and a group of bands for the OH-stretching system of water absorbed in I-S, glass, KBr, and OH groups in the glass, located between 3600–3000 cm^{-1} . There is uncertainty about the position and width of some of these bands, and most are broad. For these reasons, the 3600–3000- cm^{-1} range of the spectrum was simulated using the number of bands permitting a good fit (although they may not have necessarily a physical meaning). The number of bands varied between four and nine and all were Gaussian type (Papin *et al.*, 1997). The positions were fixed in a first calculation and left free for the final calculation. The uniqueness of the results was tested by changing the original positions of the bands to determine if final results changed.

RESULTS AND DISCUSSION

The calibration lines show a good correlation between measured band areas and the amount of I-S for both diffuse reflectance and transmission (Figure 1). One transmission data point plots off the line (square in Figure 1) probably because of an error in the sample preparation. This point was not used in the regression calculation. The transmission method reproduced the amount of I-S in the samples used for calibration with errors of $<2\%$ of total I-S, whereas the errors for diffuse reflectance were $<6.5\%$. For diffuse reflectance, the calibration included I-S contents from 0 to 100%. In the case of transmission, I-S contents were 0–40% and the region 0–10% was analyzed in more detail (six data points) because this is the range where most of the alteration experiments were likely

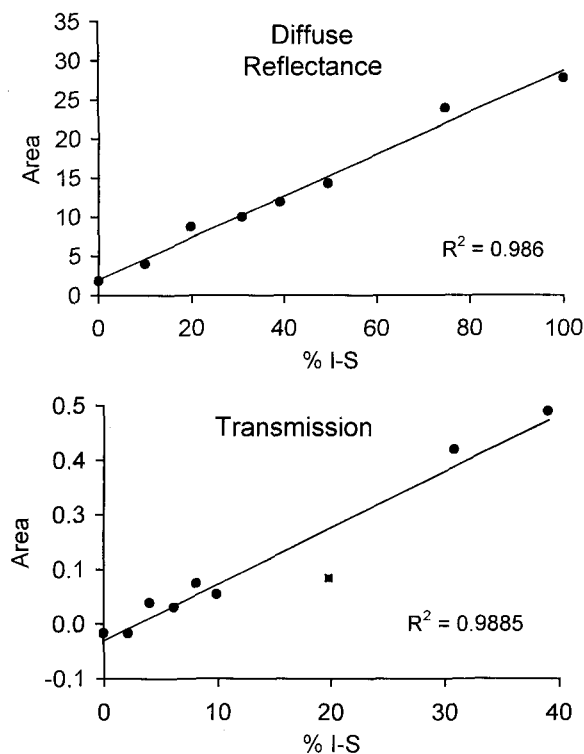


Figure 1. Calibration lines for the quantification of I-S using infrared by both diffuse reflectance and transmission: area of the OH-stretching band of I-S vs. percentage of I-S in the mixture of I-S and glass. The square in the transmission plot is not used in the regression.

to plot. The detection limit for I-S for transmission mode was $\sim 2\%$.

The intercepts of the two calibration lines are different. For transmission, the corresponding value is zero. For diffuse reflectance, the intercept is above zero. This is related to the presence of an OH-stretching band corresponding to either molecular water or hydroxyl groups in the glass. This band exactly superposes with OH stretching in I-S and the intensities are added. The fact that this band is not present in transmission, where hydration was lower, suggests that it is related to molecular water. In fact, there is one band at 3650 cm^{-1} assigned to hydration water in smectites (Madejová *et al.*, 1994). This band could also be present in the glass.

The spectra obtained by diffuse reflectance show a series of intense bands corresponding mainly to adsorbed water and thus, the band of interest is not clearly visible (Figure 2a). This poses a difficulty for the curve-fitting process. The calculated position of the I-S band varied from 3630 to 3655 cm^{-1} , slightly away from 3620 cm^{-1} . The displacement toward lower frequencies was approximately proportional to the amount of I-S present. The calculated I-S contents in some of the altered samples are given in Table 1. The

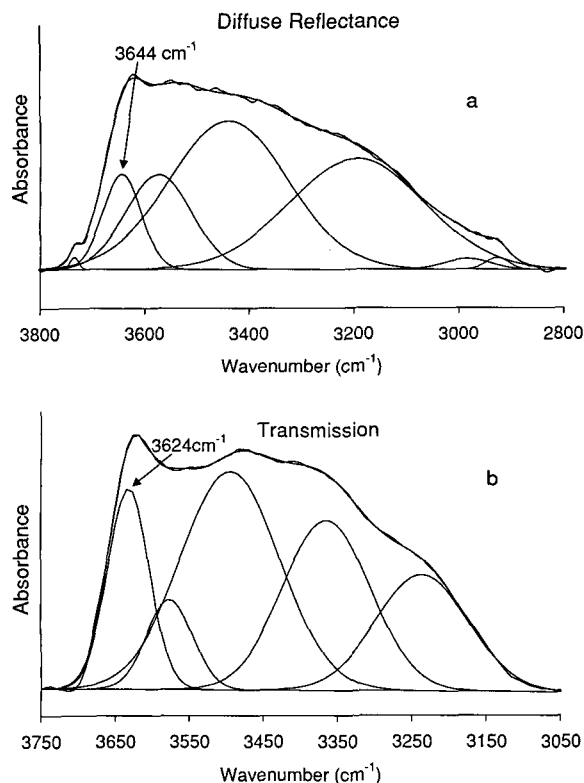


Figure 2. Curve-fitting calculation for sample 42af in the OH-stretching region. The bands corresponding to I-S are indicated by the arrows. The other bands correspond to hydroxyls in the glass and water adsorbed in I-S and KBr. (a) Diffuse reflectance and (b) transmission.

Table 1. I-S amounts determined by FTIR, using diffuse reflectance and transmission modes, for selected samples. Samples correspond to different temperature and Na/K conditions of some of the longer experiments. d.w. = deionized water.

Sample	T (°C)	Time (days)	Na/K	% I-S	
				Diff. Reflect.	% I-S Transm.
7af	60	180	0.01	6.2	5.2
8af	60	180	0.1	2.7	2.5
9af	60	180	1	5.5	3.9
12af	60	180	d.w.	8.2	4.8
1af	60	360	0.01	6.1	3.4
2af	60	360	0.1	5.3	4.8
3af	60	360	1	5.2	4.7
4af	60	360	10	8.2	4.6
5af	60	360	100	4.6	4.6
6af	60	360	d.w.	4.2	3.3
27af	120	360	1	5.8	3.7
30af	120	360	d.w.	6.3	8.3
37af	160	360	0.01	6.3	6.3
39af	160	360	1	8.7	7.7
41af	160	360	100	17.4	6.6
42af	160	360	d.w.	29.3	31.2

estimated precision of the method is 10% of the measured value.

The transmission spectra showed less intense bands associated with adsorbed water, so that a precise calculation for the I-S band was possible (Figure 2b). The intensity of the absorbed-water bands was proportional to the amount of I-S present, which indicates that water adsorbs mostly in the I-S. The position of the I-S band maxima varied between 3623–3646 cm^{-1} . In contrast to diffuse reflectance, there was no relationship between the amount of I-S and the position of the band. The estimated error in the I-S quantification for transmission is 7% of the determined value.

Table 1 compares the calculated I-S contents using transmission and diffuse reflectance. Regrettably, all values except the one for sample 42af are below 9%, so that there is not a wide range of weight percent abundance of I-S in the samples. The values are similar, the larger relative differences corresponding to 12af, 1af, 4af, and especially 41af. The determined values for transmission are more accurate because of the lower amount of water in the samples. Nevertheless, the similar results suggest that the intense water bands do not greatly affect the curve-fitting results. Previous studies used band heights for quantification (Pandya *et al.*, 1992; Yanagisawa *et al.*, 1997; Zhang *et al.*, 1997). As this study shows that the band of interest may have a slightly different width from sample to sample, the use of band areas is more appropriate.

The displacement of the I-S band (Figure 2) in the decomposed spectra from diffuse reflectance is primarily caused by the water band at 3650 cm^{-1} . Both the I-S band and the water band overlap to produce a single band. For transmission, the I-S band is sometimes also displaced from 3620 cm^{-1} , but to a lesser degree. The causes for this displacement may be, in part, different from that of diffuse reflectance because of the different extent of displacement and the lack of dependence with I-S content. The displacement may be related to glass grains in an advanced state of alteration to I-S and there is TEM-AEM evidence for the presence of such grains. Hydroxyl groups in structural environments similar but not the same as that in I-S are likely to produce variations in vibration frequencies. Obviously, this would also affect I-S band frequencies in the diffuse-reflectance analyses.

In summary, both techniques are useful for quantitative determination of Al-rich smectite, I-S, or illite in a glass matrix. The elimination of adsorbed water improves results, although it is not critical to eliminate all the water, which requires high temperatures or a vacuum (Farmer, 1974; Cuadros *et al.*, 1994). Diffuse reflectance is the better method, provided samples can be satisfactorily dehydrated, because

sample preparation is faster, simpler, and most importantly, it has a higher reproducibility than the transmission mode. Diffuse reflectance has a higher reproducibility because samples require only to be homogeneously mixed with KBr, and the intensity of the IR band of interest will depend only on the sample concentration in the mixture. For transmission, the sample requires suspension in a homogeneous water dispersion, which may be difficult to achieve. A drop of the suspension is dried on the window for IR analysis. An assumption is that the resulting film is also homogeneous, because the IR-beam cross section is smaller than the cross section of the film. The intensity of the resulting IR bands depends on these preparation steps.

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REFERENCES

- Bishop, J.L., Pieters, C.M., and Edwards, J.O. (1994) Infrared spectroscopy analyses on the nature of water in montmorillonite. *Clays and Clay Minerals*, **42**, 702–716.
- Cuadros, J. and Altaner, S.P. (1998) Compositional and structural features of the octahedral sheet in mixed-layer illite/smectite from bentonites. *European Journal of Mineralogy*, **10**, 111–124.
- Cuadros, J. and Linares, J. (1996) Experimental kinetic study of the smectite-to-illite transformation. *Geochimica et Cosmochimica Acta*, **60**, 439–453.
- Cuadros, J., Huertas, F., Delgado, A., and Linares, J. (1994) Determination of hydration (H_2O^-) and structural (H_2O^+) water for chemical analysis of smectites. Application to Los Trancos smectites, Spain. *Clay Minerals*, **29**, 297–300.
- Farmer, V.C. (1974) The Layer Silicates. In *The Infrared Spectra of Minerals*, V.C. Farmer, ed., Mineralogical Society, London, 331–363.
- Kortüm, G. (1969) Experimental Testing of the “Kubelka-Munk” theory. In *Reflectance Spectroscopy. Principles, Methods, Applications*, Springer Verlag, New York, 170–216.
- Madejová, J., Komadel, P., and Čičel, B. (1994) Infrared study of octahedral site populations in smectites. *Clay Minerals*, **29**, 319–326.
- McMillan, P.F. and Hofmeister, A.M. (1988) Spectroscopic Methods in Mineralogy and Geology. In *Infrared and Raman Spectroscopy, Reviews in Mineralogy, Volume 18*, F.C. Hawthorne, ed., Mineralogical Society of America, Washington, D.C., 99–159.
- Pandya, N., Muenow, D.W., and Sharma, S.K. (1992) The effect of bulk composition on the speciation of water in submarine volcanic glasses. *Geochimica et Cosmochimica Acta*, **56**, 1875–1883.
- Papin, A., Sergeant, J., and Robert, J. (1997) Intersite OH-F distribution in an Al-rich synthetic phlogopite. *European Journal of Mineralogy*, **9**, 501–508.
- Russell, J.D. (1987) Infrared methods. In *A Handbook of Determinative Methods in Clay Mineralogy*, M.J. Wilson, ed.,

- Blackie, London, UK, and Chapman and Hall, New York, USA, 133–173.
- Schroeder, P.A. (1992) Far-infrared study of the interlayer torsional-vibrational mode of mixed-layer illite/smectites. *Clays and Clay Minerals*, **40**, 81–91.
- Yanagisawa, N., Fujimoto, K., Nakashima, S., Kurata, Y., and Sanada, N. (1997) Micro FT-IR study of the hydration-layer during dissolution of silica glass. *Geochimica et Cosmochimica Acta*, **61**, 1165–1170.
- Zhang, Y., Belcher, R., Ihinger, P.D., Wang, L., Xu, Z., and Newman, S. (1997) New calibration of infrared measurement of dissolved water in rhyolitic glasses. *Geochimica et Cosmochimica Acta*, **61**, 3089–3100.

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