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Spectral Response (VNIR-SWIR) Associated to the Octahedral Sheet of Smectites.

Adrián Lorenzo [1]*, Andrea García [1], Juan Morales [1], Emilia García [2-3], and Mercedes Suárez [1].

[1] Department of Geology, University of Salamanca. Plaza de la Merced, S/N, 37008 Salamanca
[2] Department of Mineralogy and Petrology. Complutense University of Madrid. C/. José Antonio Novais. 28014 Madrid.
[3] Geoscience Institute (UCM-CSIC), 28014 Madrid.
* Correspondence: adrianlorenzo@usal.es

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Abstract: A mineralogical characterization of a group of bentonite samples was done by X-ray diffraction (XRD), chemical analysis by inductively coupled plasma mass spectroscopy (ICP-MS) and visible-near infrared and short-wave infrared spectroscopy (VNIR-SWIR). As tested by XRD, all samples are very pure, composed mainly by smectites with very small amounts of impurities like quartz and feldspar. The results of the chemical analysis show high contents of Al_2O_3 in all the samples except COU(V), which has high contents of Fe_2O_3, and R4 which is a trioctahedral smectite. Within VNIR-SWIR spectra, absorption features characteristics of the smectites due to the presence of Fe are observed at lowest wavenumber, while at the SWIR region the absorptions are related to the M-OH bonds, and there are differences among the samples according to their octahedral content.

Keywords: dioctahedral smectites; trioctahedral smectites; Fe-rich smectite; XRD; VNIR-SWIR spectroscopy.

1. Introduction

The bentonites are smectite-rich rocks that have a wide number of industrial applications, mainly in the sector of ad/absorbents. Their industrial properties are related to their structure, crystal-chemistry, and small particle size, together with their swelling ability. Recently, these minerals are widely investigated for their use as nanocomposites and bionanocomposites [1].

Variations in the crystal-chemistry of the smectites due to tetrahedral and octahedral substitutions produce different layer charge and influence their application properties. According to the octahedral content, the smectites are classified in dioctahedral and trioctahedral, being more abundant the dioctahedral smectites.

VNIR-SWIR spectroscopy is a technique which allows obtaining structural information of the minerals in short time, without previous treatment of the sample, and it is especially useful for the smectites study since these minerals have a good spectral response in this range of wavelengths. The results of the characterization with this technique can be applied in different fields, such as remote sensing, mineral deposits mapping, soil characterization and heritage conservation [2, 3, 4], among others.

In this work, the spectral response VNIR-SWIR of a group of smectites, including dioctahedral, Fe-rich, and trioctahedral smectites, is studied with the aim of obtaining a relation of the spectral response in the wavelength selected and the crystal-chemical parameters of smectites.

2. Materials and methods

For this work we selected 7 samples shown in Table 1. The samples come from different localities: 3 from USA, 3 from Spain, and 1 from Italy. The samples coming from USA were obtained from the Source Clay Repository and the rest of the samples were collected from the field sites.

Table 1. Samples selected with their localization.

Samples	Localization
APA	Arizona, USA (Clay Repository)
COU(V)	Washington, USA (Clay Repository)
PUT	Putifigari, Italy
R4	Esquivias, Spain
SAN	Arizona, USA (Clay Repository)
SUD	Cabo de Gata, Spain
CGA	Cabo de Gata, Spain

For their mineralogical and chemical characterization, the samples were manually ground in an agate mortar until reaching a particle size < 50μm. The mineralogical characterization was carried out by X-ray diffraction and VNIR-SWIR spectroscopy analysis. In the X-ray diffraction study, the samples were analyzed using two methods: randomly oriented powders and oriented powder aggregates (under ambient conditions, after solvation with ethylene-glycol, and after heating at 550°C for 2 hours). A Bruker D8 Advance ECO diffractometer, with LYNXEYE SSD160 high resolution detector, theta-2theta configuration, and Cu anode was used, working at 40 kV and 30 mA and a speed of $0.05°\text{min}^{-1}$. The High Score Plus (PANalytical) software was used to interpret all the results. The VNIR-SWIR spectroscopy study was done with the field spectroradiometer ASD FieldSpec 4 Standard-Res. This equipment has 3 detectors: VNIR, SWIR1, and SWIR2, which measure wavelength comprises from 350 to 1000 nm, from 1001 to 1800 nm, and from 1801 to 2500 nm, respectively. The samples were measured in direct contact with the sounding line, protected with a glass without response. The results were interpreted with the Spectragryph software [6].

The chemical analyses of major elements were done in the Activation Laboratories Ltd., Ontario (Canada), using FUS-ICP to mayor elements and FUS-MS to trace elements and FeO was determined by titration.

3. Results

3.1. X-ray diffraction

The X-ray study showed that all the samples are high purity bentonites constituted mainly by smectites-group minerals, quartz and plagioclase as accessory minerals, as can be appreciated on Figure 1. Based on the 060 reflection, we observed that the samples APA, PUT, SAN, SUD, and CGA are dioctahedral, while R4 is trioctahedral. Position of 060 reflection in COU(V) sample agrees with the high Fe^{3+} content which produces the high background of its XRD-pattern. All samples, except for R4, present good crystallinity with relatively narrow 001 reflection, as shown in Figure 1.

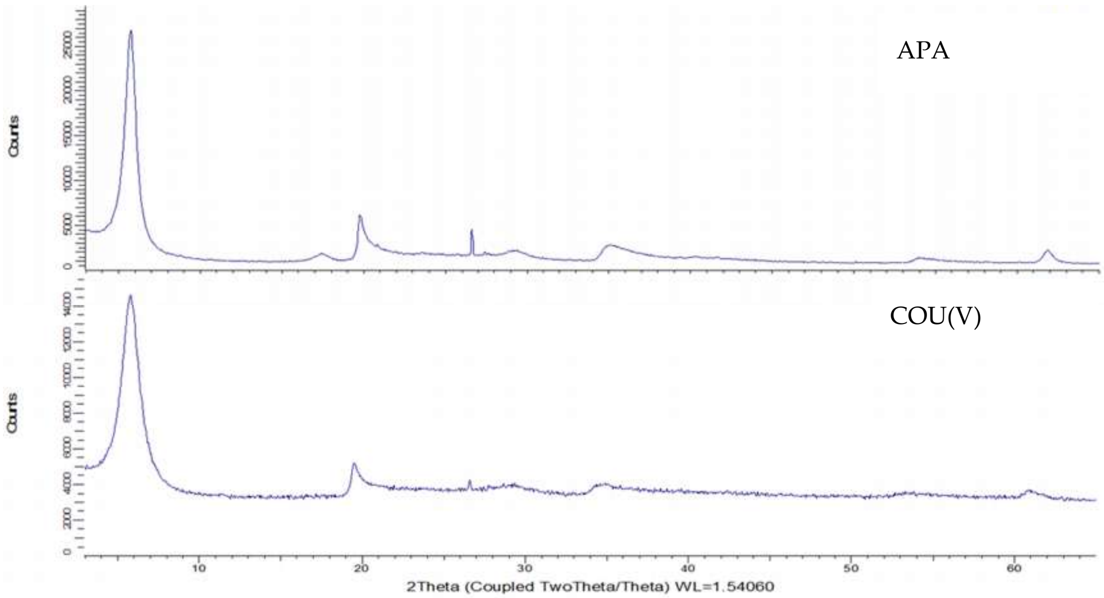

Figure 1. XRD-Powder patterns of representative samples APA and COU(V).

3.2. *Chemical analysis*

The results of the chemical analysis, expresed as percentaje of oxides of major elements, are in Table 2. As the samples are almost pure smectites, their chemical analysis can be interpreted according to the general structural formula of the smectites. The contents of Al, Fe, Mg, and Mn are mainly related to octahedral cations and the contents in Ca, Na, and K are then related to the interlaminar space, although Mg can be also an interlayer cation in both dioctahedral and trioctahedral smectites [7]. Although Fe in smectites appears mainly as Fe^{3+} [8], FeO has been also analyzed. Because the smectites are hydrated minerals, all samples present high values of loss of ignition tests (LOI), between 17.27% and 22.89%, for R4 and APA samples, respectively. Samples APA, PUT, SAN, SUD, and CGA are Al-rich samples, ranging between 14.18% and 16.82% of Al_2O_3. On the other side, COU(V) and R4 samples have the highest contents in Fe_2O_3 and MgO, respectively. COU(V) has 18.17% of Fe_2O_3. R4 is a trioctahedral smectite, according to its high percentage of MgO (25.81%). The main exchangeable cation is Ca^{2+} according to the content in this oxide; the samples SUD and CGA contain also Na^+ in similar proportions as exchangeable cation.

Table 2. Oxide percentage of the major elements.

Samples	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	MnO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI
APA	51.95	14.18	1.23	0.00	5.04	0.08	2.48	0.08	0.17	0.20	0.03	22.89
COU(V)	49.90	7.41	18.17	0.50	1.41	0.02	1.61	0.02	0.02	0.51	0.03	19.74
PUT	50.52	14.02	5.06	0.00	4.11	0.07	1.17	0.50	0.18	0.68	0.19	21.90
R4	52.91	1.83	0.00	1.00	25.81	0.01	0.46	0.03	0.32	0.08	0.03	17.27
SAN	53.71	14.52	0.98	0.40	5.16	0.09	2.57	0.16	0.17	0.23	0.04	22.35
SUD	53.82	16.60	3.15	0.40	4.27	0.02	1.26	1.05	0.56	0.15	0.02	18.77
CGA	53.03	16.82	2.20	0.20	5.10	0.06	1.38	0.99	0.34	0.14	0.02	20.57

3.3. *VNIR-SWIR spectroscopy*

The VNIR-SWIR spectra are shown in Figures 2 and 3. In order to better understand the spectral response, they were divided into two parts: 1) the visible and near wavelength range (from 350 nm to 1000 nm), and 2) the short wavelength range (from 1001 nm to 2500 nm). In visible and near infrared wavelength of the spectra, the absorptions are due to the electronic transitions of Fe and other transition elements [9]. The samples COU(V) and SUD show the most intense absorption bands in this region (Figure 2). This is due to the high amount of Fe that these two samples contain, mainly as Fe^{3+} (Table 2). Both samples present broad bands centered at ~650 nm and 950 nm.

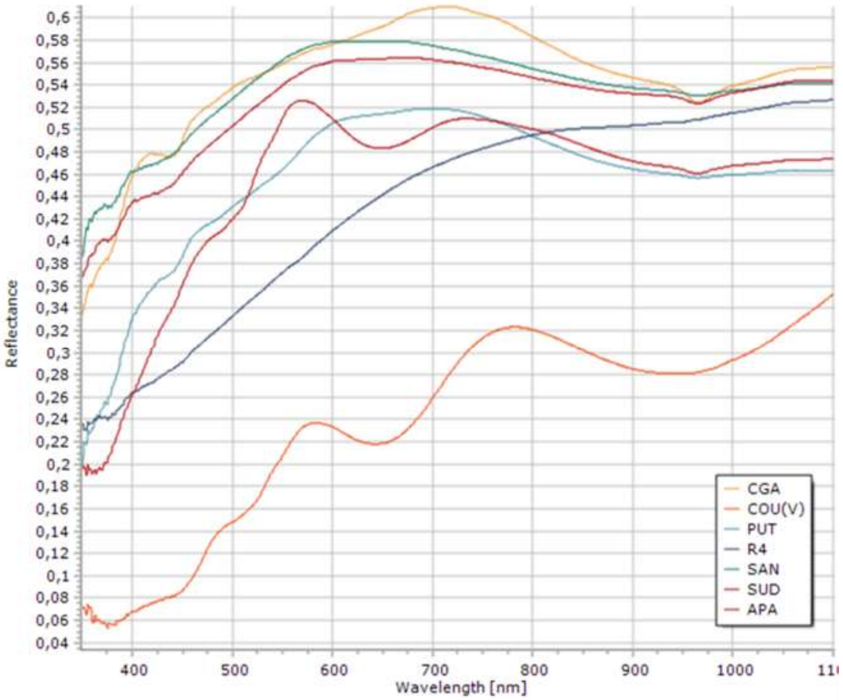

Figure 2. Spectral response of the samples in the visible near wavelength.

In the short-wave zone of the spectra, the samples show two intense absorptive features near 1410 nm and 1910 nm (Figure 3) related to the combinations of the vibration modes of H_2O [10]. These broad bands are characteristic of the hydrated minerals.

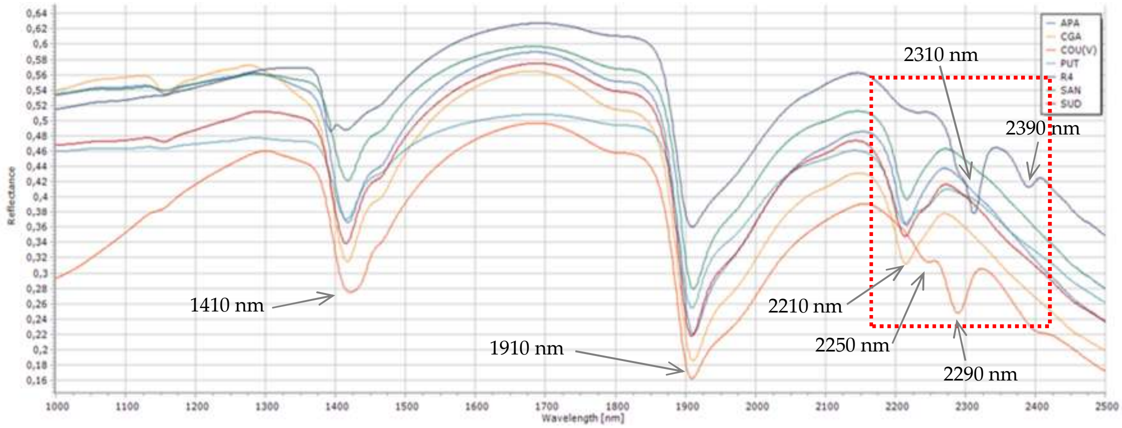

Figure 3. Spectra of the samples in the short-wave zone.

In the region of the spectra with the wavelengths higher than 2200 nm (framed in red in Figure 3) the assignation of the absorption band has been done according to [10, 11, 12] and the samples can be divided into three groups by their characteristic absorption features at 2210 nm, 2290 nm, 2310 nm, and 2390 nm.

4. Discussion

The classification of the smectites of these highly pure bentonites from XRD-patterns agrees whit the chemical analysis. The samples APA, PUT, SAN, SUD, and CGA are Al-rich samples, and they have been identified as dioctahedral smectites by their 060 reflection values, while COU(V) and R4 samples are Fe and Mg-rich smectites, respectively.

The differences in the spectral response are related to the different composition of the smectites. In the lower wavelength region, in the VNIR range, the richest in Fe samples exhibit the more intense absorptions as wide bands. These bands do not correspond to the most frequent Fe-oxide minerals, hematite and goethite, of which characteristic absorption bands are centered at 530 nm and 890 nm in hematite, and 480 nm and 969 nm in goethite. However, the most intense absorption in these two Fe-rich smectites is located at 650 nm and it is due to the octahedral Fe in these smectites.

In the short-wave region of the spectra, the samples show singular absorption features associated to the octahedral cations, due to the vibrations of the M-OH bonds [10, 11, 12]. The samples with a high content in Al show an intense feature near 2210 nm. APA, PUT, SAN, SUD, and CGA have absorption features ~ 2210 nm. These absorption features are due to the Al-Al-OH in the octahedral sheet. This agrees with the results of the chemical analysis that showed high amount of Al in these 5 samples. More specifically, the concentrations of Al^{3+} are 14.18% for APA, 14.02% for PUT, 14.52% for SAN, 16.60% for SUD, and 16.82% for CGA. On the other hand, the smectites with a high Fe content show an intense absorption close to 2290 nm. COU(V) sample has a deep absorption feature at ~ 2290 nm related to the bond vibration of Fe^{3+}-Fe^{3+}-OH in the octahedral sheet. The presence of octahedral Fe also causes the absorption at 2250 nm in COU(V) sample, this absorption appears as a shoulder in PUT sample. They are probably related to the dioctahedral Al-Fe^{3+}-OH bonds. On the other hand, the only trioctahedral smectite here studied, R4 sample, has two characteristic absorption features at ~ 2310 nm and ~ 2390 nm, both related to the 3Mg-OH bonds vibration in the octahedral sheet, according to the content of MgO (25.81%) obtained in the chemical analysis.

5. Conclusions

The samples present clear and discriminatory absorption bands related to the octahedral content of the smectites. Dioctahedral Al-rich smectites are characterized by the absorption at 2210 nm while most Fe-rich dioctahedral smectites present the most intense absorption at 2290 nm. The presence of dioctahedral Al-Fe^{3+}-OH bonds causes an adsorption located at 2250 nm. Finally, trioctahedral 3Mg-OH bonds produce significant absorption bands located at ~ 2310 nm and ~ 2390 nm. These discriminatory absorptions allow to identify the smectite type by means of the field spectroscopy.

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References

1. Bergaya, F., Jaber, M., Lambert, J.-F. Clays and Clay Minerals as Layered Nanofillers for (Bio)Polymers. Green Energy and Technology 2012, 50, pp. 41-75. doi: 10.1007/978-1-4471-4108-2_3.
2. Bishop, J. L.; Gates, W. P.; Makarewicz, H. D.; McKeown, N. K.; Hiroi, T. Reflectance spectroscopy of beidellites and their importance for mars. Clays Clay Miner 2011, 59, 378–399. doi: 10.1346/CCMN.2011.0590403
3. Rajendran, S.; Sobhi, N. Characterization of ASTER spectral bands for mapping of alteration zones of volcanogenic massive sulphide deposits. Ore Geology Reviews 2017, 217, 88, 317–355. doi: https://doi.org/10.1016/j.oregeorev.2017.04.016

4. Ogena, Y.; Goldshlegerb, N.; Ben-Dorc, E. 3D spectral analysis in the VNIR–SWIR spectral region as a tool for soil classification. Geoderma 2017, 302, 100–110. doi: https://doi.org/10.1016/j.geoderma.2017.04.020
5. Camaiti, M.; Benvenuti, M.; Costagliola, P.; Di Benedetto, F.; Moretti, S. Hyperspectral Sensors for the Characterization of Cultural Heritage Surfaces. In Sensing the Past. Geotechnologies and the Environment. Masini, N., Soldovieri F. Eds.; 2017, pp 289–311. doi: https://doi.org/10.1007/978-3-319-50518-3_13.
6. Menges, F. Spectragryph - optical spectroscopy software, Version 1.x.x, 201x, 2019, http://www.effemm2.de/spectragryph/.
7. Christidis, G. E. Validity of the structural formula method for layer charge determination of smectites: A re-evaluation of published data. Applied Clay Science 2008, 42, 1–7. doi: https://doi.org/10.1016/j.clay.2008.02.002
8. García-Romero, E.; Manchado, E.; Suárez, M. & García-Rivas, J. Spanish Bentonites: A Review and New Data on Their Geology, Mineralogy, and Crystal Chemistry. Minerals 2019, 9, 696. doi: https://doi.org/10.3390/min9110696
9. Burns, R.G. Mineralogical Applications of Crystal Field Theory. Cambridge: Cambridge University Press. 1993. doi: https://doi.org/10.1017/CBO9780511524899
10. Bishop, J. L.; Lane, M. D.; Dyar, M. D.; Brown, A. J. Reflectance and emission spectroscopy study of four groups of phyllosilicates: smectites, kaolinite-serpentines, chlorites and micas. Clay Miner 2008, 43, 35–54. doi: 10.1180/claymin.2008.043.1.03
11. Bishop, J. L.; Pieters, C. M.; Edwards, J. O. Infrared spectroscopic analyses on the nature of water in montmorillonite. Clays Clay Miner 1994, 42, 702–716. doi: 10.1346/CCMN.1994.0420606
12. Bishop, J. Visible and Near-Infrared Reflectance Spectroscopy: Laboratory Spectra of Geologic Materials. In Remote Compositional Analysis: Techniques for Understanding Spectroscopy, Mineralogy, and Geochemistry of Planetary Surfaces. Bishop, J., Bell III, J., Moersch, J., Eds.; Cambridge University Press: Cambridge, 2019, pp 68–101. doi: 10.1017/9781316888872.006