Structural Characterization of Octahedral Sheet in Dioctahedral Smectites by Thermal Analysis

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Abstract: The structures of octahedral sheets of dioctahedral phyllosilicates show cis-vacant (cv) and trans-vacant (tv) configurations due to the different distributions of the octahedral cations over cis- and trans-sites. On the basis of the different dehydroxylation temperatures, a thermal analysis is an effective method used to identify the cv and tv configurations of an octahedral sheet in dioctahedral smectites. The proportions of cv and tv configurations were determined by fitting the derivative thermogravimetry (DTG) curves. A wide range of cv and tv proportions were detected in the samples. The dehydroxylation temperatures of samples consisting of cv configuration are about 150 to 200 °C higher than those consisting of tv configurations. The samples were classified as tv varieties when octahedral Fe3+ > 0.46 mol/FU, and the pure tv dioctahedral smectites were found when Fe3+ > 1.8 mol/FU. A clear linear relationship was found between the content of octahedral Fe3+ and Al3+ and the proportion of cv and tv configurations. The substitution of Al3+ by Fe3+ in the octahedral sheets is the main factor for the formation of tv varieties. There was no relationship detected between the layer charge density, octahedral Mg2+ content, and the proportion of tv and cv. The present results indicate that the iron content has a significant effect on the structure of the octahedral sheet.

Keywords: cis-vacant; trans-vacant; dioctahedral smectites; dehydroxylation; thermal analysis

1. Introduction

Smectites are used widely in industrial and environmental applications due to their physical and chemical properties, for example, cation exchange capacity, swelling behavior, and adsorption capacity [1]. The properties of smectites are closely related to their structural features [2,3].

Smectites are typical 2:1 layers of clay minerals, composed of two tetrahedral silicate sheets (T) and one octahedral sheet (O). In each layer, the octahedral sheet is sandwiched between the two tetrahedral sheets (TOT) (Figure 1). In the tetrahedral sheets, the dominant cation is Si4+, but it can often be substituted by trivalent cation such as Al3+. In the octahedral sheet, the common cations are Al3+, Mg2+, Fe3+, or Fe2+, but other cations, such as Li+, Ni2+, and Cr3+ have also been identified in octahedral sites. Two arrangements exist in the octahedral sheet, if all octahedral sites are filled with bivalent cations such as Mg2+ and Fe2+, the structure is called trioctahedral; if two-thirds of octahedral sites are occupied by trivalent cations such as Al3+ and Fe3+, the structure is known as dioctahedral. The general chemical formula for dioctahedral smectites is:

\[(\mathrm{M}_{x+y}^{+} \cdot n\mathrm{H}_{2}\mathrm{O})\left(\mathrm{R}_{3-x}^{2+}\cdot \mathrm{R}_{y}^{3+}\right)\left(\mathrm{Si}_{4-x}^{4+}\cdot \mathrm{Al}_{x}^{3+}\right)\mathrm{O}_{10}^{2-} (\mathrm{OH})_{2}\]

where M+ represents the exchangeable interlayer cations; R2+ and R3+ refer to divalent and trivalent octahedral cations, respectively; x and y indicate the tetrahedral and octahedral layer charge, respectively [2]. The most important species of dioctahedral smectites are montmorillonite, beidellite, and nontronite. In general, octahedra shows two different configurations related to the disposition of
hydroxyl groups, for example, cis- and trans-octahedron. In the cis-octahedron, the OH groups are on the same side, whereas in the trans-octahedron, the OH groups are on the opposite side (Figure 2).

![Figure 1. General structure of smectites.](image)

**Figure 1.** General structure of smectites.

![Figure 2. Structure of (a) cis-octahedron and (b) trans-octahedron.](image)

**Figure 2.** Structure of (a) cis-octahedron and (b) trans-octahedron.

In dioctahedral smectites, one third of the octahedral positions are vacant. Thus, the octahedral sheet with cis-sites vacant is called the cis-vacant (cv) configuration (Figure 3a), and with trans-sites vacant it is called the trans-vacant (tv) configuration (Figure 3b). This kind of cations’ distribution was first proposed by Méring and Oberlin in 1971 [4]. Then, Tsipursky and Drits [5] found that natural dioctahedral smectites cover a wide range of proportions of cv and tv structures, and normally, montmorillonites are cv and illites are tv.

![Figure 3. Octahedral sheet of (a) cis-vacant configuration and (b) trans-vacant configuration in dioctahedral smectites.](image)

**Figure 3.** Octahedral sheet of (a) cis-vacant configuration and (b) trans-vacant configuration in dioctahedral smectites.

In general, 2:1 dioctahedral phyllosilicates show structural defects such as a stacking disorder which makes it difficult to obtain precise structural information by the X-ray powder diffraction (XRD) method, especially for the smectite group [6]. Drits et al. [7] found that the dehydroxylation
temperature is related to the structure of the octahedral layer. Since then, the structural transformations have been extensively studied during dehydroxylation of dioctahedral 2:1 dioctahedral phyllosilicates [8–15]. These studies showed that the chemical composition and the distribution of cations over cis- and trans-sites in the octahedral sheet are two major factors affecting the dehydroxylation of micas, smectites, and illite/smectite (I/S). The dehydroxylation of tv clay minerals occurs in one stage; each two adjacent OH groups form a water molecule and leave one residual oxygen atom, the octahedral cations become five-coordinated. The dehydroxylation of cv clay minerals occurs in two stages. First, each two adjacent OH groups are replaced by the residual oxygen atom and the octahedral cations become five- and six-coordinated in cis- and trans-sites, respectively. Secondly, the cations migrate from trans-sites into the former cis-vacant site [7,10]. This requires additional thermal energy. Therefore, varieties containing cv configuration have dehydroxylation temperature from 100 to 200 °C higher than those consisting of tv configuration. The relationships between structural properties and tv, cv structures has been investigated [16–18]. The octahedral iron content is highly related to the tv configuration. The Fe-rich dioctahedral phyllosilicates occur most as a tv configuration, and the Al-rich dioctahedral phyllosilicates prefer to form a cv configuration [16]. Wolters et al. found that the main influence on the tv configuration was due to Fe$^{2+}$ substitution for Al$^{3+}$ in the octahedral sheet [17]. Kaufhold et al. confirmed the relationship between iron content and the ratio of cv and tv sites from an energy point of view [18]. The dehydroxylation temperature also depended on the iron content.

The information of octahedral structure reflects the thermal reactions which are important for the industrial applications of smectites, for example, the production of supplementary cementitious materials and geopolymers [19]. In addition, the thermal stability of bentonite determines their amount during the foundry process. Therefore, further research about the relationship between the octahedral structure, including cv and tv varieties, and the physicochemical properties of smectites is necessary in order to gain a better understanding of the formation mechanism of 2:1 dioctahedral phyllosilicates and their industrial application.

The thermal analysis is considered to be an effective method to discriminate the structure of the octahedral sheet. According to Drits et al. [7,8], the tv smectites have a dehydroxylation temperature between 500 to 550 °C, and the cv smectites have a dehydroxylation temperature about 700 °C. The proportion of the peak areas in different temperatures reflects the proportion of cis- and trans-vacant configurations. In this study, the thermogravimetric (TG) analysis was used to characterize the structure of the octahedral sheet. The proportions of cv and tv configurations were calculated by fitting the derivative thermogravimetry (DTG) curves which provided the information of the dehydroxylation reaction, for example, the temperature when water molecules exit the structure from each of the two OH groups. The purpose of this study is to characterize the tv and cv configurations in dioctahedral smectites by thermogravimetric (TG) analysis and classify samples, to (1) characterize the structure of the octahedral sheet in dioctahedral smectites by thermal analysis and (2) verify the relationships between the proportions of tv and cv and the structural properties, such as cation distribution in the octahedral and tetrahedral sheets and the layer charge density.

2. Materials and Methods

2.1. Sample Preparation and Characterization

A series of well-investigated dioctahedral smectite samples [17,20] and international reference samples (Source clays, CMS) were used in this study to avoid additional sampling and screening (Table 1). All samples were purified firstly. Only carbonates were found in the bulk samples. The chemical pretreatment to eliminate this impurity was performed according to Tributh and Lagaly [21]. After purification, samples were Na$^+$-saturated, and the remaining salt was removed by dialysis. The separation of <0.2 μm fraction was obtained by centrifugation and was applied in order to remove most of impurities, such as quartz [22]. The raw and purified samples were analyzed by XRD. The measurements were performed on an URD 6 instrument using CoKa radiation in 5° to 80° 2θ range, 0.03°
step, and 3 to 5 s/step counting time. An example of one sample before and after purification is shown in Figure 4. The intensity of reflections of smectite was enhanced significantly after purification. The chemical composition of samples was determined by the X-ray fluorescence analysis (XRF) (Table 2). The measurement was performed on a MagiXPRO XRF-spectrometer. The chemical formula was calculated using the method described by Köster based on one formula unit (FU) \([\text{O}_{10}(\text{OH})_2]\) [23]. The layer charge density (LCD) was determined by the alkylammonium method (AAM) [24,25]. The results of chemical formula and the LCD of samples are listed in the studies of Wang et al. [26] and Wang and Liao [27]. The structural information such as octahedral cation content and the LCD obtained by these methods were used to investigate the relationships among the proportions of \(cv\) and \(tv\) layers, the cation distribution in octahedral sheet, and the LCD. All the experiments were performed on <0.2 \(\mu m\) fraction. The experimental data of sample characterization originate from studies of Wang et al. [26] and Wang and Liao [27].

Table 1. Origin of samples.

| Samples       | Description | Source          | Supplier                                      |
|---------------|-------------|-----------------|-----------------------------------------------|
| XL_01_B8     | Montmorillonite | Wyoming, USA    | Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) |
| XL_02_B9     | Montmorillonite | Wyoming, USA    |                                               |
| XL_04_B14    | Beidellite   | Hungary         |                                               |
| XL_06_B22    | Montmorillonite | Hungary         |                                               |
| XL_09_SWy1   | Montmorillonite | Wyoming, USA    | Society’s Source Clays Repository, Clay Minerals  |
| XL_10_STx1   | Montmorillonite | Texas, USA      |                                               |
| XL_11_NAu1   | Nontronite   | South Australia |                                               |
| XL_12_NAu2   | Nontronite   | South Australia | Society(CMS)                                   |
| XL_13_14TR03 | Montmorillonite | Unidentified    |                                               |
| XL_14_41ValC18 | Beidellite | Valdagno, Italy |                                               |
| XL_16_4JUP   | Montmorillonite | Argentina       | Karlsruhe Institute of Technology (KIT)       |
| XL_17_2LP    | Montmorillonite | Argentina       |                                               |
| XL_18_Valdol | Beidellite   | Valdagno, Italy |                                               |
| XL_19_NWa    | Nontronite   | Washington, USA |                                               |

Figure 4. X-ray powder diffraction (XRD) patterns of Sample XL_09_SWy1 before and after purification.
Table 2. Chemical compositions of samples measured by XRF analysis (<0.2 μm fraction).

| Samples          | Oxides (%) |          |          |          |          |          |          |          |          |          |          |          | LOI *  | Sum    |
|------------------|------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|---------|---------|
|                  | SiO₂       | Al₂O₃    | Fe₂O₃    | MnO      | MgO      | CaO      | K₂O      | Na₂O     | TiO₂     | CuO      | P₂O₅     | Cr₂O₃    | NiO     | LOI     |
| XL_01_B8         | 55.18      | 19.98    | 4.40     | 0.01     | 1.74     | 0.05     | 0.03     | 0.00     | 0.14     | 3.42     | 0.00     | 0.00     | 15.05   | 100.01 |
| XL_02_B9         | 60.25      | 17.03    | 3.74     | 0.01     | 2.19     | 0.03     | 0.03     | 0.00     | 0.12     | 2.86     | 0.01     | 0.00     | 13.74   | 100.00 |
| XL_04_B14        | 46.63      | 18.17    | 11.10    | 0.02     | 1.95     | 0.04     | 0.50     | 0.00     | 2.24     | 3.01     | 0.12     | 0.03     | 16.16   | 100.00 |
| XL_06_B22        | 59.93      | 16.24    | 1.22     | 0.00     | 3.53     | 0.03     | 0.04     | 0.00     | 0.15     | 3.79     | 0.00     | 0.00     | 15.07   | 100.00 |
| XL_09_SWy1       | 55.19      | 19.78    | 4.19     | 0.01     | 2.66     | 0.03     | 0.03     | 0.00     | 0.10     | 3.12     | 0.00     | 0.00     | 14.89   | 100.00 |
| XL_10_STx1       | 58.03      | 18.10    | 2.00     | 0.01     | 2.93     | 0.04     | 0.06     | 0.00     | 0.27     | 3.16     | 0.02     | 0.00     | 15.37   | 100.00 |
| XL_11_NAu1       | 43.63      | 7.36     | 30.25    | 0.01     | 0.00     | 0.03     | 0.01     | 0.00     | 0.03     | 3.82     | 0.00     | 0.01     | 14.48   | 100.00 |
| XL_12_NAu2       | 48.35      | 2.49     | 32.67    | 0.00     | 0.01     | 0.04     | 0.02     | 0.00     | 0.04     | 3.07     | 0.00     | 0.00     | 13.30   | 100.00 |
| XL_13_14TR03     | 55.14      | 16.60    | 1.76     | 0.01     | 4.98     | 0.03     | 0.02     | 0.00     | 0.09     | 4.09     | 0.00     | 0.00     | 17.27   | 100.00 |
| XL_14_41ValC18   | 52.29      | 16.06    | 8.40     | 0.01     | 3.65     | 0.03     | 0.98     | 0.00     | 0.29     | 3.18     | 0.04     | 0.04     | 15.00   | 100.00 |
| XL_16_4JUP       | 52.29      | 18.24    | 7.44     | 0.03     | 2.13     | 0.04     | 0.32     | 0.00     | 0.93     | 3.11     | 0.03     | 0.00     | 15.45   | 100.00 |
| XL_17_2LP        | 54.20      | 18.62    | 4.48     | 0.02     | 3.00     | 0.03     | 0.06     | 0.00     | 0.15     | 2.99     | 0.00     | 0.00     | 16.44   | 100.00 |
| XL_18_Valdol     | 49.85      | 15.26    | 10.44    | 0.02     | 3.70     | 0.05     | 1.07     | 0.00     | 0.39     | 3.04     | 0.11     | 0.04     | 16.00   | 100.00 |
| XL_19_NWa        | 46.53      | 8.64     | 23.02    | 0.02     | 1.65     | 0.02     | 0.05     | 0.00     | 0.60     | 2.97     | 0.02     | 0.01     | 16.46   | 100.00 |

* LOI: loss on ignition.
2.2. Thermal Analysis

The thermogravimetric (TG) and differential thermal analysis (DTA) measurements were performed on the device SETARAM TGA 92-16.18. Before analysis, samples were stored in a desiccator over a saturated magnesium nitrate solution Mg(NO₃)₂ (53% RH) for at least 24 h to create a constant humidity condition. Then, a 30 mg sample was used for each measurement, with a heating rate of 10 °C/min in the temperature range of 25 to 1000 °C. The proportions of cis- and trans-vacant configurations were calculated by fitting the derivative thermogravimetry (DTG) curves in the range of 300 to 900 °C using the PeakFit program v4.12 (Systat Software Inc., 2007). According to Drits et al. [8], the areas of DTG peaks with the temperature below and above 600 °C correspond to the amount of trans- and cis-vacant configurations, respectively, in dioctahedral smectites. Each sample was fitted until the coefficient of determination R² was >0.999. The classification of cv and tv varieties was based on Wolters and Emmerich [28] (Table 3).

### Table 3. Classification of dioctahedral smectites according to the thermal reaction (according to Wolters and Emmerich [28]).

| Varieties | cv        | cv/tv     | tv/cv     | tv        |
|-----------|-----------|-----------|-----------|-----------|
| the area of dehydroxylation peaks above 600 °C/% | 100–75    | 74–50     | 49–25     | 24–0      |

3. Results and Discussion

3.1. Characterization and Classification of Octahedral Structure

Figure 5 shows the thermal behavior of samples with mainly cv and tv configurations. The dehydration of both samples was at around 120 °C. The dehydroxylation temperature of the samples with mainly cv structure was around 700 °C and the sample with mainly tv structure was around 500 °C, which agreed well with previous studies [7,8,28,29].

![Figure 5](image)

**Figure 5.** Thermal analysis of (a) sample XL_01_B8 with mainly cv structure; (b) Sample XL_12_NAu2 with tv structure.

The results of the classification are presented in Table 4. Fourteen samples covered a wide range of cis- and trans-vacant varieties and the mixtures of them, i.e., cv, cv/tv, tv/cv and tv (Table 4). Five samples were considered to be cv varieties with a small amount of tv configurations (Table 4). Samples XL_06_B22, XL_09_SWy1, and XL_17_2LP showed a similar peak profile with that of sample XL_01_B8, as shown in Figure 6a, and they showed a main peak near 700 °C. Additionally, sample XL_10_STx1 had a small broad peak around 500 °C, which indicated a small amount of tv (Figure 6b).
Table 4. The cations content and the proportions of trans- (W\text{t}) and cis-vacant (W\text{cv}) configurations of samples and the classification.

| Sample   | Tetrahedral Cation (mol/FU) | Octahedral Cations (mol/FU) | Octahedral Sheet | Classification |
|----------|-----------------------------|-----------------------------|------------------|----------------|
|          | AL\textsuperscript{b}       | AL\textsuperscript{b}       | Fe\textsuperscript{b} | Mg\textsuperscript{b} | W\text{t} (%) | W\text{cv} (%) |
| XL_01_B8 | 0.12                        | 1.58                        | 0.24             | 0.19            | 82.5        | 17.5          |
| XL_06_B22| 0.09                        | 1.53                        | 0.08             | 0.45            | 90.0        | 10.0          |
| XL_09_SWy1| 0.12                        | 1.53                        | 0.22             | 0.28            | 87.7        | 12.3          |
| XL_10_STx1| 0.00                        | 1.57                        | 0.11             | 0.32            | 92.8        | 7.2           |
| XL_17_2LP | 0.10                        | 1.48                        | 0.24             | 0.32            | 95.7        | 4.3           |
| XL_02_B9 | 0.41                        | 1.55                        | 0.27             | 0.32            | 57.0        | 43.0          |
| XL_13_14TR03| 0.00                       | 1.42                        | 0.10             | 0.54            | 51.1        | 48.9          |
| XL_16_4JUP| 0.20                        | 1.40                        | 0.41             | 0.24            | 47.6        | 52.4          |
| XL_04_B14| 0.44                        | 1.23                        | 0.65             | 0.23            | 1.3         | 98.7          |
| XL_11_NAu1| 0.49                        | 0.21                        | 1.83             | 0.00            | 0.0         | 100.0         |
| XL_12_NAu2| 0.19                        | 0.04                        | 1.94             | 0.00            | 0.0         | 100.0         |
| XL_14_41ValC18| 0.17                    | 1.22                        | 0.47             | 0.40            | 15.0        | 85.0          |
| XL_18_Valdol| 0.25                        | 1.10                        | 0.59             | 0.42            | 17.1        | 82.3          |
| XL_19_NWa | 0.42                        | 0.43                        | 1.46             | 0.21            | 0.8         | 99.2          |

Samples XL_02_B9 and XL_13_14TR03 can be classified as cv/tv varieties. They had a main peak above 600 °C which indicate one dehydroxylation reaction (Figure 7). Thus, the cv configurations dominated in these two samples (Table 4).
Figure 7. Examples of derivative thermogravimetry (DTG) curves of $cv/tv$ smectites. Sample XL_13_14TR03 with 51.1% $cv$ layers and 48.9% $tv$ layers.

Sample XL_16_4JUP was $tv/cv$ varieties. It contained two well resolved peaks in the $cv$ and $tv$ region which indicated two main dehydroxylation reactions, i.e., around 490 °C and 650 °C (Figure 8). The sum of the peak area below 600 °C (52.4%) was larger than the area above 600 °C (47.6%), even though the peak at around 630 °C was stronger than the peak at around 490 °C. Therefore, the amount of $tv$ is larger than the amount of $cv$. Thus, the $tv$ configurations dominated in this sample.

Figure 8. Examples of derivative thermogravimetry (DTG) curves of $tv/cv$ smectites. Sample XL_16_4JUP with 52.4% $tv$ layers and 47.6% $cv$ layers.

Six samples were classified as $tv$ varieties (Table 4), i.e., three nontronite samples XL_11_NAu1, XL_12_NAu2 and XL_19_NWa; three beidellite samples XL_04_B14, XL_18_Valdol and XL_14_41ValC18. Tsipursky and Drits [5] showed that montmorillonite and some Al-rich smectites are cis-vacant structure, beidellites and nontronites typically have a trans-vacant structure. As expected, nontronite samples XL_11_NAu1 and XL_12_NAu2 were found to be purely trans-vacant configurations, another nontronite sample XL_19_NWa contained 99.2% $tv$ structure. These three nontronites samples show similar dehydroxylation behavior to sample XL_04_B14; they had only one strong peak around 450 °C as shown in Figure 9a. It indicated one dehydroxylation reaction at this temperature. Two resolved peaks were also found in $tv$ samples XL_14_41ValC18 and XL_18_Valdol, that showed similar derivative thermogravimetry (DTG) curves with a DTG peak at around 500 °C than the peak at around 630 °C (Figure 9b).

In summary, five samples were classified as the $cv$ variety with the main dehydroxylation reaction near 700 °C and six samples were classified as the $tv$ variety with the main dehydroxylation reaction near 500 °C. The remaining three samples contained two well resolved peaks corresponding
to two main dehydroxylation reactions between 500 and 700 °C. Two of these samples were considered to be the cv/tv type; one of them was considered to be the tv/cv type, and the ratio between the peak areas reflected the ratio between cv and tv layers. The results of the proportions of cv and tv configurations by thermal analysis agree with the expectations and confirm the classification of the selected samples.

3.2. Relationship between Octahedral Cations and Octahedral Structure

Drits et al. [16] considered that there was a compositional control on the distribution of octahedral cations over trans- and cis sites in dioctahedral smectites. Therefore, the relationships between the cation distribution in the octahedral sheet and the cv, tv varieties were investigated. No relationship between the octahedral Mg\(^{2+}\) content and the proportion of tv and cv was detected (Figure 10). It indicated that the octahedral Mg\(^{2+}\) content is not correlated to the configuration of the octahedral sheets. In contrast, the influences of octahedral Fe\(^{3+}\) and Al\(^{3+}\) content on the structure of octahedral sheets is highly significant. A linear relationship was found between octahedral Fe\(^{3+}\) and Al\(^{3+}\) content and proportion of cv and tv configurations (Figure 11). The proportion of tv structure was increased with increasing octahedral Fe\(^{3+}\) content and decreasing octahedral Al\(^{3+}\) content. It indicates that the substitution of Al\(^{3+}\) by Fe\(^{3+}\) in octahedral sheet could be the main reason for the formation of tv varieties. Wolters and Emmerich [28] concluded that iron content controls the structure which is consistent with our study. Samples can be classified as tv varieties when octahedral Fe\(^{3+}\) > 0.46 mol/FU, and pure tv varieties were found when octahedral Fe\(^{3+}\) > 1.8 mol/FU (Table 4, nontronite samples XL_11_NAu1 and XL_12_Nau2). These two nontronites were found with a main dehydroxylation peak in the region around 450 °C (Figures 5b and 9a). It is worth noting that the iron content affects the thermal stability of clay minerals; high iron content can reduce the dehydroxylation temperature due to the differences in bonding energy in the order Mg–OH > Al–OH > Fe–OH [17,30]. This can be one of the reasons that nontronites show a lower dehydroxylation temperature and tv configuration.

![Figure 9](image.jpg)
3.3. Relationship between Layer Charge Density and Octahedral Structure

The present results show that there is no relation between the proportion \( tv \) and \( cv \) configurations to the total layer charge density (Figure 12a). However, the relationship between the proportion of \( tv \) configuration to tetrahedral charge is more significant (Figure 12b). Wolters et al. [17] found a positive correlation between tetrahedral charge and the proportion of \( tv \) configuration which is consistent with our results.
Furthermore, the content of tetrahedral Al\textsuperscript{3+} is positively correlated with octahedral Fe\textsuperscript{3+} content, i.e., the content of tetrahedral Al\textsuperscript{3+} increases with the octahedral Fe\textsuperscript{3+} increasing (Figure 13). Cuadros [31] concluded that this could be because the tetrahedral b dimension is bigger than the octahedral b dimension. He concluded that an increase in octahedral Mg\textsuperscript{2+} + Fe\textsuperscript{3+} causes an increase in tetrahedral Al\textsuperscript{3+} when correlating the ideal b dimension of octahedral and tetrahedral sheets. Cuadros [31] pointed out that the octahedral sheet with cv structure has a smaller b dimension than the tv structure. Therefore, when the tetrahedral sheets have a low substitution (low tetrahedral charge), the sample tends to prefer the cv structure; otherwise, it tends to be the tv structure. Kaufhold et al. confirmed that the existence of a positive correlation between iron content and tetrahedral charge from an energy point of view [18]. The authors concluded that the ratio of tv and cv depends on the iron content which is due to the octahedral iron or tetrahedral Al substitutions [18]. It can be concluded that the iron content is a dominant factor in the positive correlation between the proportion of tv, cv configurations, and the tetrahedral charge. The high iron content is another factor for the lower dehydroxylation temperature of tv configuration than cv configuration.

![Figure 13. Relationship between tetrahedral Al\textsuperscript{3+} content and octahedral Fe\textsuperscript{3+} content.](image)

### 4. Conclusions

As expected, the dehydroxylation temperature of samples with mainly cv configuration is about 680 °C and for samples with mainly tv configuration it is around 500 °C. The proportions of cv and tv can be determined by fitting the derivative thermogravimetry (DTG) curves. On the one hand, samples which were classified as the cv variety showed a main dehydroxylation peak near 680 °C. On the other hand, samples which were classified as the tv variety showed a main dehydroxylation peak between 450 and 500 °C. Samples of cv/tv and tv/cv varieties presented one main peak with a broad shoulder in their own region or two well resolved peaks in the cv and tv region which indicated two main dehydroxylation reactions. The content of cv and tv configurations is dependent on the chemical composition. The octahedral Fe\textsuperscript{3+} and Al\textsuperscript{3+} contents were highly related to the proportion of trans- and cis-vacant structures. With an increasing amount of octahedral Fe\textsuperscript{3+} and a decreasing amount of octahedral Al\textsuperscript{3+}, the proportions of the tv increased. Pure tv dioctahedral smectites were formed when Fe\textsuperscript{3+} > 1.8 mol/FU. No pure cv configuration was found in these samples. No relationships among the total layer charge, octahedral Mg\textsuperscript{2+} content, and the proportion tv and cv were detected. A positive correlation between the tetrahedral charge and trans-vacancies was found and the octahedral iron content influences the tetrahedral charge. The present results indicate that the iron content has a significant effect on the structure of the octahedral sheet.

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