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Research paper

Influence of organic matter on the reactivity of clay minerals in highly alkaline environments

Kerstin Elert *, Eduardo Sebastián Pardo, Carlos Rodriguez-Navarro

Department of Mineralogy and Petrology, University of Granada, Fuentenueva S/N, 18002 Granada, Spain

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ABSTRACT

Soil organic matter has important implications in dissolution reactions of clay minerals and their transformation. Under acidic conditions increased dissolution rates are generally reported. However, in high pH environments, organic matter (OM) might have a passivation effect on the mineral surface, thereby hindering dissolution and transformation substantially. The reduced reactivity of clay minerals is an important consideration when clays are used as backfill materials in nuclear waste disposals or when lime is used for soil stabilization. Here the outcome of a comparative study is presented using soil, containing common clay minerals such as smectite, interstratified illite–smectite, illite and kaolinite, that was treated with highly concentrated alkaline solutions in the presence and absence of naturally occurring organic matter. The results clearly show that clay mineral dissolution and the formation of new zeolitic phases at room *T* are delayed in the presence of OM. The soils' OM content is, thus, an important parameter to be considered in systems where clay minerals are exposed to highly alkaline environments.

1. Introduction

The interaction of organic matter (OM) with clay minerals has been studied extensively in the past and it has been established that OM stabilization occurs through the formation of organo-mineral complexes (Allison, 1973; Mayer, 1994; Leinweber et al., 1999). Especially, expandable clays and allophanic materials have been found to be responsible for the reduction in bioavailability of organic molecules (Mayer, 1994). However, little attention has been paid to the fact that the presence of OM might, to a significant degree, influence reactions between clay minerals and pore waters, in particular in high pH environments. Wattel-Koekkoek (2002) stated that the sorption of OM would render the clay surface hydrophobic, resulting in its passivation. Reduced reactivity modifies clay minerals stability and their transformation into new phases. This aspect needs to be considered not only when clay is used as a backfill material for nuclear waste disposal or as waste water barrier where clay minerals are in direct contact with high-pH alkali-rich solutions generated by water-induced concrete alteration (Wilson et al., 2006), but also in the case of soil stabilization using lime or cement (Lunt, 1980). Reduced mineral reactivity in the presence of OM might also have implications in the alkaline treatment of clays at high pH, a novel treatment method proposed by the authors for the consolidation of earthen architecture (Elert et al., 2008).

According to Cornejo and Hermosin (1996) humic substances are the main components of soil OM interacting with the soil inorganic components (i.e., clays) and forming organo-mineral complexes. Conventionally, humic substances are divided according to their solubility characteristics: (i) humic acid is not soluble under acidic conditions but is soluble in alkali; (ii) fulvic acid is soluble in acid and alkali; (iii) humin is not soluble in acid and alkali.

The chemical weathering of minerals, including clay minerals, at low pH by organic acids has been studied extensively and increased mineral dissolution is often reported as a result of the formation of metal-organic complexes or the catalytic effect of organic acids on proton promoted mineral dissolution (Huang and Keller, 1971; Ganor et al., 2009). However, interactions depend on the organic acid species. Chin and Mills (1991) determined that low molecular weight organic ligands increased kaolinite dissolution rate, whereas humic acid inhibited dissolution. The inhibiting effect of humic acid is not surprising, considering its insolubility under acidic conditions. At high pH, some humic substances, especially those being insoluble in alkaline solutions, might exert a similar dissolution inhibiting effect by causing the passivation of the mineral surface. Claret et al. (2002) studied the reactivity of clay minerals from the Callovo-Oxfordian formation which is considered a potential host for nuclear waste storage. The authors detected very limited mineral transformation of these clays under high pH conditions which they associated with the presence of OM. Furthermore, Lunt (1980) suggested that the presence of OM inhibited the setting of cement or impaired pozzolanic reactions when lime was used for the stabilization of soils. Thompson (1967) also observed a retardation of pozzolanic reactions in lime-stabilized soils containing more than 1 wt.% OM which he attributed to a "masking effect" of OM and/or an organic matter chelation reaction. Despite the previous studies, information on the

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* Corresponding author. Tel.: +34 958 246616; fax: +34 958 243368.
E-mail address: kelert@ugr.es (K. Elert).

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inhibiting effect of OM on the dissolution of clay minerals is very limited and no attempt has been made so far to directly compare the mineralogical evolution (i.e. dissolution and transformation) of clay minerals in contact with highly alkaline solutions in the presence and absence of OM.

Here, the outcome of a laboratory study is presented which was conducted in order to evaluate the suitability of an alkaline treatment for the consolidation of earthen architecture by reducing the soils swelling capacity. In contact with highly alkaline solutions clay minerals dissolve and transform into non-expandable reaction products (i.e., zeolites) which have cementing properties and improve water resistance and mechanical strength of the earthen material (Elert et al., in press). However, a preliminary study showed that transformation was very limited, possibly as a result of the presence of OM (Elert et al., 2008). In order to determine the effect of OM on the clay minerals reactivity one batch of soil was treated with H_2O_2 to remove OM prior to the alkaline treatment and its mineralogical evolution was compared to that of a batch of the same soil containing OM. The direct comparison of the mineralogical evolution of soil from the Alhambra Formation with and without OM exposed to high pH conditions is presented here which allows the determination of a global retardation effect on the dissolution and transformation of clay minerals exerted by OM.

The soil chosen in this study was collected from the Alhambra Formation in Granada, Spain. This soil was used historically for the construction of earthen architecture such as the historic city walls and the Alhambra fortress (de la Torre et al., 1996; Ontiveros et al., 1999). It contains illite, kaolinite and interstratified illite–smectite as main clay minerals, with minor amounts of paragonite and chlorite. A bibliographic review of the mineralogical composition of earthen constructions revealed that these minerals, maybe with the exception of paragonite which is a mineral of rather rare occurrence, are the most common in the majority of earthen structures around the world (Houben and Guillaud, 1994). This is not surprising since they are also the most common clay minerals in soils (Velde, 1992). Thus, the results of this study will be relevant to many applications using common clayey soils in contact with alkaline solutions.

2. Materials and methods

2.1. Materials

Soil samples were taken from the Alhambra Formation in close proximity to the Alhambra Fortress, Granada (Spain). The Alhambra Formation outcrops at the east margin of the Granada Basin and constitutes a good example of a fluvial (delta-fan) debris-flow deposit from the Pleistocene-Early Pliocene age (Martin, 2000). The clay-rich soil samples were taken from the upper horizon of the Alhambra Formation and constitute a typical example of Mediterranean red soils (Martin-Garcia et al., 1998). Carbonates were eliminated using acetic acid (0.2 N) and the clay fraction (<2 μm) was separated by centrifugation (Kubota KS-8000). Semiquantitative X-ray analysis of oriented aggregates showed that the <2 μm fraction was composed of 45 ± 5% illite, 30 ± 5% kaolinite, 15 ± 5% smectite/interstratified illite–smectite and <10% paragonite and chlorite. TEM-AEM data revealed the beidellitic character of smectites. Deconvolution of the diffractogram of the oriented aggregate after an ethylene glycol treatment suggested the presence of an illite–smectite interstratification of variable proportions, dominated by smectite-rich phases. For a complete mineralogical characterization of the Alhambra Formation soil see Elert et al. (2008).

Prior to alkaline treatment, the OM of one batch of the clay was eliminated using hydrogen peroxide. The clay dispersion (10 g/10 ml H_2O) was mixed at room *T* (20 °C) with 50 ml of 20% H_2O_2 (wt/wt) solution and stirred until frothing subsided. The treatment was repeated twice. Afterwards the sample was washed with deionised water.

Note that we will refer to samples treated with H_2O_2 prior to alkaline activation as samples without OM, while samples not treated with H_2O_2 prior to alkaline activation will be referred to as samples with OM.

For the alkaline treatment, 5 g of the clay fraction was mixed with 100 ml of 5 M NaOH or 5 M KOH solution. The starting pH of the NaOH and KOH solutions was >13. Samples of the alkaline-treated clay suspensions were kept in air-tight polyethylene bottles at room *T*. The bottles were shaken periodically and aliquots were collected after 1 day, 2 weeks, 4, 6 months, 1 and 6 years. Dispersed clay samples (3 ml) were washed with deionised water until a pH of 7 was reached. After decanting excess water, oriented aggregates (OA) were prepared and dried at room *T*.

2.2. Methods

The amount of OM was determined using thermogravimetric analysis (TG) on a Shimadzu TGA-50H coupled with Fourier transform infrared spectroscopy (FTIR; Nicolet 550) for evolved gas analysis. Analyses were performed in flowing air (100 ml/min) and at a constant heating rate of 20 °C $\min^{-1}$ (25–950 °C). One analysis per sample was performed.

Elemental analysis of nitrogen, carbon and hydrogen was performed to verify the organic carbon content using a Fisons Carlo Erba EA 1108 CHNS-O equipped with TCD detection system. The samples were heated to 1020 °C during 800 s and calculations were carried out employing Eager 200 software. One analysis per sample was performed.

The mineralogical evolution of the clay fraction of the Alhambra Formation soil upon alkaline treatment was determined by means of X-ray diffraction (XRD). XRD patterns of oriented aggregates (OA) were collected using a X'Pert PRO diffractometer (PANalytical B.V.) equipped with Cu-Kα radiation; Ni filter; 45 kV voltage; 40 mA intensity; spinner; exploration range of 3° to 60° 2θ and goniometer speed of $0.05° \ 2\theta \ s^1$.

The morphology and composition of the clay fraction and the new phases formed during the alkaline treatment were studied by means of field emission scanning electron microscopy (FESEM, AURIGA, Carl Zeiss SMT) coupled with EDS microanalysis (INCA-200, Oxford) as well as transmission electron microscopy (TEM, Philips CM20, CIC-UGR) operated at 200 kV and equipped with an EDAX solid-state ultra-thin window energy dispersive X-ray (EDS) detector.

Nitrogen sorption isotherms of powdered clay samples before and after alkaline treatment were obtained at 77 K on a TriStar 3000 (Micromeritics). About 0.2 g of sample was degassed at 150 °C for 3 h prior to analysis using a sample degas system (VacPrep 061, Micrometics). Two analyses per sample were performed.

3. Results

3.1. Determination of OM content in Alhambra Formation soil (<2 μm fraction) using TG coupled with FTIR for evolved gases and elemental analysis

The major weight loss observed during TG analysis in the H_2O_2-treated and in the untreated soil samples can be attributed to adsorbed and structural water of clay minerals (Fig. 1). The sample with OM showed a more pronounced weight loss between 300 and 500 °C, the temperature range commonly associated with the thermal decomposition of OM (Boyle, 2004). The difference in weight loss between the untreated samples and the samples treated with H_2O_2 was 1.1 wt.%, which is attributed to the OM content.

The evolved gas spectrum taken at 356 °C of the clay sample treated with H_2O_2 did not show any detectable amounts of CO and only a small amount of CO_2, whereas the spectrum of the untreated clay sample revealed the presence of CO in addition to a much larger amount of CO_2 (Fig. 2). These results suggest that the H_2O_2 treatment was effective in destroying OM. The release of a small amount of CO_2 in the sample

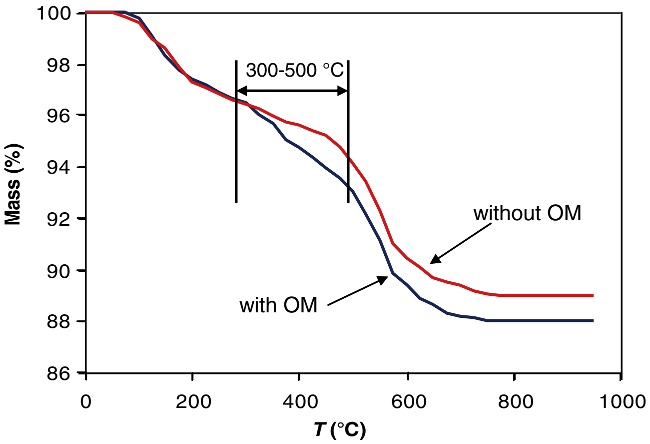

Fig. 1. Thermogravimetric curves of untreated Alhambra Formation soil with and without OM.

treated with H_2O_2 implies that traces of OM still persist. However, CO gas, being an indicator for incomplete combustion, was only released during the combustion of the samples which were not treated with H_2O_2 and contained a much larger amount of OM (Fig. 2a).

Elemental analysis revealed a total carbon content of 0.91 wt.% (Table 1) in the untreated soil sample which is attributed to organic and black carbon. In order to calculate the OM content of the soil sample we considered the difference in carbon content between the untreated clay sample and the sample treated with H_2O_2, which was 0.66 wt.%. Schumacher (2002) stated that OM in soils is constituted of ~58% organic carbon, the rest corresponding primarily to oxygen, hydrogen and nitrogen. Thus, the calculated OM content of the untreated soil amounts to 1.14 wt.%. This value is in good agreement with that calculated from TG. It cannot be ruled out that the calculated OM content from TG and elemental analysis data is slightly underestimated because organic carbon might not have been destroyed completely by the H_2O_2 treatment. Plante et al. (2005) reported that it is possible to remove about 87% of the initial organic carbon from clay samples by hydrogen peroxide treatment. According to the same authors, the remaining carbon corresponds to black carbon, a term used to describe the carbon which withstands strong chemical or thermal oxidation and is considered inert. Black carbon includes graphitic and pre-graphitic phases such as charcoal, graphite, soot and coal.

Note that the initial treatment of the clay fraction with acetic acid eliminated any carbonates (inorganic carbon) that could have masked the TG results. In any case, the decomposition of carbonates occurs at $T > 500$ °C at a heating rate 2 °C/min (Rodriguez-Navarro et al., 2009, 2012) and only CO_2 is released during their thermal decomposition.

Overall, the values of the OM content of the studied soil calculated from TG and elemental analysis data are in good agreement with published data by Martin-Garcia et al. (1998) for the Alhambra Formation soil.

Table 1
Elemental analysis results of samples heated up to 1020 °C.

Sample	wt.%		
	Nitrogen	Carbon	Hydrogen
Clay, untreated	0.21	0.91	1.36
Clay treated with H_2O_2	0.09	0.25	1.33

3.2. Mineralogical evolution of Alhambra Formation soil (<2 μm fraction) treated with 5 M NaOH or 5 M KOH

3.2.1. XRD

The XRD patterns of the untreated Alhambra Formation soil before and after removal of OM showed that the smectite-rich interstratified illite–smectite suffered minor degradation as a result of the H_2O_2 treatment (Fig. 3). A partial destruction of 2:1 clays induced by H_2O_2 treatment and indicated by a reduction of the Bragg peak intensity has been reported previously (Douglas and Fiessinger, 1971; van Langeveld et al., 1978). However, clays other than interstratified illite–smectite were not affected by the H_2O_2 treatment in our study, as can be deduced from the absence of any changes in 001 Bragg peak intensities of illite and kaolinite before and after H_2O_2 treatment (Fig. 3).

XRD analysis revealed that the presence of OM clearly modified the clay minerals reactivity towards alkaline attack using NaOH or KOH solutions. The mineralogical evolution was faster and changes in the XRD patterns were more pronounced in the case of the samples treated with H_2O_2 prior to alkaline treatment. However, the zeolitic phases formed upon alkaline treatment were the same in the presence and absence of OM and depended on the cation (i.e. Na or K) in the alkaline solution.

The mineralogical evolution upon alkaline treatment in the presence of OM using 5 M NaOH and 5 M KOH is shown in Fig. 4a and b, respectively. Both treatments caused a partial destruction of smectites and interstratified illite–smectites after only 2 weeks, resulting in a reduction in the intensity of the broad Bragg peak (shoulder) around 12–14 Å. The intensity of the 001 Bragg peak of kaolinite started to decrease after 4 months using either 5 M NaOH or 5 M KOH. This mineral disappeared completely after 1-year treatment with 5 M KOH and only a trace amount remained in the case of soil samples treated with 5 M NaOH. Illite only suffered a partial destruction upon treatment with 5 M NaOH after 6 months which continued over the course of the treatment. However, even after 6 years illite was still detectable. During the treatment with 5 M KOH the intensity of the 001 Bragg peak of illite remained unchanged as a result of the stabilizing effect of K^+ present in the alkaline solution. Newly formed zeolitic phases, a faujasite with the following formulae: $Na_2Al_2Si_{2.5}O_9 \cdot 6.2H_2O$ (JPDF card no. 380237) and a hydroxysodalite ($Na_{2.16}Al_2Si_{1.68}O_{7.44} \cdot H_2O$, JPDF card no.

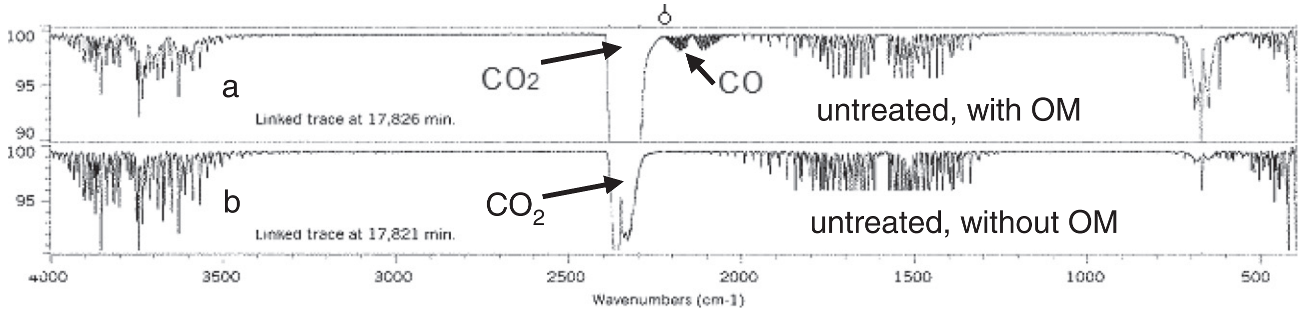

Fig. 2. Evolved gas analyses (FTIR) of untreated Alhambra Formation soil with OM (a) and without OM (b).

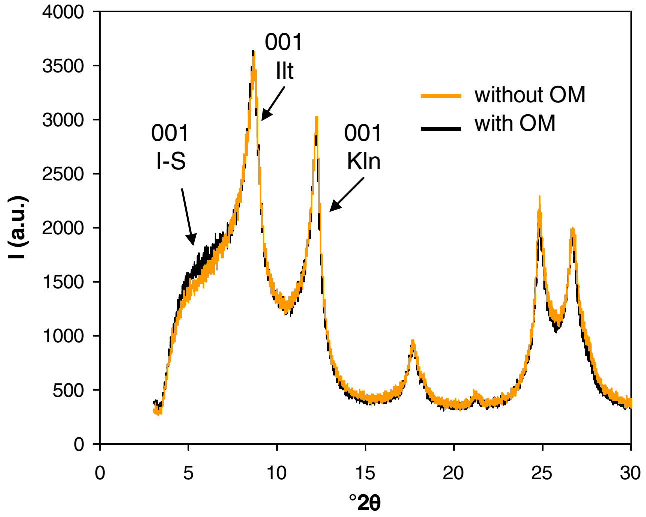

Fig. 3. XRD patterns of Alhambra Formation soil (OA of clay fraction) before (with OM) and after (without OM) H_2O_2 treatment. I–S = smectite-rich interstratied illite–smectite, Ilt = illite, Knl = kaolinite.

311271) were detected after 6 months and 1 year, respectively, in samples treated with 5 M NaOH. The treatment with 5 M KOH resulted in the formation of zeolite K-I ($K_2Al_2Si_2O_8 \cdot 3.8H_2O$, JPDF card no. 180988) and chabazite ($K_2Al_2SiO_6 \cdot H_2O$, JPDF card no. 120194) after 4 months and 1 year, respectively.

The comparison of the mineralogical evolution of soil samples treated with alkaline solutions in the presence and absence of OM revealed a slower dissolution of clay minerals and a delayed formation of zeolitic phases in the presence of OM. After 6 months of alkaline treatment with 5 M NaOH, a faujasite-type zeolite (Fig. 5a) was identified in the Alhambra Formation soil with and without OM. However, the intensities of the 111, 220 and 311 Bragg peaks of faujasite were significantly higher in the sample without OM. Furthermore, the sample without OM showed a more severe reduction of the 001 kaolinite Bragg peak intensity if compared to the sample with OM. The 001 illite Bragg peak intensity of the sample without OM was also slightly lower than the one of the sample with OM. The effect of OM on smectite and interstratified illite–smectite dissolution could not be detected using XRD because of the great inhomogeneity (i.e., illite–smectite interstratification with

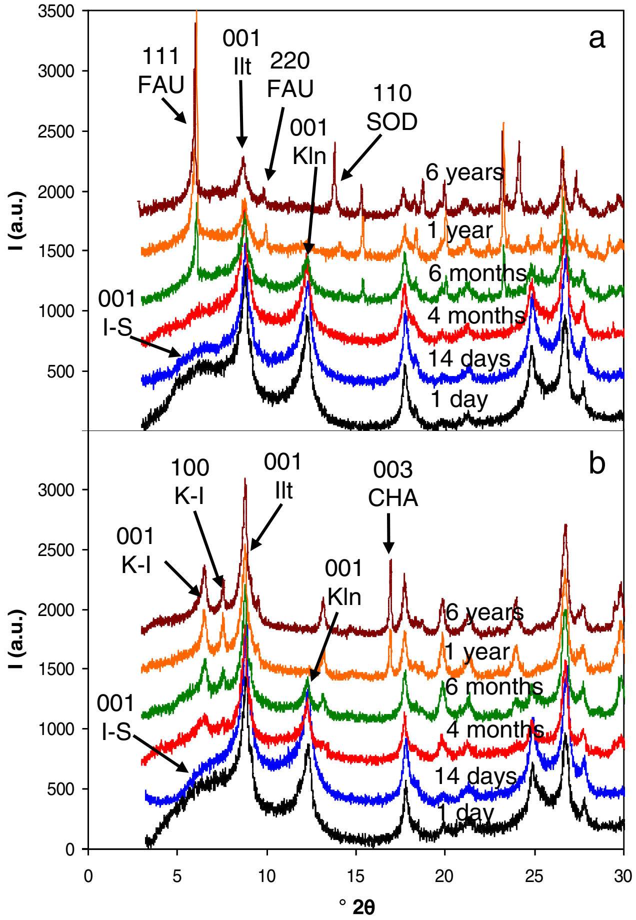

Fig. 4. XRD patterns of Alhambra Formation soil (OA of clay fraction with OM) treated with a) 5 M NaOH and b) 5 M KOH for various periods of time. FAU = faujasite, I–S = smectite-rich interstratied illite–smectite, Ilt = illite, Knl = kaolinite, K-I = zeolite K-I, CHA = chabazite, SOD = hydroxysodalite.

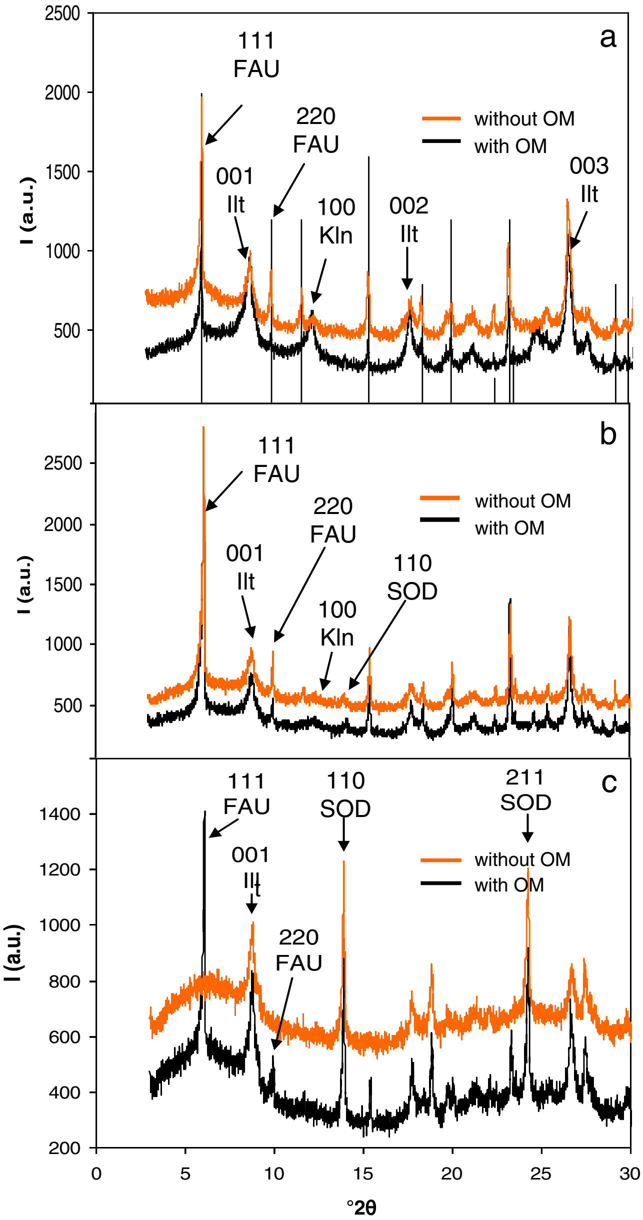

Fig. 5. XRD patterns of Alhambra Formation soils (OA of clay fraction) treated with 5 M NaOH solution for 6 months (a), 1 year (b) and 6 years (c). FAU = faujasite, Ilt = illite, SOD = hydroxysodalite, Kln = kaolinite, black line pattern: faujasite-type zeolite (JPDF card no. 380237).

variable proportions) and low crystallinity of these phases in the Alhambra Formation soil.

After one year of treatment with 5 M NaOH, XRD data (Fig. 5b) revealed that kaolinite had practically disappeared in Alhambra Formation soil samples with and without OM. However, the intensity of the 111 and 220 Bragg peaks of the faujasite-type zeolite was still higher in the sample without OM if compared to the sample with OM. Furthermore, an additional Bragg peak at 6.3 Å, presumably corresponding to a sodalite-type zeolite was observed in both samples.

Clear evidence for the presence of the sodalite-type zeolite was observed after 6 years of alkaline treatment. The amount of this phase increased over time at the expense of the faujasite-type zeolite. While the 111 and 220 Bragg peaks of faujasite were still detectable in the sample with OM, this phase had transformed completely into the sodalite-type zeolite in the sample without OM as indicated by the absence of the above mentioned Bragg peaks (Fig. 5c).

The mineralogical evolution of the sample treated with 5 M KOH without OM was also faster than the one of the sample with OM during the first 6 months. The XRD patterns of both samples showed the presence of zeolite K-I. However, in the sample without OM the decrease of the 001 kaolinite Bragg peak intensity was more pronounced, and an additional peak at 5.2 Å was observed which corresponds to the 003 Bragg peak of a chabazite-type zeolite (Fig. 6a).

After 1 year of treatment with 5 M KOH the XRD patterns of both samples were very similar and the 003 reflection of the chabazite-type zeolite was detected in the sample with OM as well. Kaolinite could no longer be detected in either of the samples (Fig. 6b). No further changes in the Bragg peaks intensities were detected in samples subjected to 5 M KOH treatment for periods of time longer than 1 year.

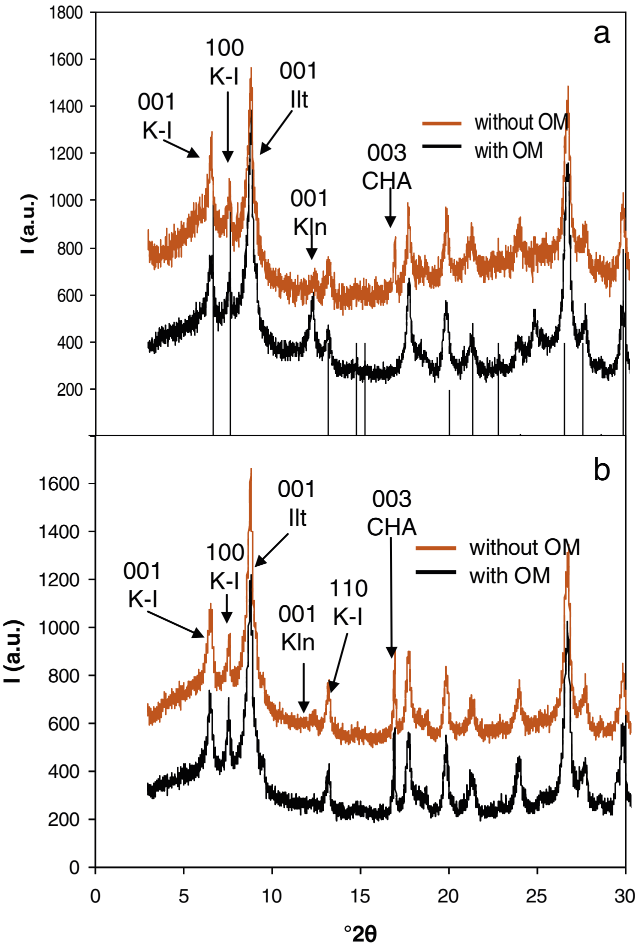

Fig. 6. XRD patterns of Alhambra Formation soil (OA of clay fraction) treated with 5 M KOH solution for 6 months (a) and 1 year (b). K-I = zeolite K-I, Ilt = illite, Kln = kaolinite, CHA = chabazite, black line pattern: zeolite K-I (JPDF card no. 180988).

3.2.2. FESEM and TEM observations

FESEM observations confirmed differences in the mineralogical evolution of the Alhambra Formation soil treated with 5 M NaOH depending on the presence or absence of OM. In contrast, the soil samples with or without OM treated with 5 M KOH did not show any significant morphological differences. A FESEM image (Fig. 7) of the untreated Alhambra Formation soil, showing the typical laminar structure of unreacted phyllosilicates, is included for comparison. The EDS analysis (inset, Fig. 7) revealed the presence of Si and Al as major elements, together with K, Na, Mg and Fe which is compatible with the presence of an assembly of clay minerals such as illite, kaolinite and/or interstratified illite–smectite as well as iron oxihydroxides.

The clay sample containing OM treated for 6 months with 5 M NaOH revealed a small amount of a faujasite-type zeolite together with a large portion of unreacted clay (Fig. 8a). The sample without OM, in contrast, showed a larger number of zeolite crystals of two distinct morphologies which correspond to a faujasite-type zeolite and a sodalite-type zeolite (Fig. 8b). The EDS spectra (insets, Fig. 8b) revealed an increased Na and Ca concentration in both zeolites if compared to the unreacted clay minerals. Note that the average crystal size of the faujasite-type zeolite was larger (~4 μm) in the sample without OM than in the one with OM (~2 μm).

Both samples showed similar textural features after 1 year of treatment (Fig. 8c and d). Abundant faujasite-type zeolite crystals together with some sodalite-type zeolite crystals were observed.

After 6 years of alkaline treatment, differences in the mineralogical evolution were detected. The sample without OM was dominated by the sodalite-type zeolite (Fig. 8e), while faujasite crystals were still observed in the samples with OM (Fig. 8f). Note that Na and Ca are the dominant cation in the faujasite-type zeolite (inset, Fig. 8e), while the sodalite-type zeolite contains almost exclusively Na (inset, Fig. 8f).

As mentioned before, FESEM analyses did not reveal any significant textural or compositional differences between the samples with and without OM following treatment with KOH. After 6 months of treatment, large amounts of nanosized crystals, zeolite K-I according to XRD results, were detected (Fig. 9a and b). EDS microanalysis (inset, Fig. 9a) revealed an increase in K and Ca in the newly formed zeolitic phase if compared to the untreated clay minerals. TEM analysis (inset, Fig. 9b) confirmed the hexagonal morphology of the nanosized crystals, typical for zeolite K-I (Barrer et al., 1968). The chabazite-type zeolite identified with XRD in the sample treated for 6 months without OM was not observed with FESEM. However, a number of crystals with

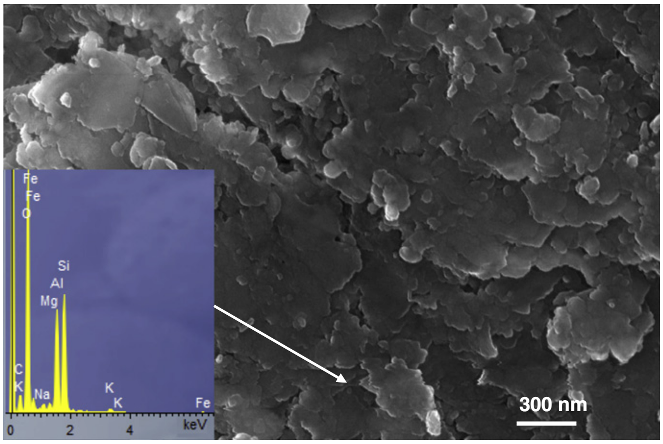

Fig. 7. FESEM image of the <2 μm fraction of untreated Alhambra Formation soil. The EDS microanalysis (inset) shows an "average" chemical composition of clay particles compatible with illite, kaolinite and/or smectites together with Fe oxy-hydroxides.

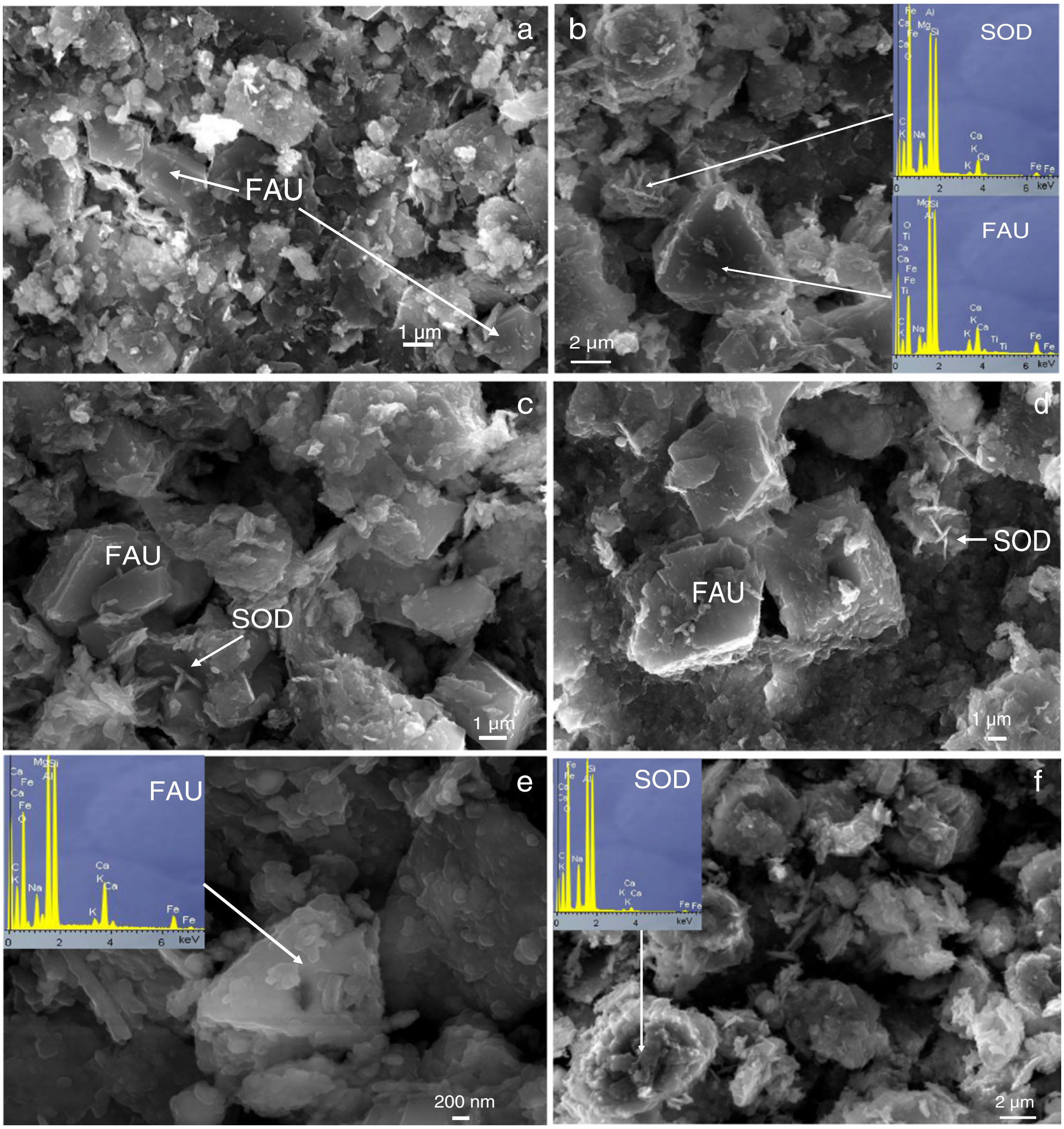

Fig. 8. FESEM images of Alhambra Formation soil with and without OM treated with 5 M NaOH for a) 6 months (with OM); b) 6 months (without OM); c) 1 year (with OM); d) 1 year (without OM); e) 6 years (with OM); f) 6 years (without OM). FAU = faujasite, SOD = hydroxysodalite. EDS microanalyses in insets.

chabazite-type morphology additional to nanosized zeolite K-I crystals were detected after 1 year of treatment in samples with and without OM (Fig. 9c and d). EDS microanalyses (insets Fig. 9c and d) showed elevated concentrations of Ca and K in the chabazite-type zeolite.

3.2.3. Nitrogen sorption

Nitrogen adsorption data revealed a slightly higher surface area of the sample without OM if compared to the one with OM before alkaline treatment (Tables 2 and 3).

After treatment with 5 M NaOH for 6 months, a significant increase in surface area of the Alhambra Formation soil was detected in samples with and without OM (Table 2). The increase was more pronounced in the sample without OM (217.48 ± 3.49 m^2/g) than in the sample with OM (147.56 ± 3.63 m^2/g). This increase was caused by the formation of a faujasite-type zeolite which has a reported surface area of 400 m^2/g (Sutarno and Arryanto, 2007) and was more abundant in the sample without OM according to XRD results.

After 1-year treatment with 5 M NaOH, surface area values were almost identical in samples with and without OM. This is in agreement with XRD and FESEM results, showing an important degree of transformation into faujasite in both samples.

After 6 years of 5 M NaOH treatment, both samples experienced a decrease in surface area which was especially severe in the case of the sample without OM (Table 2). This decrease is due to the transformation of the faujasite-type zeolite into the less porous sodalite-type zeolite. The sodalite-type zeolite has a reported surface area of 22.8 m^2/g (Li et al., 2007). Note that the transformation of the less stable faujasite into a more stable and dense hydroxysodalite during alkaline treatment is a common process (Bosnar et al., 2004). Our nitrogen sorption data are consistent with XRD and FESEM results, showing that some faujasite-type zeolite was still present in the sample with OM, whereas the sodalite-type zeolite was the dominant phase in the sample without OM after 6 years of treatment.

Surface area measurement results were less conclusive in the case of samples treated with KOH as a result of the small pore size of zeolites which formed upon alkaline treatment with KOH. The BET surface area evolution was similar for the samples with and without OM treated with 5 M KOH (Table 3). After 1 year of treatment, both samples had

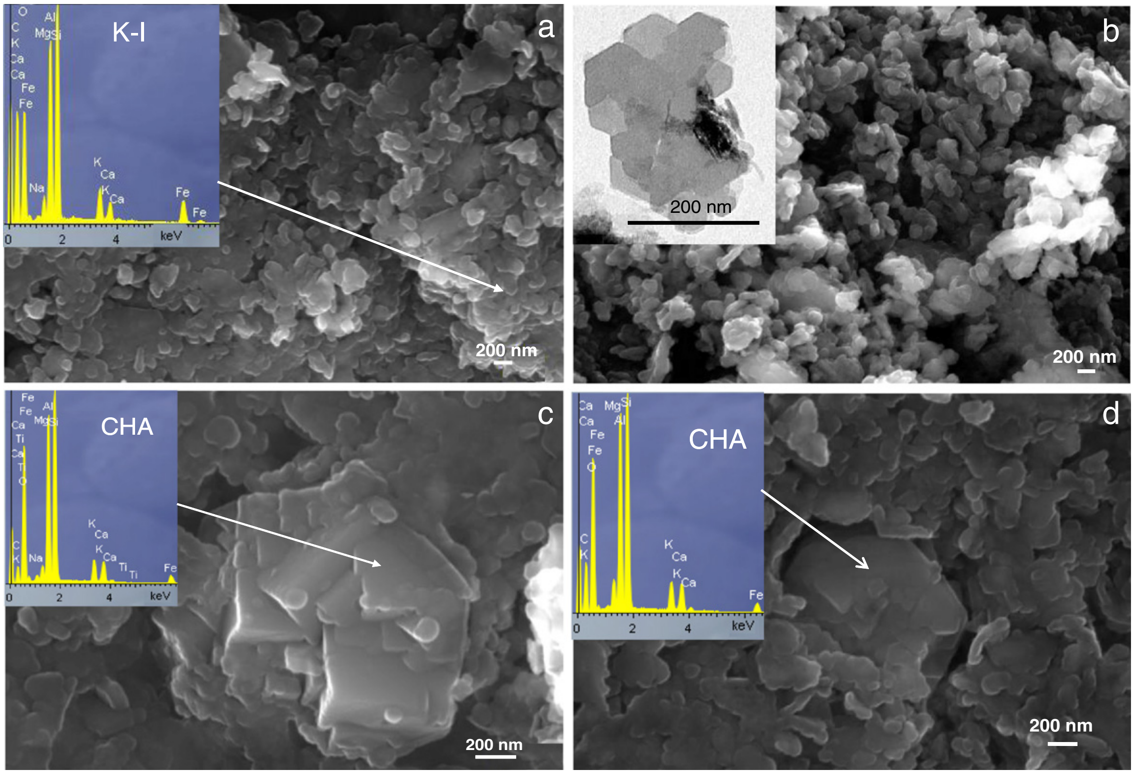

Fig. 9. FESEM images of Alhambra Formation soil with and without OM treated with 5 M KOH for a) 6 months (with OM); b) 6 months (without OM); c) 1 year (with OM); d) 1 year (without OM). K-I = zeolite K-I, CHA = chabazite. EDS microanalyses and TEM image of zeolite K-I (panel b) in insets.

suffered a surface area decrease of 13% and 20%, respectively. This decrease was provoked by a partial destruction of clay minerals, in particular smectites, and by the formation of K-zeolites. Considering the pore size reported by Breck (1974) for zeolite K-I (pore size: 0.26 nm) and chabazite (pore size: 0.4 nm) it becomes obvious that those pores are inaccessible to nitrogen which only has access to pores with a size of approximately ≥0.5 nm (Groen et al., 2003). Thus, these zeolites will have comparatively low BET surface areas if nitrogen is used as adsorbate. In fact, K-chabazite has a reported BET surface area of only 17.82 m^2/g (Ridha, 2009) using nitrogen as adsorbate. Unfortunately, no surface area data for zeolite K-I are available in the published literature. Prolonged treatment for 6 years resulted in a negligible surface area decrease in the sample with OM, while the sample without OM experienced a surface area increase of 29%. The reason for this increase is not clear.

3.2.4. TG/evolved gas analysis (FTIR)

Fig. 10 shows evolved gas FTIR spectra taken between 356 and 408 °C during TG analysis. In this T range the maximum CO emission associated with the thermal decomposition of OM was detected. The FTIR spectra of samples with OM and treated for 6 months with 5 M NaOH or 5 M KOH (Fig. 10a and e) released a significant amount of CO, while samples treated with H_2O_2 prior to alkaline attack released no CO (Fig. 10b, d, f and h). The fact that OM was still present even after 6 months of alkaline treatment explains why XRD and FESEM results showed a slower dissolution of clay minerals and a delayed formation and transformation of zeolitic phases in the soil samples which were not treated with H_2O_2 prior to alkaline treatment. After 1-year alkaline treatment, the OM content was significantly reduced in the samples treated with 5 M NaOH or 5 M KOH as shown by the small amount of evolved CO gas (Fig. 10c and g). However, even after 1 year of alkaline treatment, trace amounts of CO were still detectable, especially in the case of the sample treated with 5 M NaOH (Fig. 10c). KOH seems to be slightly more efficient in destroying OM which might be a result of the higher pH maintained during the alkaline treatment. Note that the pH of the 5 M NaOH and 5 M KOH was ~12.5 and 14, respectively, after 1 year of treatment (Elert et al., in press). Results for the total carbon content obtained using elemental analysis, confirmed TG-FTIR results (Table 4), revealing a progressive reduction in carbon content (i.e., degradation of OM) upon alkaline treatment in samples which were not treated with H_2O_2 previously. After 1 year of alkaline treatment, these samples still contained slightly more carbon than the ones which underwent H_2O_2 treatment. Black carbon was not affected, its value remaining basically unchanged over the course of the alkaline treatment.

Table 2
BET surface area of Alhambra Formation soil with and without OM and treated with 5 M NaOH for different periods of time.

Treatment time	Surface area (m^2/g)	
	With OM	Without OM
0	71.94 ± 1.63	82.10 ± 0.67
6 months	147.56 ± 3.63	217.48 ± 3.49
1 year	241.63 ± 3.90	246.27 ± 0.43
6 years	100.50 ± 13.36	30.38 ± 1.57

Table 3
BET surface area of Alhambra Formation soil with and without OM and treated with 5 M KOH for different periods of time.

Treatment time	Surface area (m^2/g)	
	With OM	Without OM
0	71.94 ± 1.63	82.10 ± 0.67
6 months	72.12 ± 6.72	82.89 ± 4.29
1 year	62.34 ± 3.97	65.54 ± 2.60
6 years	60.76 ± 0.33	84.49 ± 4.09

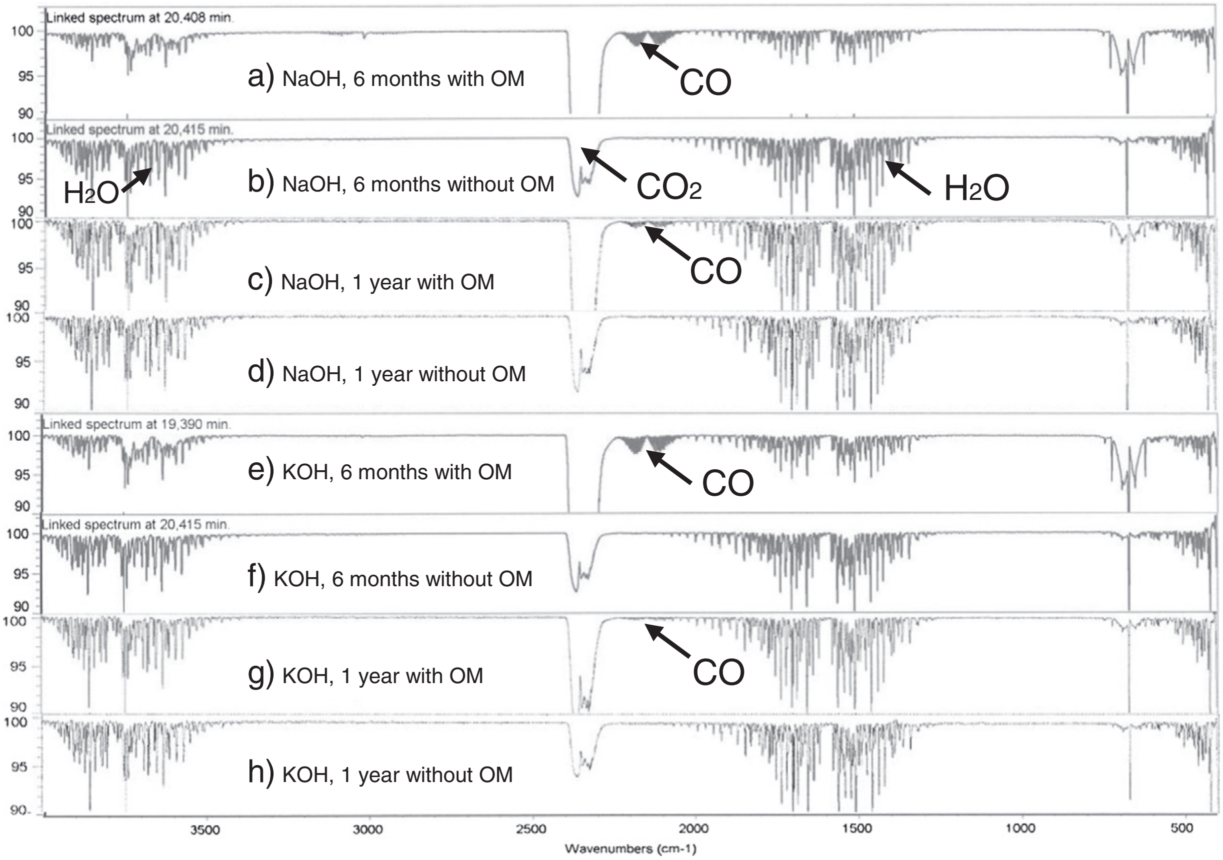

Fig. 10. Evolved gas FTIR spectra taken between 356 and 408 °C of Alhambra Formation soil treated with 5 M NaOH or 5 M KOH.

4. Discussion

Our experimental results demonstrate that mineral dissolution and transformation upon alkaline treatment with 5 M NaOH or 5 M KOH is delayed as a result of the presence of OM in the clay fraction of the Alhambra Formation soil.

The clay sample with OM revealed a 14% smaller surface area than the sample without OM which had been previously treated with H_2O_2. Theng et al. (1999) also reported an increase in surface area upon removal of OM. It is assumed that adsorption of OM reduces the electrostatic repulsion of clay particles and, thus, facilitates aggregation. This will result in a lower surface area in the case of the soil with OM. Zhang et al. (2013) came to a similar conclusion regarding reduced surface area of clay minerals in the presence of OM, OM acting as an aggregation agent for clay particles. Apart from particle aggregation, Kaiser and Guggenberger (2003); Tombacz et al. (1998) attributed the reduction in specific surface area to the clogging of micropores by adsorbed OM. The aggregation and clogging effect of OM, thus, render the clay surface less accessible for the alkaline solutions and contributes to lower reactivity of clay minerals.

Table 4
Total carbon content (wt.%) of Alhambra Formation soil with and without OM and treated with 5 M NaOH or 5 M KOH for different periods of time.

	5 M NaOH		5 M KOH	
	With OM	Without OM	With OM	Without OM
0	0.91	0.25	0.91	0.25
6 months	1.05	0.23	0.66	0.25
1 year	0.53	0.31	0.45	0.40

TG-FTIR results revealed that part of the humic substances was insoluble under alkaline conditions over a prolonged period of time. FTIR spectra showed the presence of significant amounts of OM even after 6 months of alkaline treatment with 5 M NaOH or 5 M KOH. The long-lasting passivation of the clay surface by OM significantly limited the effect of the alkaline treatment (i.e., mineral dissolution of clay minerals and transformation into zeolitic phases) in our study. Kaolinite and illite were still protected from alkaline attack by OM to a significant degree after 6 months of treatment, resulting in a slower dissolution as evidenced by XRD (Figs. 4a and 5a). Data by Claret et al. (2002) support these findings. Using scanning transmission X-ray microscopy, the authors demonstrated that the most reactive sites at the particle edges of illitic and smectitic clays were still protected by OM after 1-year treatment with highly alkaline solutions (pH ~ 13) at 60 °C.

Originally, OM was thought to be adsorbed in a monolayer covering the entire clay mineral surface. However, this theory was revised and newer findings revealed that OM adsorption takes primarily place at reactive surface sites (Mayer, 1994, 1999; Ransom et al., 1997). Experimental data by Kubicki et al. (1997), who used salicylic acid as a humic acid analogue, supported the above theory showing that organo-mineral surface complexes were predominantly formed on the edges of illite grains. Kaiser and Guggenberger (2003) studied the relation between specific surface area of minerals and different loading of OM. The authors suggested that OM sorption took place at specific reactive sites such as aluminol groups at illite edges. In a recent study, Vogel et al. (2014) determined with nano-scale secondary ion mass spectroscopy that only 19% of the clay mineral surface was covered by OM and that OM was preferentially associated with rough surfaces (i.e., etch pits, micropores or cracks). The fact that the reactive sites of clay minerals are preferentially covered by OM which is difficult to remove even under extremely high alkaline conditions (i.e., prolonged treatment with 5 M NaOH or 5 M KOH in this study) explains the delayed mineralogical evolution observed in the case of Alhambra Formation soil containing ~1.1 wt.% OM, because these sites are also the ones involved in mineral dissolution.

Our experimental results showed that kaolinite experienced a significantly slower dissolution in the presence of OM if compared to samples which were treated with H_2O_2 to remove OM prior to alkaline treatment using either 5 M NaOH or 5 M KOH. In the case of illite, the passivation induced by OM was only significant during the first 6 months of the alkaline treatment (Fig. 4a), showing a somewhat lower 001 Bragg peak intensity after treatment with 5 M NaOH. After further treatment, the 001 Bragg peak intensities of illite were identical in the presence and absence of OM. It has to be kept in mind, that illite generally shows a significantly slower dissolution than kaolinite in highly alkaline environments, especially in the presence of K which might actually induce a recrystallization process, involving Ostwald ripening (Cuevas Rodriguez, 1993). The generally lower reactivity of illite if compared with kaolinite and smectite has been pointed out by other researchers who carried out batch reactor experiments using highly concentrated NaOH (Caroll and Starkey, 1971; Jozefaciuk and Bowanko, 2002). Structural differences between illite and kaolinite can explain the lower reactivity of the former if compared with the latter. In illite, a 2:1 clay, reactive sites are located at broken edges, steps and defect sites, and the contribution of the basal layer to the overall reactivity of this clay mineral is very limited (Sposito, 1984). In contrast, kaolinite, a 1:1 clay, shows high reactivity when exposed to alkaline environments despite its relatively low surface area because hydroxyl groups at the gibbsite layer offer additional sites for reaction (Huertas et al., 1999). As previously stated, the effect of OM on the dissolution of smectite-rich interstratified illite–smectite could not be evaluated using XRD analysis. However, these phases can be considered to be very reactive in high pH environments, offering a large surface area for the interaction with alkaline solutions. Ramirez et al. (2005) also acknowledged the high reactivity of smectite-rich interstratifications treated with concentrated NaOH and KOH solutions.

Our findings also revealed that the presence of OM not only influenced mineral dissolution but also the nucleation of new phases. The formation of new zeolitic phases such as faujasite, hydroxysodalite and chabazite was significantly faster in the absence of OM in the case of the Alhambra Formation soil samples treated with 5 M NaOH or 5 M KOH. Thus, an inhibition effect on mineral precipitation exerted by OM seems to be very likely. Ganor et al. (2009) presented an exhaustive review on organic matter – mineral interactions, revealing inhibited precipitation of various minerals in the presence of a great variety of organic compounds. Our results do not allow us to determine unambiguously whether only crystal nucleation was delayed or whether crystal growth was also affected by the presence of OM. Generally, growth inhibition should be accompanied by habit modifications (Rodriguez-Navarro and Benning, 2013), which, however, were not detected in zeolites formed here. Nucleation inhibition, on the other hand, typically results in longer waiting times and the nucleation of the new phase at a higher supersaturation. This in turn leads to a higher nucleation density and smaller crystals as shown by our FESEM observations.

The findings of our study also showed that the inhibiting effect of OM was not only limited to the precipitation of new phases, but also delayed zeolite transformation after alkaline attack for more than 1 year. After 6 years, samples treated with 5 M NaOH still contained faujasite-type zeolite in the presence of OM, while all faujasite had transformed into hydroxysodalite in the absence of OM. These results suggest that the presence of OM exerted a retardation effect on faujasite dissolution and the subsequent precipitation of hydroxysodalite even after prolonged exposure to a high pH environment.

5. Conclusions

The findings of this study confirm previous assumptions, clearly showing that dissolution of clay minerals and the formation of new zeolitic phases is delayed in the presence of OM. The OM content does not need to be very high in order to exert a passivation effect on mineral dissolution and transformation, as can be deduced from our results, showing delayed reactions upon alkaline attack in Alhambra Formation soil containing ~1.1 wt.% OM. This appears to be due to the preferential adsorption of OM at active sites which are directly involved in the dissolution of clay minerals. The soils' OM content is, thus, an important parameter to be considered in systems where clay minerals are exposed to highly alkaline solutions/environments, the passivation effect being especially significant in soils with high reactive clay content (i.e., high content in kaolinite, smectites and smectite-rich interstratified illite–smectite).

The retardation effect of OM can have important implications, for example when alkaline treatments are applied as a consolidation treatment for earthen architecture or during the stabilization of soils. In such cases, the presence of OM can be detrimental. In contrast, in the case where clays are used as a backfill material for nuclear waste disposal or as waste water barrier, the presence of OM might actually be beneficial and hamper clay mineral dissolution and transformation (i.e. illitization of smectites or transformation into non-swelling phases). The addition of organic additives (i.e. humin or other organic compounds insoluble at high pH) to clay-rich soils used as barrier materials in contact with cement and its alkaline leachates, should be investigated as a possible means of passivation of clay minerals towards alkaline attack, limiting changes of the original clay characteristics (i.e., swelling and adsorption capacity) and delaying its transformation. However, possible negative side effects of organic additives will have to be considered, for example possible changes in the clays hydromechanical properties or the potential risk of organic colloid formation, favouring migration of radionuclides (Pusch, 2002).

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