

# Analysing oxygen and hydrogen isotopes in clay minerals from Lower Cretaceous palaeosols by NanoSIMS: first palaeoclimatic results

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## INTRODUCTION

Oxygen and hydrogen isotopic values have been widely used to characterize clay minerals and infer their origin (e.g., Sheldon & Tabor, 2009; Kuligiewicz et al., 2021). Nevertheless, palaeosols can contain not only authigenic clay minerals but also detrital and/or diagenetic ones. Together with the frequently micrometric or nanometric size of the clay minerals, this can generate difficulties during isotopic analyses by conventional spectroscopies (Kuligiewicz et al., 2021). To avoid this problem, in this study we use nanoscale secondary ion mass spectrometry (NanoSIMS) to analyse authigenic clay minerals (kaolinite and smectite) included in palaeosol levels from early Barremian (Lower Cretaceous) continental profiles located in the SE of the Iberian Chain (NE Spain).

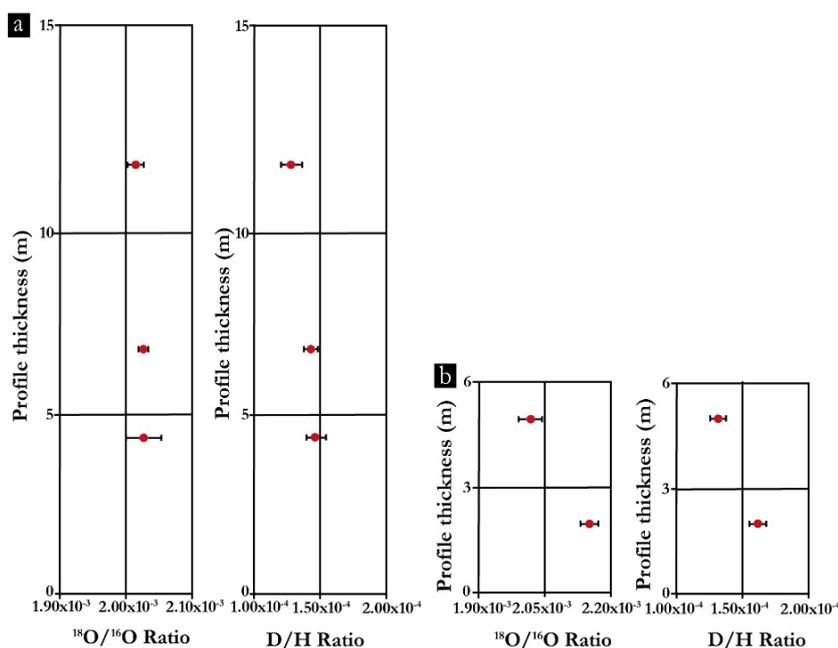
## MATERIALS AND METHODS

The palaeosol levels are composed of nanometre-sized authigenic minerals (kaolinite, smectite, goethite, hematite, anatase and rutile), detrital quartz and illite, and calcite nodules (Laita et al., 2020). The samples under study come from different palaeosol levels included in two continental profiles (labelled ALC and JO), which were previously studied by Laita et al. (2020). Three samples come from lower, middle, and upper palaeosol levels included in the ALC profile (ALC-1, ALC-4, and ALC-8, respectively), and two samples from lower and upper palaeosol levels included in the JO profile (JO-1 and JO-5, respectively). The samples were selected due to their high kaolinite and smectite contents, whose oxygen and hydrogen isotopic composition can provide palaeoenvironmental and palaeotemperature information. Thin sections of the samples were previously studied by field emission scanning electron microscopy (FESEM) to find kaolinite- and smectite-rich areas in each sample suitable for the isotopic analyses. Pure kaolinite and smectite powder standards were also previously analysed in a reference laboratory to calibrate the instrumental mass fractionation. The thin sections were heated at 150 °C for a minimum of 2 h to remove the interlayer and absorbed water in the clay minerals, and subsequently they were gold-coated and placed in the NanoSIMS vacuum chamber to prevent water reabsorption. Isotopic analyses were carried out at different selected points of the samples containing kaolinite or smectite. Several spots of 1  $\mu\text{m}^2$  were analysed in each sample with 32 x 32 pixels and a dwell time of 132  $\mu\text{s}/\text{pixel}$  and a  $\text{Cs}^+$  current of 2.0 pA, in 10 blocks of 27 measurements.

## RESULTS AND DISCUSSION

A decrease in the  $^{18}\text{O}/^{16}\text{O}$  and D/H ratios is observed in both profiles (Fig. 1). The kaolinite  $^{18}\text{O}/^{16}\text{O}$  and D/H ratios from sample ALC-1 ( $2.03 \times 10^{-3}$  and  $1.45 \times 10^{-4}$ , respectively) are higher than those of the kaolinite from sample ALC-4 ( $^{18}\text{O}/^{16}\text{O} = 2.02 \times 10^{-3}$  and  $\text{D}/\text{H} = 1.43 \times 10^{-4}$ ), and the latter are also higher than the smectite  $^{18}\text{O}/^{16}\text{O}$  and D/H ratios from sample ALC-8 ( $2.01 \times 10^{-3}$  and  $1.27 \times 10^{-4}$ , respectively). Comparing the ALC with the JO profile, the kaolinite from sample JO-1 presents higher  $^{18}\text{O}/^{16}\text{O}$  and D/H ratios ( $2.15 \times 10^{-3}$  and  $1.62 \times 10^{-4}$ , respectively) than the kaolinite from samples ALC-1 and ALC-4, whereas the smectite from sample JO-5 presents somewhat higher  $^{18}\text{O}/^{16}\text{O}$  and D/H ratios ( $2.02 \times 10^{-3}$  and  $1.32 \times 10^{-4}$ , respectively) than the smectite from sample ALC-8, but the differences in the smectite ratios between the samples from the ALC and JO samples are much

lower than the differences in the kaolinite ratios. The higher ratios in the kaolinite from sample JO-1 may be due to diagenetic processes, which could have affected this kaolinite after soil formation, altering its isotopic signature. This is also supported by mineralogical data (e.g., larger crystal sizes and higher crystallinity) (Laita et al., 2020). For this reason, the isotopic results obtained in this sample were not used for palaeoclimatic deductions.



**Fig 1.** Average  $^{18}\text{O}/^{16}\text{O}$  and D/H ratios obtained in the palaeosol samples under study showing a decrease from bottom to top in the ALC (a) and JO (b) profiles.

The  $\delta^{18}\text{O}_{\text{SMOW}}$  and  $\delta\text{D}_{\text{SMOW}}$  values obtained for kaolinite and smectite in the different samples are as follows:  $\delta^{18}\text{O}_{\text{SMOW}}=17.6\text{‰}$ ;  $\delta\text{D}_{\text{SMOW}}=-82.3\text{‰}$  (for kaolinite in sample ALC-1),  $\delta^{18}\text{O}_{\text{SMOW}}=15.8\text{‰}$ ;  $\delta\text{D}_{\text{SMOW}}=-96.6\text{‰}$  (for kaolinite in sample ALC-4),  $\delta^{18}\text{O}_{\text{SMOW}}=10.6\text{‰}$ ;  $\delta\text{D}_{\text{SMOW}}=-179.7\text{‰}$  (for smectite in sample ALC-8) and  $\delta^{18}\text{O}_{\text{SMOW}}=12.5\text{‰}$ ;  $\delta\text{D}_{\text{SMOW}}=-167.0\text{‰}$  (for smectite in sample JO-5). These values are consistent with crystallization in a weathering environment. The calculated temperature for kaolinite formation is 21–22 °C, whereas for smectite it is 16–17 °C. These data agree with a climatic change from bottom to top in the ALC and JO profiles, as was deduced by Laita et al. (2020) using mineralogical tools.

## CONCLUSIONS

The high resolution of NanoSIMS has allowed us to undertake isotopic analysis of different clay minerals separately, as well as differentiating between authigenic and diagenetic kaolinites. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values obtained for authigenic kaolinite and smectite in the palaeosol samples indicate formation during weathering processes at the Earth's surface, pointing to a decrease in the temperature from 21–22 °C to 16–17 °C in the SE area of the Iberian Chain during the early Barremian. NanoSIMS thus proves to be a useful tool for the isotopic study of nanometre-sized clay minerals.

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