

# The hydrogen and oxygen isotopic compositions of hydroxyl in clay mineral from a weathering profile: New proxies for paleo-climate change?

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**Abstract** Recent studies suggest that the hydrogen and oxygen isotopic compositions of clay minerals can indicate paleoclimate. Here, we report mineralogy and stable isotopic records ( $\delta D$  and  $\delta^{18}O_{OH}$ ) of a weathering profile located in the Fujian Province, aiming to validate whether hydroxyl stable isotopes can indicate paleo-precipitation and paleo-temperature. Our results indicate that the  $\delta D$  and  $\delta^{18}O_{OH}$  changes in the kaolinite hydroxyl of the weathering profile are basically determined by the isotopic composition of paleo-meteoric water and paleo-temperature, respectively. Nevertheless, whether the  $\delta D$  and  $\delta^{18}O_{OH}$  of kaolinite can quantitatively indicate paleo-precipitation and paleo-temperature needs to be verified further, and especially, the structural oxygen isotopic composition that is the essential element for the kaolinite formation temperature calculation has to be constrained in future work.

**Keywords** Weathering profile · Hydrogen and oxygen isotopes · Hydroxyl · Kaolinite

## 1 Introduction

The stable hydrogen and oxygen isotopic composition of hydroxylated minerals have the potential to provide paleo-environmental information, such as paleo-precipitation (Tabor and Montañez 2005; Bauer et al. 2016), the isotopic

composition of soil water (Vitali et al. 2002; Tabor et al. 2002) and paleo-temperature (Sheldon and Tabor 2009; Gilg et al. 2013). Recently, stable isotopic compositions of clay minerals, especially kaolinite and smectite have been widely used as paleo-environmental proxies (Feng and Yapp 2009; Caballero and de Cisneros 2010; Mix and Chamberlain 2014; Hall et al. 2015; Bauer et al. 2016). Despite these studies, the indication of stable isotopes of clay minerals awaits further investigation. For instance, only a few studies focused on the weathering profile, which contains rich paleo-climatic information.

In this study, we present the stable isotopes ( $\delta D$  and  $\delta^{18}O$ ) of clay minerals and mineralogical compositions of a 7.7 m long granodiorite-developed weathering profile from southeast China (Fujian Province). It is important to note that structural oxygen can be divided into two groups: hydroxyl oxygen and non-hydroxyl oxygen (Girard and Savin 1996), and only hydroxyl oxygen isotopic compositions (hereafter referred to as  $\delta^{18}O_{OH}$ ) are reported in this study. The purpose of this study is: (1) to investigate the stable isotopic composition in the weathering profile and (2) to validate whether the hydroxyl stable isotopes can indicate paleo-precipitation and paleo-temperature.

## 2 Samples and methods

The granodiorite-developed weathering profile samples were collected from Xianyou County of Fujian Province (118°44.694'E, 25°21.853'N), southeast China in January 2014 (Fig. 1). The observed profile thickness above the ground was around 8.7–9.2 m, and only the upper 7.4 m was sampled at 10–30 cm intervals. A total of 31 soil samples were collected from the weathering profile. For more detailed information about the analytical methods for mineral identification, one can refer to Su et al. (2015).

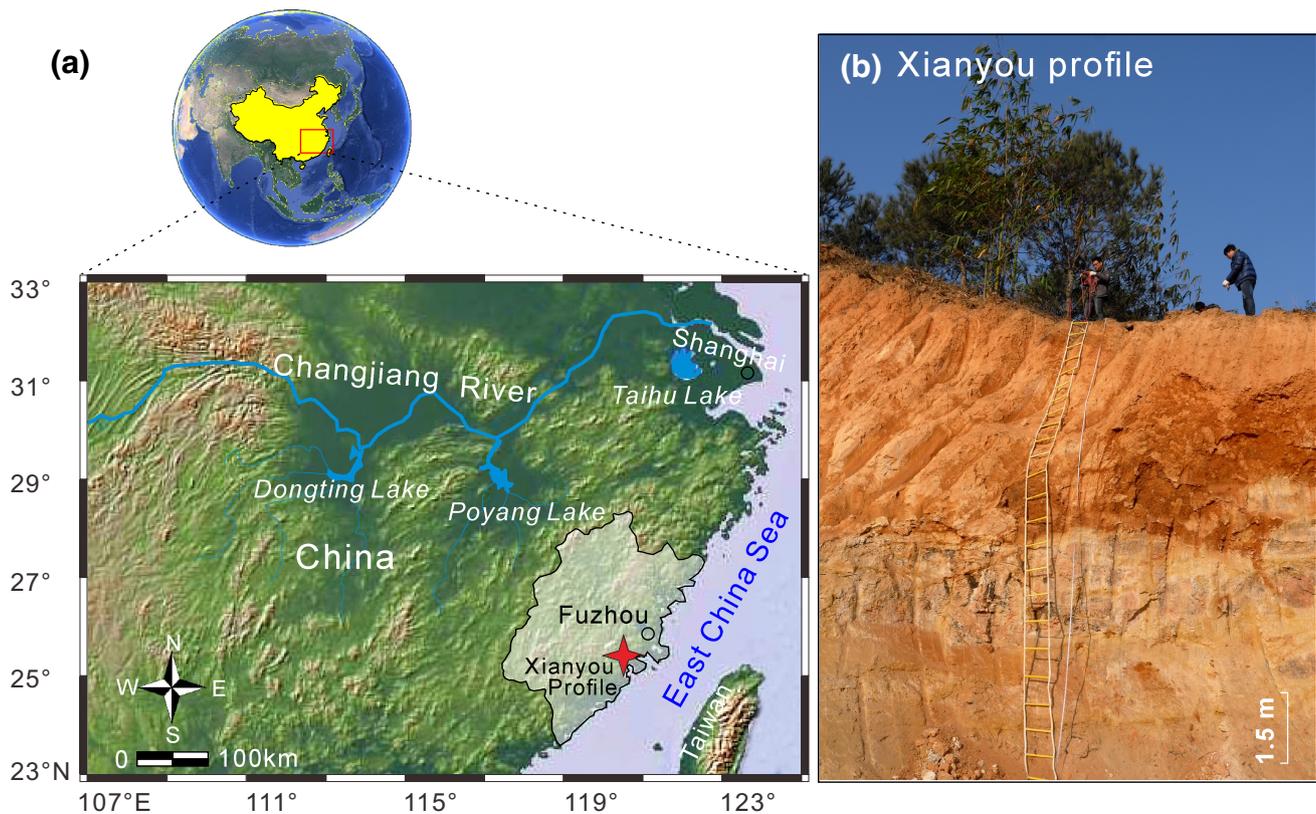
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**Fig. 1** Map showing the study area (a) and the granodiorite-developed weathering profile (b) in Fujian Province, China

The hydrogen and oxygen isotopic measurement followed Yang et al. (2016), and the detailed procedures are given as follows. The samples were vacuum-degassed at 300 °C to remove the absorbed and interlayer water. Then, they were heated to 600 °C for extracting constitution water. A liquid nitrogen trap was used to collect water vapor. Finally, the liquid water was stored in a sealed glass tube, and then transferred into a specific bottle for stable isotopes analyses. It is important to note that the structural oxygen isotopic composition ( $\delta^{18}\text{O}_k$ ), which is studied in previous research, cannot be measured by using the heating method in this study. Hydrogen and oxygen isotopic compositions of clay minerals are reported in the conventional delta notation ( $\delta$ ) in per mill (‰) relative to Vienna Standard Mean Ocean Water (V-SMOW). The analytical uncertainties of the isotope measurements on clay samples are estimated at  $\pm 3\%$  for hydrogen and  $\pm 0.3\%$  for oxygen at one sigma.

### 3 Results

X-ray Diffraction (XRD) results indicate that quartz is the major mineral in the whole profile, with an average content of 47.3%. Clay minerals are dominated by kaolinite (14.3%–56.0% of bulk minerals). Illite mainly occurs at the top 1 m, and chlorite is mainly observed in the middle part of

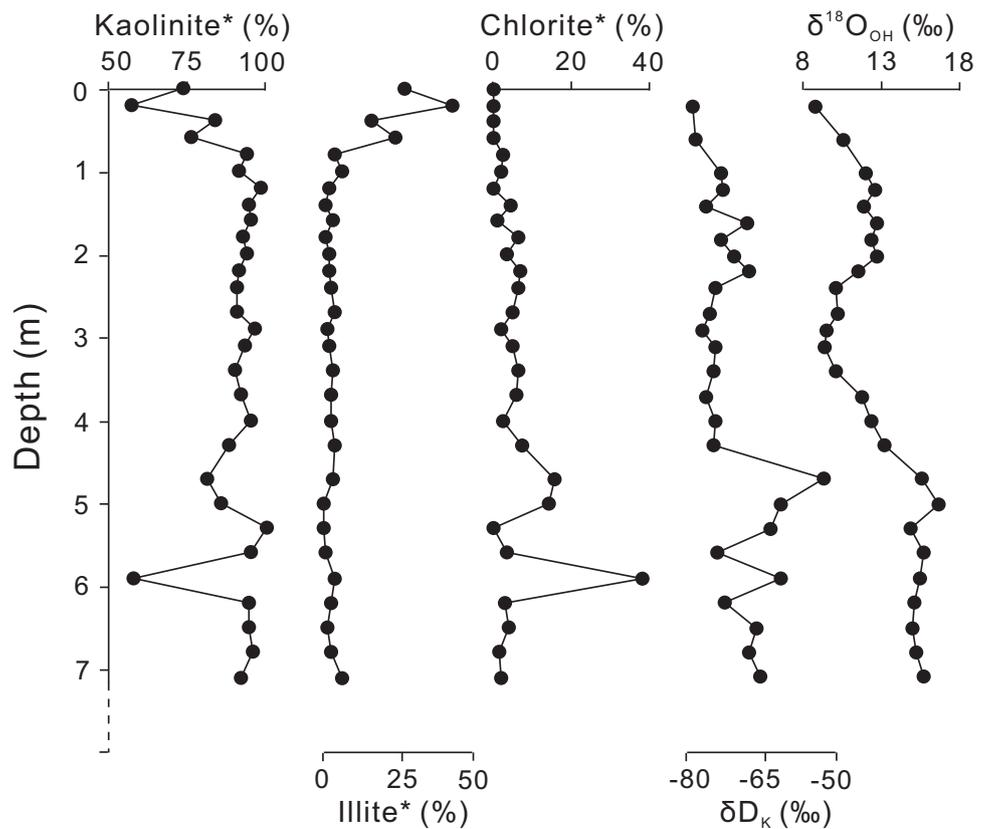
the profile with contents mostly below 3% (Fig. 2). Other hydrous minerals, such as mica, goethite and gibbsite, only occur in a few samples. Feldspar including microcline, albite and sanidine, only exists below 4.3 m of the profile, and increases downward with an average content of 21.2%.

The  $\delta\text{D}$  and  $\delta^{18}\text{O}_{\text{OH}}$  values of hydroxyl vary from  $-78.3\%$  to  $-52.7\%$  and from  $9.4\%$  to  $16.7\%$ , respectively (Fig. 2). The most prominent feature of the hydrogen isotope variation is a pronounced negative shift of about  $22.0\%$  at 4.3 m of the profile. The  $\delta\text{D}$  values are relatively constant between 1.6 and 4.3 m and decrease gradually in the upper profile. However, the variations of  $\delta^{18}\text{O}_{\text{OH}}$  are different from hydrogen isotope. The oxygen isotopic compositions of hydroxyl are relatively constant at the bottom ( $15.0\%$ – $16.7\%$ ), and decrease gradually from 4.3 to 3 m ( $9.4\%$ – $13.3\%$ ), and then increase upward ( $9.6\%$ – $12.8\%$ ), and finally decrease from 1.6 m toward the surface ( $8.8\%$ – $12.8\%$ ).

### 4 The controlling factors and indication of $\delta\text{D}$ and $\delta^{18}\text{O}_{\text{OH}}$ in kaolinite

The hydrogen and oxygen isotopic composition in clay minerals depend on several factors: (1) the isotopic composition of water; (2) the isotopic composition of reactant minerals; (3) the water/rock ratio; (4) the temperature and (5) the mineral-water

**Fig. 2** Depth variation of calibrated clay mineral contents and stable hydrogen and oxygen isotopic compositions. The content of clay mineral  $X$  is calibrated by using the total clay contents, and referred to  $X^*$  ( $X^* = 100 \times X/\text{total clay content}$ )



fractionation factor (Faure 1998). Based on the XRD results, the variations of  $\delta D$  and  $\delta^{18}O_{OH}$  predominantly reflect the isotopic variation in kaolinite hydroxyl in this study. To our knowledge, the kaolinite-water fractionation factor is a temperature-dependent parameter, and the isotopic composition of reactant minerals have little impact on the isotopic composition of secondary minerals in the supergene environment, due to the huge water/rock ratio. Therefore, only factors (1) and (4) need to be considered carefully. However, the temperature for kaolinite formation cannot be estimated because we do not measure the isotopic composition of structural oxygen in kaolinite. According to previous studies (Wolfe et al. 1997; Mix and Chamberlain 2014), we assume that temperature variation during the weathering profile development can reach at most 20 °C in a supergene environment. In theory, the variation of 20 °C can lead to about 3.4 and 4.5‰ variation for  $\delta D$  and  $\delta^{18}O_k$  in kaolinite, respectively (Sheppard and Gilg 1996). It is obvious that the theoretical variation for  $\delta D$  is much less than the actual variation in kaolinite, while it is similar to actual  $\delta^{18}O_{OH}$  variation in this study, if we assume the fractionation factor between non-hydroxyl and hydroxyl oxygen isotopes is constant for all samples. In addition, 3.4‰ variation is within analytical uncertainty of the analytical method for hydrogen in mineral. Hence, we infer that factors (1) and (4), i.e. meteoric water stable isotope and paleo-temperature, respectively, control the  $\delta D$  and  $\delta^{18}O_{OH}$  in kaolinite. The

meteoric water isotopic variation in Fujian Province in the present day is predominantly controlled by the amount effect (Zhang and Yao 1998; Chen et al. 2010). Hence,  $\delta D$  variation in kaolinite from the weathering profile may reflect paleoprecipitation changes, while  $\delta^{18}O_{OH}$  changes may indicate paleo-temperature variability during the development of the weathering profile.

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