Applied Clay Science 143 (2017) 10–21

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

# Clay mineralogy of altered tephra beds and facies correlation between the Permian-Triassic boundary stratigraphic sets, Guizhou, south China

Hanlie Hong [a,b,*], Qian Fang [b], Chaowen Wang [b], Gordon Jock Churchman [c], Lulu Zhao [b], Nina Gong [b], Ke Yin [b]

[a] State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, Hubei 430074, China
[b] School of Earth Sciences, China University of Geosciences, Wuhan 430074, China
[c] School of Agriculture, Food and Wine, Waite Campus, The University of Adelaide, SA 5005, Australia

ARTICLE INFO

*Article history:*
Received 18 January 2017
Received in revised form 24 February 2017
Accepted 9 March 2017
Available online xxxx

*Keywords:*
K-bentonite
Tephra
Weathering
Illite-smectite
Kaolinite-smectite
Sr isotopic composition
Nd isotopic composition

ABSTRACT

The Permian-Triassic boundary (PTB) successions in south China contain numerous altered volcanic ash (tephra) beds (K-bentonites), which presents the opportunity to correlate the PTB position in both marine and non-marine sections, especially when no feasible biostratigraphic markers are available in the profiles. Clay mineralogical and geochemical studies of two altered ash beds in the Zhongzai (ZZ) and Tucheng (TC) sections, in Guizhou Province, south China, deposited in littoral and interactive marine-terrestrial environments, respectively, permit an investigation of the alteration of ash and correlation of ash beds between disparate facies. The results show that the two ZZ altered ashes consist of mainly R1 I/Sm and minor R0 I/Sm. Sample ZZ-1 has slightly more R1 I/Sm but less R0 I/Sm relative to sample ZZ-2. The TC ash samples contain mainly kaolinite and mixed-layer kaolinite/smectite (K/Sm). The poorly-crystallized kaolinite is present in pseudo-hexagonal plates, and the well-crystallized kaolinite occurs in book-like aggregates in veins or cavities. K/Sm minerals are derived from the transformation of smectite to kaolinite. Obviously, the TC ashes experienced terrestrial weathering and resedimentation prior to final burial and preservation, and local microenvironmental conditions control the formation of clay minerals. The ZZ ash samples have markedly higher $^{87}Sr/^{86}Sr$ values than those of the TC samples. The notable difference in $^{87}Sr/^{86}Sr$ value of ash beds between the sections is attributed to variations in Rb—Sr partitioning during the chemical weathering process in different environments. The ZZ ash samples have notably higher $^{143}Nd/^{144}Nd$ ratios than those of the TC samples, suggesting that the ZZ ashes are likely derived from eruptions involving continental crust and the TC ashes originate from eruptions involving new continental island arcs, in agreement with the REE distributions and the Ti vs. Zr, $TiO_2$ vs. $Al_2O_3$, and $Zr/TiO_2$ vs. Nb/Y discrimination plots. The occurrence of tephras from such markedly different volcanic source materials different in PTB stratigraphic sets previously believed to be synchronous, Guizhou, south China, suggests that correlation between disparate facies by an ash marker requires geochemical fingerprinting of the materials to confirm correlations or otherwise.


## 1. Introduction

Volcanic ashes (tephras) are usually reactive in the presence of water, which can rapidly alter them into clay minerals (Hints et al., 2008; Huff, 2016). Formation of clay minerals by the weathering and alteration of the dominant constituent, amorphous siliceous volcanic glass, is generally associated with intensive leaching of mobile elements, and therefore, depends on conditions of their sedimentary environments, including the interaction of the glass with water, environmental pH, organic matter, and pore water of the sediment, and early diagenetic environment (Naish et al., 1993; Ver Straeten, 2004; Ddani et al., 2005; Hints et al., 2006; Kiipli et al., 2007; Hong et al., 2016). In saline alkaline lakes under arid climate conditions volcanic materials usually alter to zeolite and K-feldspar (Sheppard and Gude, 1973); in coal-bearing sequences volcanic ashes are altered usually to kaolinite (Bohor and Triplehorn, 1993). However, in marine environments with various water depths, volcanic ashes are typically altered to smectite or I/Sm, though there are certain differences in clay mineralogy between various facies (Ver Straeten, 2004; Hong et al., 2011; Huff, 2016).

Ash layers occur widely in sedimentary sequences and have been considered as key stratigraphic markers for regional correlation, and they can also provide geochronologic age dates to better constrain chronostratigraphic time (Cant, 1992; Zhang et al., 2006; Christidis and Huff, 2009; Lowe, 2011; Rocha-Campos et al., 2011). In south China the Permian-Triassic boundary (PTB) sequences of marine facies generally contain 5 to 10 individual, closely spaced volcanogenic beds, which are interbedded with claystone, siliceous mudstone, and carbonate sediments. The individual thickness of ash beds usually ranges from 2 to 40 cm. However, the number of ash beds in the PTB sequences

* Corresponding author.
*E-mail address:* honghl8311@aliyun.com (H. Hong).

http://dx.doi.org/10.1016/j.clay.2017.03.014
0169-1317/

changes with different sedimentary environments and locations; the marine PTB sequences may contain up to 10 ash beds and the terrestrial PTB sets only contain 1 to 3 ash beds (Peng and Shi, 2009; Yu et al., 2015). Although zircons are commonly found in the ash beds and are useful for age determination and stratigraphic correlation, the dating results are sometimes very different from different researchers, especially when different testing methods are employed (Bowring et al., 1998; Mundil et al., 2004).

The stratigraphic persistence and stability of ash beds across south China have been considered as providing effectively an alternative marker for recognizing and correlating the PTB position in both marine and non-marine PTB sections in the area (Mitchell et al., 1994; Peng et al., 2001; Metcalfe et al., 2009). However, weathering and alteration of volcanic ashes may form authigenic minerals in correspondence with the sedimentary environment, and thus, the primary volcanogenic materials will produce different authigenic minerals in various environments (Ver Straeten, 2004; Kiipli et al., 2007). Previous studies of the PTB volcanic ashes in different facies focused mainly on clay mineral composition and heavy minerals, and the detailed stacking structures and formation of clay minerals are still not well known (Zhang et al., 2004, 2006). In order to better understand the alteration of volcanic ash in corresponding environments, and to employ the ash beds as regional scale chronostratigraphic markers in sedimentary sequences under differing, complex geological situations, knowledge of authigenic minerals of volcanic ash in various depositional environments is essential for understanding the alteration, diagenetic processes, and later metamorphism of the material. The purpose of this study is to investigate the clay mineralogy of ash beds in the PTB stratigraphic sets in Guizhou, south China, and thus, to shed light on weathering and alteration of volcanic ashes in littoral and interactive marine-terrestrial depositional environments and correlation of ash beds between disparate facies in the area.

## 2. The PTB stratigraphic successions and sampling

The two sections are located in the southwestern part of Guizhou Province, south China (Fig. 1). The Zhongzai (ZZ) PTB stratigraphic set is situated at the Zhongzai village, Liuzhi County, Guizhou Province. The Permian-Triassic boundary sequences crop out well from excavation alongside the highway from Langdai to Zhongzai. Two ash layers are found in the PTB succession, with thicknesses of 3 and 5 cm (Fig. 2). The PTB stratigraphic set consists mainly of calcareous siltstone, silty mudstone, limestone, argillaceous limestone, marl, and shale, and the distinctive white and poorly consolidated ash layers are interbedded with thin-bedded argillaceous limestones. The Zhongzai Permian-Triassic sequence consists of the conformably contacted upper Longtan Formation and lower Yelang Formation. The PTB sequences contain abundant fossils of cephalopods, bivalves, gastropods, brachiopods, and ostracods, indicating that the Zhongzai succession was formed in a nearshore littoral environment during the period (Zhang et al., 2014; Yu et al., 2015).

The Tucheng (TC) PTB stratigraphic set is located in at the Qingshui village, 9 km south of Tucheng town, Panxian County, Guizhou Province, south China (Fig. 1). It is approximately 220 km from the Zhongzai section. The Tucheng section was exposed by excavation for the highway from Panxian to Shuicheng. It consists of the upper Xuanwei Formation and lower Kayitou Formation, and the Xuanwei Formation is conformably overlain by the Kayitou Formation. The lithology of the PTB stratigraphic succession is mainly mudstone, sandstone, siltstone, interbedded with coal seams and ash beds. Permian plants and Triassic floras, bivalves and brachiopods (*Lingularia* spp.) were commonly found in the sediments, and thus the Tucheng succession was formed in a terrestrial-marine transitional zone, where the terrestrial environment could change to a nearshore marine environment when flooded by seawater (Yu et al., 2007, 2015).

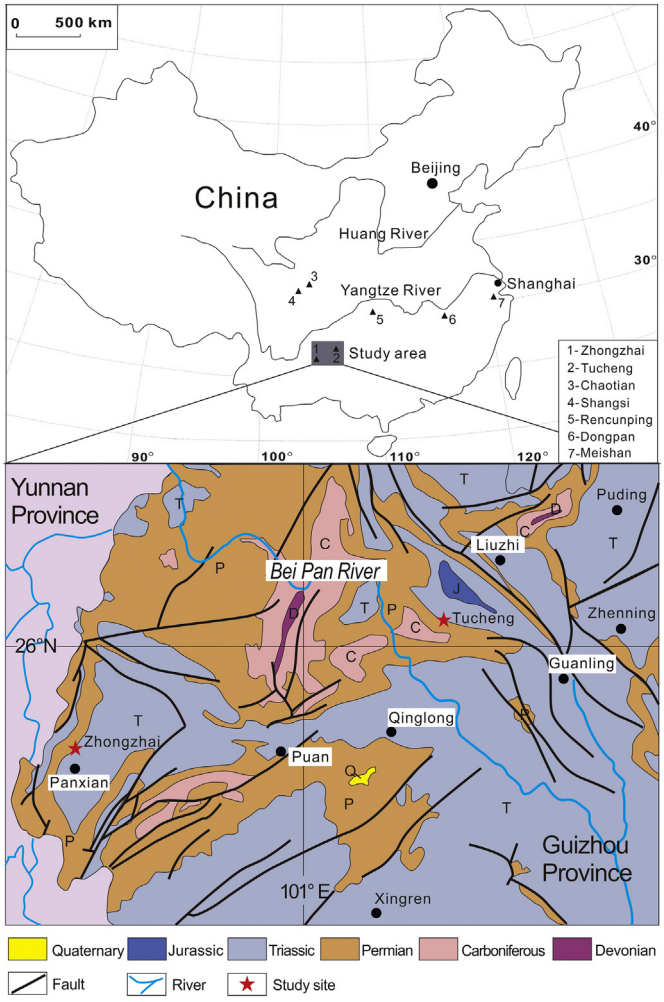


**Fig. 1.** Simplified regional map showing the locations of the PTB sections and the regional geology of the studied area.
(Modified from Guizhou Bureau of Goelogy and Mineral Resoueces (GBGMR) (1987).)

In the western Guizhou and eastern Yunnan area, south China, the continuous PTB successions are well-exposed within a short distance, with depositional environments ranging from continental facies through paralic facies to marine settings. Stratigraphic correlations between different PTB successions were previously undertaken with high resolution and confidence by Peng and Shi (2009). Two ash beds within the PTB stratigraphic sets in the Zhongzai and Tucheng sections were selected for our study, and clay samples each with a weight of ~500 g were collected from the ash beds of the two PTB stratigraphic successions.

## 3. Experimental methods

### 3.1. XRD analysis

The bulk clay samples were dried in an electric oven at 60 °C overnight, then ground to powder passing through a 200 mesh sieve with a mortar and pestle, and the <2 μm clay fraction was obtained by a sedimentation method, which was converted to Ca-form, as described in Zeelmaekers et al. (2015). The bulk clay samples were prepared by mounting the powders into sample holders using a back-press technique, and the oriented clay samples were prepared by pipetting the purified clay suspension onto glass slides and allowed to air-dry at room temperature. Ethylene glycol-saturated clay samples were prepared by treating the air-dried oriented samples with ethylene glycol vapor in a desiccator at 65 °C for 4 h.