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Fluorine speciation and origin of Early-Middle Triassic bentonite deposits in Sichuan Basin, South China

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Fluorine (F) is one of the most important environmentally harmful elements released by volcanic activity, and the bentonite deposits that formed from volcanic ashes are potentially harmful to the environment. However, the mechanisms governing F-rich bentonite formation and its F speciation composition remain enigmatic. The F-rich bentonite deposits are widely distributed in the Early-Middle Strata of the Sichuan Basin, South China. Detailed mineralogical and geochemical studies were conducted on the bentonite deposits from five sections of the Sichuan Basin. X-ray diffraction (XRD) analyses indicate that the F-rich bentonites mainly contain quartz, carbonates (calcite and dolomite) or gypsum, and clay minerals, while the clay minerals are dominated by illite and illite/smectite (I/S). Clay mineralogical studies suggest that bentonites were transformed from volcanic ashes during diagenesis by smectite illitization. The major and trace element distribution in F-rich bentonite deposits altered from volcanic ashes is most likely derived from felsic magmas, and alteration of the parent rocks (e.g., rhyolites) to bentonite is associated with leaching and subsequent removal of F. The total fluorine content (F_{TOT}) of the bentonite samples ranged from 1,162 mg/kg to 2,604 mg/kg (average = 1773 mg/kg), well above the average F_{TOT} contents of soils in the world. The results of the sequential extraction experiments show that the highest content is residual-fluorine (F_{res}), followed by carbonate-fluorine (F_{car}) with a mean value of 1,556 mg/kg and 186 mg/kg, indicating carbonate is an important F sink in bentonite deposits. The average fluorine value of organic fluorine (F_{or}), Fe/Mn oxide-fluorine (F_{fm}) and exchangeable fluorine (F_{ex}) are relatively low with an average value of 17.5 mg/kg, 6.8 mg/kg and 4.1 mg/kg, respectively. However, water-soluble fluorine (F_{ws}) has a mean value of 4.0 mg/kg, which is higher than the corresponding average value in soils in an area susceptible to endemic fluorosis in China. Based on the characteristic of fluorine speciation, the fluorine in bentonite deposits may pose a risk to the environment. This study makes an important contribution to a better understanding of the characteristic of fluorine speciation in bentonites and the formation mechanism that governs fluorine enrichment in bentonites.

KEYWORDS

fluorine speciation, bentonite, altered volcanic ashes, Sichuan Basin, Early-Middle Triassic

1 Introduction

Fluorine (F) is the 13th element found in abundance on the Earth and one of the most important natural pollutants receiving increasing attention because of its high toxicity and reactivity, which are potentially harmful to the environment and humans (Halmer et al., 2002; Fuge, 2019; Schlesinger et al., 2020). Volcanoes are one of the most important natural sources of fluorine, and the global volcanogenic fluorine flux is estimated to range from 50 to 8,600 Gg/yr (Symonds et al., 1988; Halmer et al., 2002; Schlesinger et al., 2020). Volcanic eruptions are associated with the release of magmatic fluorine in the form of hydrogen fluoride through volcanic degassing and the huge volume of volcanic ash that likely delivers fluorine large distances from its source (Rubin et al., 1994). Although fluorine has been assumed to move rapidly from volcanic ash to water through dissolution of the glass fraction and mineral coatings precipitated on glass surfaces (Rubin et al., 1994; Bia et al., 2020), volcanic ash may be largely enriched in total fluorine relative to the original magmatic contents, e.g., a 6 − fold increase in volcanic ash from Ruapehu volcano (Cronin et al., 2003). Bentonite is an important type of clay deposit commonly formed from the alteration of volcanic ash (Altaner et al., 1984; Huff, 2016). Therefore, the bentonite deposits formed from volcanic ash in the marine and continental basins always had high fluorine concentrations (Starkey, 1982; Haamer and Karro, 2006), which may be potential long-term sinks or sources of fluorine in the environment.

Water-soluble fluorine in the sediments is most important for groundwater toxicity and contamination, making it a key factor in the retention and mobility of F in sediments (i.e., soil) (Wenzel and Blum, 1992; Deng et al., 2022). The environmental hazard of fluorine in volcanic ash is generally assessed by analyzing the content of water-soluble fluoride in the ash (Bellomo et al., 2007; Delmelle et al., 2021). However, the fluoride in volcanic ash also occurs in the form of poorly water-soluble compounds (Delmelle et al., 2021). Fluorine can likely be released under a variety of environmental conditions, which should be considered when evaluating the input and potential environmental hazards from F-rich volcanic eruptions (Bellomo et al., 2007). Few studies have been conducted on the bentonite deposits with high total fluorine concentrations regarding its F speciation, which complicates appropriate risk management for fluoride-rich altered volcanic ash (Starkey, 1982; Haamer and Karro, 2006). In addition, the material source of the F-rich bentonite deposits and their formation conditions remain enigmatic (Bellomo et al., 2007).

Distribution and development of bentonite in Early-Middle Triassic strata in the Sichuan Basin, South China, resulting in significant fluorine accumulation in the marine basin (Yan et al., 2015; Lin et al., 2020; Feng M. S. et al., 2021), making it an ideal field site to constrain the process of F-rich bentonite formation. In this study, we aim to characterize the fluorine speciation of bentonite deposits in the Sichuan Basin, South China using mineralogical methods and batch leaching experiments to decipher the formation process of F-rich bentonite deposits. This study is useful to evaluate appropriate risk management for F-rich bentonite deposits and improve our understanding of the behavior of volcanic fluorine accumulating in altered volcanic ash.

2 Geological setting

The Sichuan Basin was a stable craton basin located in the western region of the Yangtze block, northwest South China, bounded by the Qinling-Dabie orogen to the north, the Jiangnan orogen to the southeast, Songpan-Ganzi Terrance to the west, and the Sanjiang orogen to the southwest (Cawood et al., 2018; Liu et al., 2021) (Figure 1). The Yangtze Platform was stable and formed shallow-water carbonates from the Late Proterozoic to Middle Triassic (Lehrmann et al., 2005). The Early-Middle bentonite deposits are widely distributed in the Upper Yangtze Platform, South China. These bentonites are so-called “mung bean rock” (or “green bean rock”) which contains a high concentration of lithium and fluorine and has an area of about $7 \times 10^6\ km^2$ and a thickness of several tens of centimeters to tens of meters (Lin et al., 2020; Feng M. S. et al., 2021; Li et al., 2021). These altered volcanic ashes were believed to originate from the eruption of episodic volcanism caused by Large Igneous Province (Ma et al., 2019; Ju et al., 2020), and the extensive volcanic eruption caused by amalgamation and collision of terranes and continents during the closure of the Paleo-Tethys Ocean (Feng M. S. et al., 2021; Li et al., 2021), and the Indosinian movement (Xiao and Hu, 2005; Wang et al., 2019).

3 Materials and methods

3.1 Sampling

Five bentonite samples were collected from outcrops in five sections in South China, including the Yongchuan section, the Pinghong section, the Xiejiacao section, the Pianyazi section and the Kai section (Figure 1). The bentonite samples exhibit light yellowish, consolidated, and locally

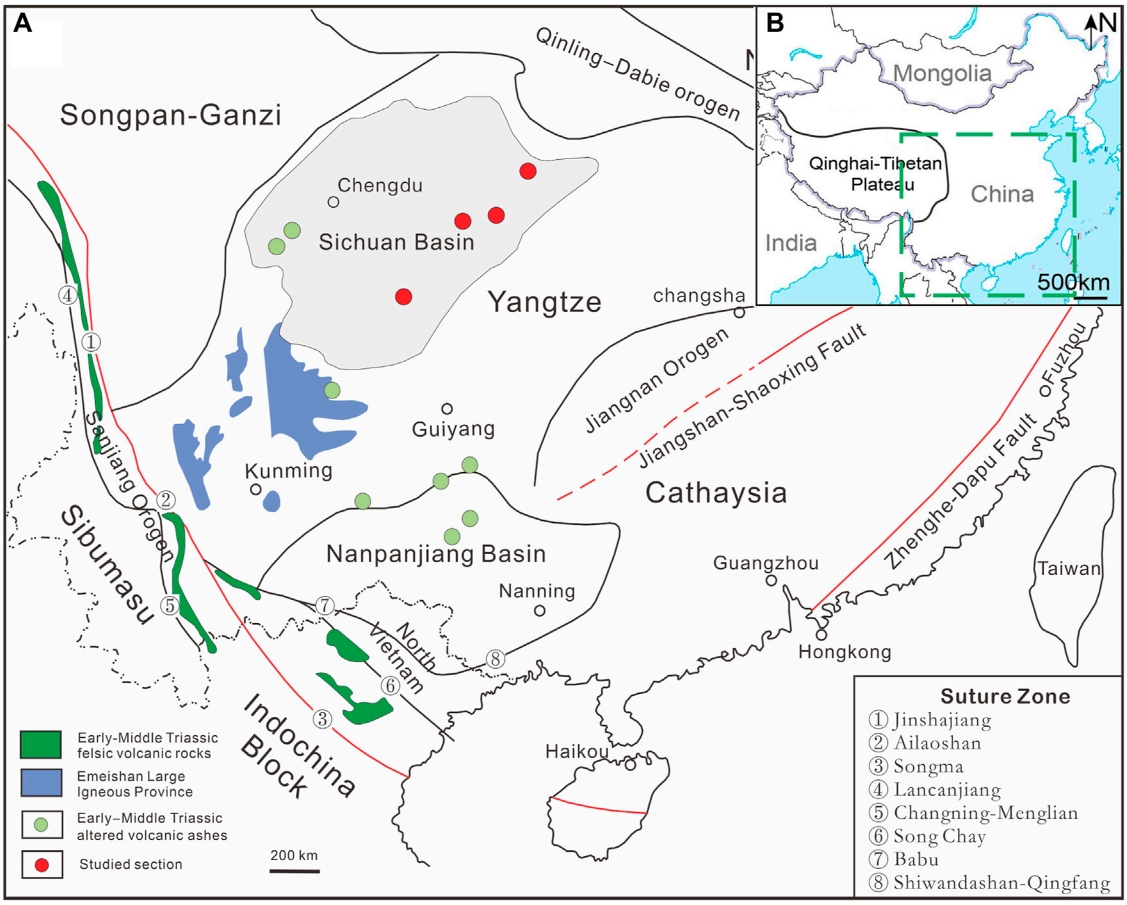

FIGURE 1
(A) Schematic geological map for South China and the distribution of Early-Middle Triassic bentonite deposits (based on the 1: 5,000,000 geology map of China); **(B)** Insert map showing the location of the study area in China.

contain elliptical siliceous particles. It occurs as a stratified bed ranging from 30 cm to 2 m thick with no discernible stratification features in the layers. In the Pianyazi section, the altered volcanic ash occurs near the bottom of the Middle Triassic Leikoupo Formation, which is underlain and overlain by anhydrite (Figure 2). In other sections, the altered volcanic ashes usually occur at the bottom of the Middle Triassic Leikoupo Formation, which is underlain by the Lower Triassic Jialingjiang Formation in a shallow-water carbonate basin setting. The lower part of Leikoupo Formation consists of dolomite and the upper part of Jialingjiang Formation consists of limestone in the study area (Li et al., 2021).

3.2 Sample characterization

Clay minerals (<2 μm) were separated from bentonite samples according to the methods of Köster et al. (2021a). The mineralogy of bentonite samples was confirmed by XRD using an X-ray diffractometer (TTR-3, Rigaku Crop, Tokyo, Japan), and Cu Kα radiation ($\lambda = 1.54056\mathring{A}$) generated at 45 kV and 30 mA. To constrain the clay mineralogy, XRD was performed on the clay mineral fractions (<2 μm) of bentonite powers, on the air-dried oriented clay sample (N), on the ethylene glycol solvated (EG), and on the 550°C heated (T) states. The XRD patterns calculations were performed using the Clayquan program (version 2016) with Rietveld refinement methods. The relative analysis error is ±5%. The major and trace element compositions of the bentonites were analyzed using X-ray fluorescence spectrometry (XRF). Fusion glasses were prepared by mixing the sample with lithium borate flux at a ratio of 1:10. Loss on ignition (LOI) was determined by weighing the samples before and after heating to 1,075 ± 25°C for 1 h. Fluorine in the altered volcanic ash samples was analyzed using a pyrohydrolysis-ion-selective electrode (ISE). The relative analytical error was better than 5% for repeated analyses. The chemical index of

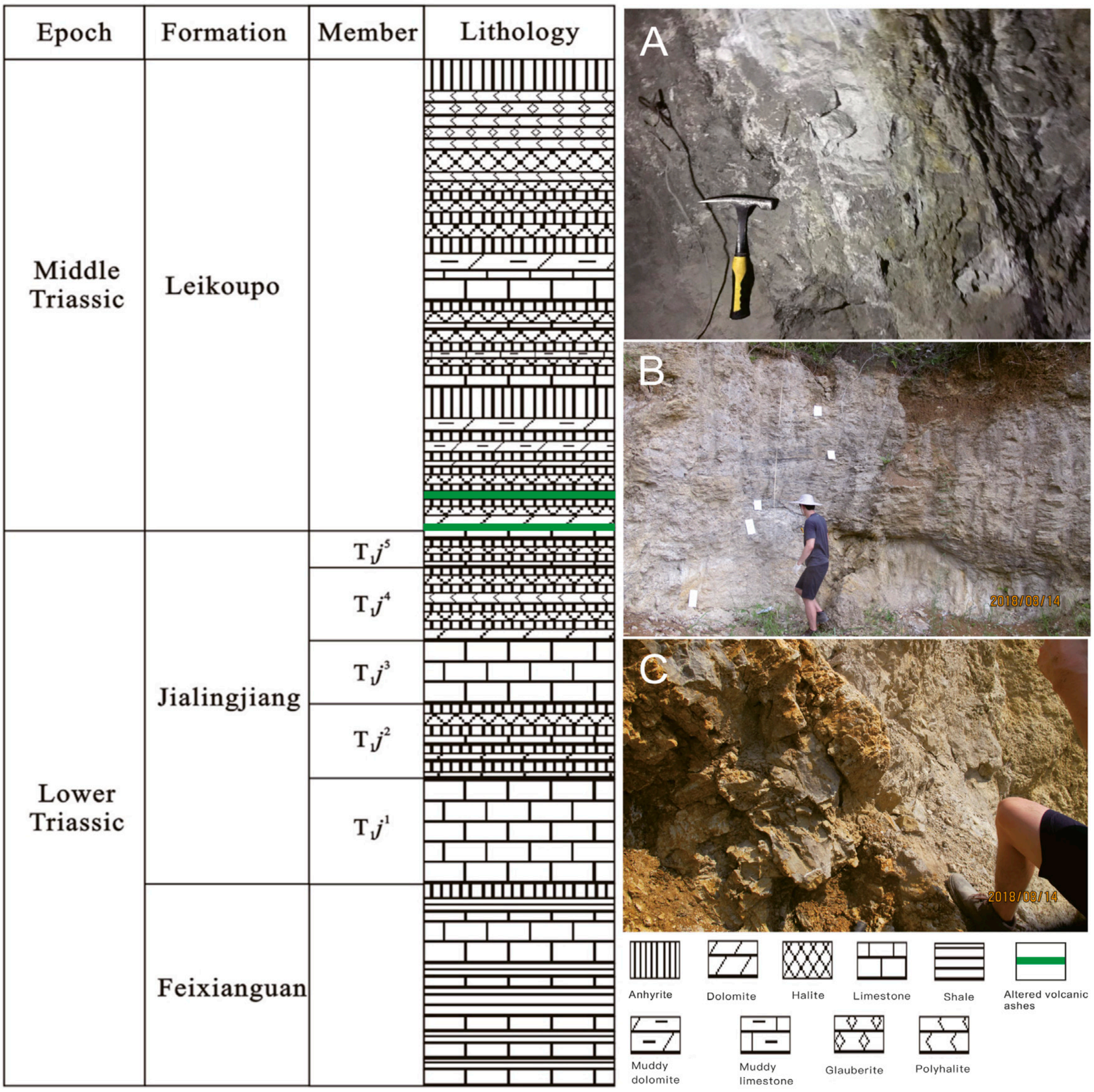

FIGURE 2
Generalized stratigraphy of the Early-Middle Triassic in the study area, South China (modified from Zhao et al. (2020)) and the representative photography showing outcrop of altered volcanic ashes; **(A)** Pianyazi section; **(B)** Pinghongcun section; **(C)** Kai section.

alteration (CIA) was used to assess the degree of weathering and alteration in altered volcanic ashes, which can be calculated using the following formulae (Nesbitt and Young, 1984):

$$\mathrm{CIA} = [\mathrm{Al_2O_3} / (\mathrm{Al_2O_3} + \mathrm{CaO^*} + \mathrm{Na_2O} + \mathrm{K_2O})] \times 100 \quad (1)$$

In this formula, $\mathrm{CaO^*}$ is the CaO residing only in the silicate fraction. In absence of carbonate and apatite, the CaO concentration of the silicate fraction was defined as the CaO content of the bulk samples. However, carbonates are observed in our studied samples, so the CaO value was defined as the content of $\mathrm{Na_2O}$ when CaO >$\mathrm{Na_2O}$.

3.3 Sequential chemical extraction experiments

Fluorine species in bentonite samples were determined separately in six categories: water-soluble fraction (F_{ws}), exchangeable fraction (F_{ex}), fraction bound to carbonates (F_{car}), fraction bound to Fe-Mn oxides (F_{fm}), fraction bound to organic matter (F_{or}) and a residual fraction (F_{res}). Sequential chemical extraction experiments were performed following a improved method based on the methods of Tessier et al. (1979), to study the speciation of fluorine in bentonites by soaking samples in different solutions: 1) water soluble fraction, 50 ml of H_2O (20°C, bentonites: DI water = 1:25, 30 min); 2)

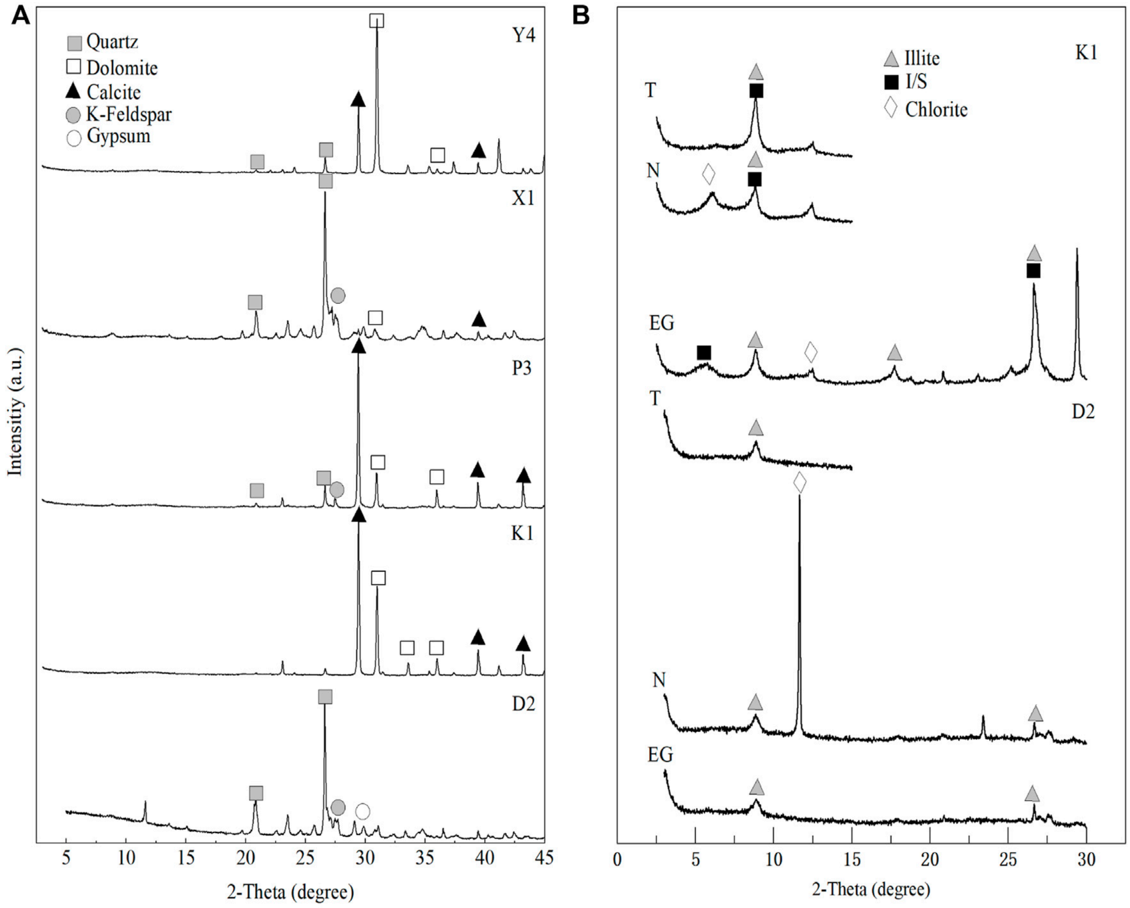

FIGURE 3
XRD pattern of bulk bentonites samples in Sichuan Basin, South China; **(A)** Bulk samples; **(B)** The diffraction pattern of clay minerals in representative samples (K1 and D2). N, Air-dried oriented clay samples; EG, Ethylene glycol-saturated clay samples; T, clay samples post heating to 550°C.

exchangeable fraction, 1 M $MgCl_2$ (pH = 7.0, 20°C, bentonites: solution = 1:25, 1 h); 3) fluorine bound to carbonates, 1 M NaOAc (pH = 5.0, 20°C, bentonites: solution = 1:25; 5 h); 4) fluorine bound to Fe-Mn oxides, 25 ml 0.2 M NH_4OAc (pH = 3.25, 20°C in a water batch, bentonites: solution = 1:25; 30 min); 5) fluorine fraction bound to organic matter, 50 ml of 0.02 M HNO_3 + 30% H_2O_2 (bentonites: solution = 1:25); and 6) residual fluorine fraction, the fluorine concentration in this step was determined by subtracting the other five fractions from the total fluorine content.

4 Results

4.1 Mineralogical and chemical composition of bentonites

The XRD data of the bulk bentonite samples show that the bentonites in the Pianyazi section consist of clay minerals (46%), quartz (36%), gypsum (10%), and K-feldspar (8%) (Figures 3A; Table 1). In other sections, the mineral compositions are variable and mainly consist clay minerals (1%–37%), quartz (2%–34%), K-feldspar (0%–19%), dolomite (7%–79%) and calcite (3%–63%). The clay minerals are composed of illite (0%–99%), I/S (0%–86%), smectite (0%–13%) and C/S (0%–27%) (Figures 3B; Table 2). The dominance of I/S in bentonites could be an indication of the digenetic transformation of smectite into illite. The relative proportion of smectite in the I/S of the bentonite is around 15% in Xiejiacao and Yongchuan, indicating R3 ordered I/S, and is around 65% in other sections, indicating R1 ordered I/S.

The chemical compositions of the bentonites are different in the study sections, which is consistent with the XRD results (Table 3). In Xiejiacao and Pianyazi sections, the most abundant major constituent of the bentonite was SiO_2 (67.73% and 58.96%), followed by K_2O (10.04% and 9.47%). In the other sections, the bentonite samples mainly consist of CaO (36.22%, 31.74%, and 42.86%) and volatiles, measured as LOI (33.51%, 41.82% and

TABLE 1 Mineralogical compositions of bulk bentonites.

Sample	Location	Quartz	K-feldspar	Calcite	Dolomite	Gypsum	Clay minerals
P3	Pinghong section	5	4	72	15	0	5
X1	Xiejiacao section	34	19	3	7	0	37
Y4	Yongchuan section	3	0	17	79	0	1
K1	Kai section	2	0	63	33	0	3
D2	Pianyazi section	36	8	0	0	10	46

TABLE 2 Clay mineralogical compositions of bentonites.

Sample	Location	Smectite	Illite/Smectite	Illite	Kaolinite	Chlorites	Chlorites/Smectite
P3	Pinghong section	0	22	43	0	8	27
X1	Xiejiacao section	13	86	0	1	0	15
Y4	Yongchuan section	0	24	32	0	17	27
K1	Kai section	0	46	33	0	6	15
D2	Pianyazi section	0	0	99	0	1	0

TABLE 3 Major element (%) and selected trace element (ppm) compositions of bentonites.

Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	TiO_2	P_2O_4	FeO	LOI	Nb	Y	Zr
P3	17.23	4	1.59	5.29	36.22	0.011	1.74	0.027	0.28	0.073	0.72	33.51	6.54	18	73.8
X1	67.73	12.41	0.944	4.18	0.418	0.015	10.04	0.009	0.238	0.029	0.21	3.74	9.63	22.3	102
Y4	10.43	1.65	0.717	12.88	31.74	0.015	0.593	0.016	0.123	0.006	0.4	41.82	1.49	2.7	12.5
K1	5.58	1.42	0.444	7.49	42.86	0.01	0.428	0.009	0.07	0.025	0.24	41.6	1.52	2.52	12.8
D2	58.96	11.41	0.422	2.91	3.26	0.089	9.47	<0.004	0.186	0.019	0.35	7.16	11.3	27.8	158

41.6%). The geochemical characteristic of the bentonites was partly derived from the parental volcanic ashes but was probably also influenced by post-depositional alteration under various sedimentary environments.

4.2 Speciation of fluorine

The total F content (F_{TOT}) of bentonite ranges from 1,162 to 2,604 mg/kg with a mean value of 1773 mg/kg, which is higher than the average F_{TOT} content of soils in China (478 mg/kg) (Yi et al., 2013) and that of average F_{TOT} content of soils in the world (329 mg/kg) (Kabata-Pendias, 2000). F_{ws} is the fluoride extracted with distilled water, ranging from 2.911 to 6.548 mg/kg with a mean value of 4.035 mg/kg, which is higher than the corresponding average value in soils in Chinese endemic fluorosis areas. F_{ex} is the fluoride adsorbed by electrostatic attraction to positively charged clay, organic particles, and hydrated oxides. F_{ex} content in bentonites ranged from 1.715 to 4.082 mg/kg with an average of 2.535 mg/kg. F_{fm} is the fluorine absorbed by Fe, Mn, and Al oxides, oxyhydroxides, and hydrated oxides and precipitated with these chemicals, and ranged from 2.497 to 11.052 mg/kg with an average of 6.767 mg/kg. F_{car} is the fluorine bound to precipitated calcite in the samples and ranged from 46.383 to 497.893 mg/kg with an average value of 185.893 mg/kg. F_{or} is the fluorine bound to the organic matter in the samples and ranges from 3.803 to 33.711 mg/kg with an average value of 17.496 mg/kg. F_{res} is the residual fluorine present in the mineral lattice of the samples (e.g. clay minerals), ranging from 934.538 to 2,509.532 mg/kg with an average value of 1,556.296 mg/kg. Overall, the order of the six-fluorine species from smallest to largest is that $F_{ex} < F_{ws} < F_{fm} < F_{or} < F_{car} < F_{res}$ (Figure 4; Table 4).

4.3 Risk assessment of F-rich bentonites

Li et al. (2005) proposed a method for assessing the risk of fluorine in soil based on the statistical relationship between the

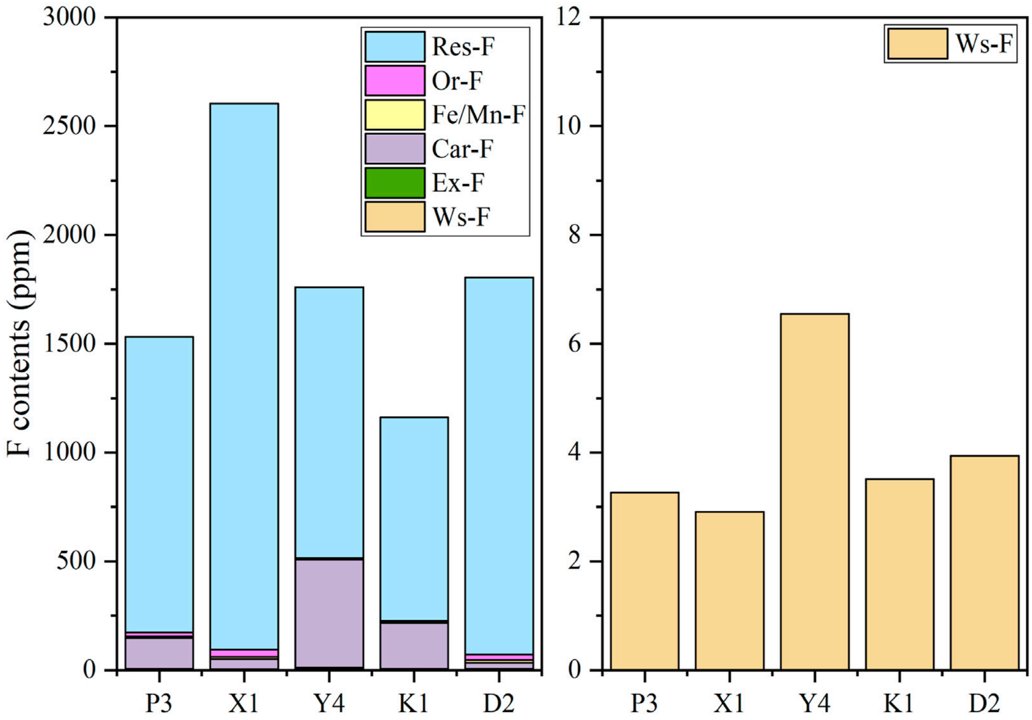

FIGURE 4
F speciation of bentonite samples in Sichuan Basin, South China.

TABLE 4 Contents of F speciation (mg/kg) in bentonite deposits in Sichuan Basin, South China.

Sample no.	F_{ws}	F_{ex}	F_{car}	F_{fm}	F_{or}	F_{res}	F_{TOT}
P3	3.264	2.697	142.851	5.718	18.538	1359.644	1532.712
X1	2.911	1.715	46.383	9.843	33.711	2509.535	2604.098
Y4	6.548	4.082	497.893	2.497	3.803	1244.036	1758.859
K1	3.512	2.015	211.405	4.725	6.109	934.538	1162.304
D2	3.939	2.166	28.450	11.052	25.320	1733.727	1804.654

geochemical characteristics of fluorine in soils with high fluorine content and the local occurrence of endemic fluorosis in China, which were described as follows:

$$C_i < S_1 \rightarrow \text{soil deficient in F} \quad (2)$$

$$S_1 \leq C_i < S_2 \rightarrow \text{soil normal in F} \quad (3)$$

$$C_i > S_2 \rightarrow \text{soil excessive F} \quad (4)$$

where C_i (mg/kg) is the analyzed content of fluorine in the samples; S_1 and S_2 (mg/kg) are the lower and upper limits, respectively, of the standard concentrations of fluorine for the assessment. C_i denotes the measured concentrations of F_{ws} in the samples when the pH of samples is alkaline (pH>7). S_1 was defined as 0.5 mg/kg, which is the average F_{ws} content in the world's uncontaminated surface soils (National Soil Pollution Survey of China, CNEMC, 1990). The S_2 was defined as 2.5 mg/kg, which is the equivalent in soils in areas with fluorosis prevalence in China. Then, a soil health index for fluorine (P_i) was also defined as follows:

$$P_i = \frac{C_i}{S_2} \quad (5)$$

If the P_i is greater than 1, it means that the evaluated soil has high-fluorine content and its health quality related to fluorine is inferior. To assess the health quality of the altered volcanic ash, F_{ws} content in the altered volcanic ash was taken as the C_i since the pH of all the altered volcanic ash is alkaline. All bentonite samples were assessed as having excessive F in their soils.

Furthermore, the water-extractable F contents in altered volcanic ash generally have higher concentrations than those of soils in fluorosis areas in China.

5 Discussion

5.1 The formation process of F-rich bentonites

Bentonites are volcanic ashes that have undergone significant devitrification to dioctahedral smectite, and volcanic ashes are a precursor material for bentonites (Altaner et al., 1984; Huff, 2016; Namayandeh et al., 2020). Generally, smectite formed in marine subaqueous environments during diagenetic alteration of volcanic glass shards, releasing alkalis and alkaline Earth elements after initial hydration and cation exchange between the fluids and volcanic glass shards (De La Fuente et al., 2000; Huff, 2016; Hong et al., 2019). Under these conditions, the pH and salinity increased, favoring smectite formation (Hong et al., 2019; Milesi et al., 2019). In this study, the clay minerals of bentonites are composed of illite and I/S. The I/S in bentonites were derived from the illitization of smectite in subaqueous environments (McCarty et al., 2009; Gong et al., 2018). The transformation of smectite to illite by a mixed-layer I/S is a common mineralogical reaction that occurs during the diagenesis of altered volcanic ashes, with temperature and potassium availability being the main controlling factors (Nesbitt and Young, 1984; Cuadros, 2006; McCarty et al., 2009). The simplest form of smectite illitization can be described as the following reaction pathway (Bethke et al., 1986):

$$\text{smectite} + Al^{3+} + K^{+} \rightarrow \text{illite} + Si^{4+} + Fe^{2+} + Na^{+} + Mg^{2+} \quad (6)$$

$$\text{smectite} + K^{+} \rightarrow \text{illite} + Si^{4+} + Fe^{2+} + Na^{+} + Mg^{2+} \quad (7)$$

However, smectite illitization starts at about 70 ~ 80 °C and lead to a decrease in smectite content according to the following reaction pathway: smectite → random I/S → ordered I/S → illite (e.g., Altaner and Ylagan, 1997; Cuadros, 2006; Abedini and Calagari, 2012; Gong et al., 2018). In this study, the mineralogy and geochemical composition of the bentonite are variable, which were probably controlled by the depositional environments (Hong et al., 2019). In the Pianyazi section, the presence of gypsum suggests that the bentonites at this site were probably formed in a restricted, subaqueous environment. In other sections, however, the presence of calcite and the absence of gypsum indicate that the bentonite at this site was probably formed in a subaqueous environment. Alteration of volcanic ash releases bicarbonate and cations drive precipitation of authigenic carbonate and clay minerals (Köster et al., 2021b). Furthermore, the high field strength elements (e.g., Nb, Zr) and TiO_2 are indicative of magmatic origin due to their immobile behavior during diagenesis and weathering (Berry, 1999; He et al., 2014; Hong et al., 2019, 2020). The Al_2O_3/TiO_2 ratio is generally considered a useful indicator of the provenance because the concentrations of Al and Ti in the materials remain constant during diagenesis and weathering (Nesbitt and Young, 1982; Sugitani, 1996; Abedini and Calagari, 2012; Abedini, 2017; Abedini and Calagari, 2017; Abedini et al., 2018; Abedini et al., 2019a; Abedini et al., 2019b; Abedini et al., 2020a; Abedini et al., 2020b; Kiaeshkevarian et al., 2020; Leontopoulou et al., 2021; Abedini and Khosravi, 2022). According to the classification model, the volcanic ashes corresponding to the bentonite deposits are classified as felsic magmas in all sections and in the fields of rhyolite (Figure 5).

Volcanoes emit a variety of gases that include hydrogen fluoride and hydrogen chloride, which are the main components of high-temperature volcanic gas (Cronin et al., 2003; Bia et al., 2020; Delmelle et al., 2021). The volcanic gases interact rapidly with volcanic ash particles and especially with atmospheric water to form acidic aerosols (Gutmann et al., 2018; Zelenski et al., 2020). The smaller volcanic ash particles have a large surface area relative to their mass, which can transport significant amounts of soluble fluorine to pastures far downwind from an erupting volcano. Total fluorine in volcanic ash can be enriched by many factors compared to the original magmatic content, for example, by a factor of six relative to the original magmatic content in Ruapehu volcano (Cronin et al., 2003). Another important source of Early-Middle Triassic altered volcanic ash is the chemical weathering of F-rich volcanic rocks in the vicinity of the basin. High fluorine concentrations have always been found in felsic igneous rocks (Chowdhury et al., 2019; Liu et al., 2020; Amézaga-Campos et al., 2022). In this study, the altered volcanic ashes were considered to be derived from the eruption of episodic volcanism (e.g., Xiao and Hu, 2005; Lin et al., 2020; Feng M. S. et al., 2021). F is removed from minerals by chemical weathering at almost the same rate as other elements (Jacks et al., 2005). The CIA values in the collected samples vary between 54 and 76 with an average value of 65, which is lower than the PAAS value of 70 but higher than the UCC value of 48 (Taylor and McLennan, 1985). The presence of clay minerals (e.g., I/S and illite) in the samples is also evidence of chemical weathering and alteration of volcanic ash. Bentonites show Ca enrichment compared to the probable source rocks, most likely due to precipitation of the Ca-carbonate precipitation by alteration of volcanic ashes. The F contents in the samples show a strong negative correlation with the CIA values, which is most likely due to the fixation of fluorine in clay and secondary minerals in altered volcanic samples (Figure 6).

5.2 Enrichment mechanism of fluorine speciation

5.2.1 Adsorption of fluorine by clay minerals

Most of the F in bentonites was stored in residual silicates. F_{res} is the residual fluorine present in the mineral lattice of the samples (e.g., clay minerals), ranging from 934.538 to 2509.532 mg/kg, with an average value of 1556.296 mg/kg. The percentage of clay minerals in the bulk rock shows a positive correlation with F_{res} (R^2 = 0.71). Clay

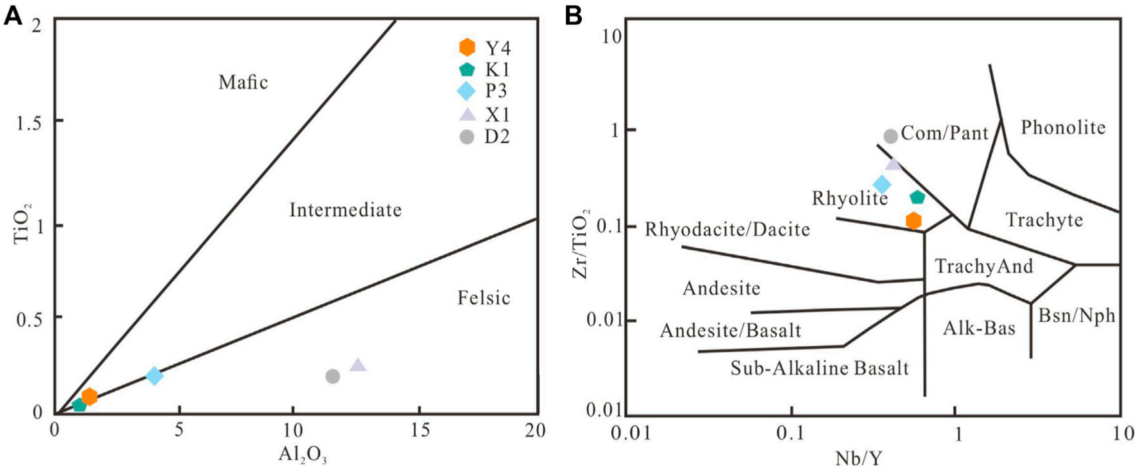

FIGURE 5
(A) Plot of TiO_2 and Al_2O_3 **(B)** Bulk rocks ratios of Nb/Y and Zr/TiO_2 for bentonite samples and the source fields defined by Winchester and Floyd (1977).

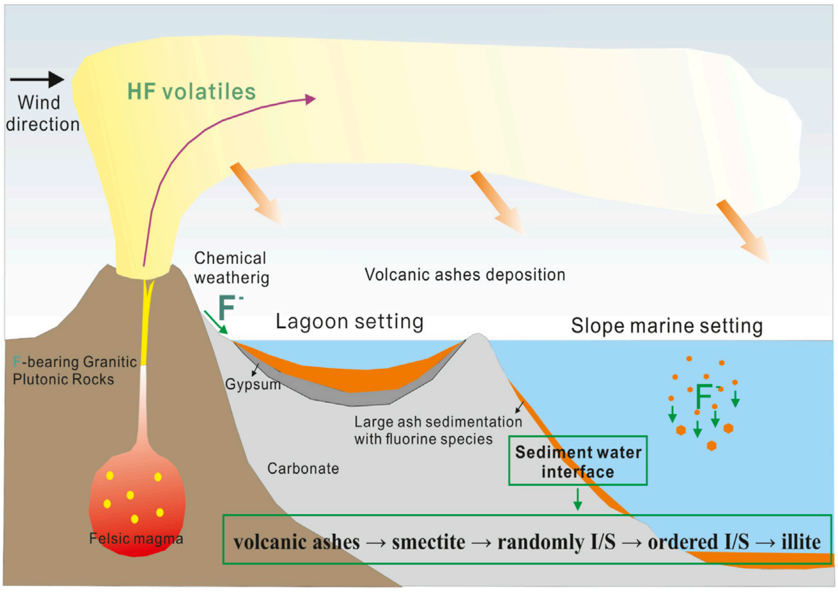

FIGURE 6
Conceptual model of bentonite deposits formation in Sichuan Basin, South China.

minerals are an important component of bentonites. Volcanic ash is an important precursor material of clays in marine environments with a diagenetic process. The K, Mg, and Ca in the past seawater are readily available for the formation of smectite, and the bentonite layers are generally dominated by smectite and subsequently consist of illite due to the smectite illitization (Cuadros, 2006; Hong et al., 2019). Alteration of volcanic ash releases bicarbonate and cations that drive precipitation of authigenic carbonate and clay minerals (Calagari et al., 2015; Köster et al., 2021a). The fluorine in seawater and volcanic ash could be removed from seawater by authigenic clay minerals. In this process, the fluorine in seawater can be taken up by clay minerals which transfer the fluorine from seawater to the solid phase by physical and chemical adsorption and surface precipitation (Du et al., 2010). The fluorine ion is crystal chemically very similar to the hydroxyl ion and replaces hydroxy in 2:1 layer silicates, such as illites and smectites (Chipera and Bish, 2002).

5.2.2 Adsorption of fluorine by carbonates

In this study, bentonites have high F_{car} concentrations, ranging from 46.383 to 497.893 mg/kg, with an average value of 185.893 mg/kg, and F_{car} shows a positive relationship with carbonate contents in bulk rocks ($R^2 = 0.63$). Alteration of volcanic ash releases bicarbonate and cations that drive precipitation of authigenic carbonate and clay minerals (Köster et al., 2021a). Ca-carbonate precipitation is thought to dominate the removal of dissolved fluorine from seawater (Carpenter, 1969; Schlesinger et al., 2020). Greater removal of fluorine from seawater by authigenic carbonates is 0.94 Tg/yr (Schlesinger et al., 2020), which will be higher during the period when there is additional fluorine input, e.g., volcanic eruptions. Calcite in altered volcanic ash is another important F sink. Due to the strong affinity of fluorine to calcite, calcite is often used as an adsorbent in wastewater-treatment technologies (Budyanto et al., 2015). F in parent solutions promotes calcite formation, and magnesium in parent solutions is thought to cause the co-precipitation of F with calcium carbonate. The amount of fluoride coprecipitated with calcite increases with increasing concentration of magnesium ions in parent solutions (Kitano and Okumura, 1973). Feng X. et al. (2021) used first-principle calculations to show the incorporation mechanisms of F into crystalline calcite, and suggest that a fluorine atom is most strongly favored as a substituent of two fluorine ions for a carbonate, forming a CaF_2 defect.

5.2.3 Adsorption of fluorine by Fe (hydr)oxides

In this study, F_{fm} ranges from 2.497 mg/kg to 11.052 mg/kg with an average value of 6.767 mg/kg. The adsorption of F on Fe/Mn-(hydr)oxides has been extensively studied and is mainly based on electrostatic attraction and ion exchange (Farrah et al., 1987; Hiemstra and Riemsdijk, 2000; Rathore and Mondal, 2017). The kinetics of adsorption by Fe (hydr)oxides is relatively fast and the process is pH dependent, as higher adsorption occurs at lower pH values. Hiemstra and Riemsdijk (2000) suggested that the absorption of F in Fe (hydr)oxides can be described as an exchange reaction for OH of surface groups, where the main reaction can be described as follows:

$$\mathrm{FeOH}^{-\frac{1}{2}} + \mathrm{F}^{-}(aq) = \mathrm{FeF}^{-\frac{1}{2}} + \mathrm{OH}^{-}(aq) \tag{8}$$

Farrah et al. (1987) confirmed the capacity of $Al(OH)_3$ to scavenge F^- from aqueous phases from pH 4 to 7, and the oxides dissolve and form F–Al complexes under strongly acidic conditions. Ren et al. (2021) suggested that F uptake by layered double hydroxides is enhanced under alkaline conditions.

6 Conclusion

The Early-Middle Triassic bentonite deposits in the Sichuan Basin, South China have anomalous high F contents that pose a major potential environmental hazard. In this work, the F speciation, mineralogical, and chemical composition of bentonites were studied in detail. The detailed mineralogical and geochemical composition of the bentonites suggests that the bentonites were transformed during diagenesis from volcanic ash by smectite illitization, and volcanic ashes are most likely derived from felsic magmas. The F_{TOT} of bentonites ranged from 1,162 to 2,604 mg/kg (average = 1773 mg/kg), and the order of six-fluorine species from smallest to the largest is that $F_{ex} < F_{ws} < F_{fm} < F_{or} < F_{car} < F_{res}$. The highest content was F_{res} and followed by F_{car} with a mean of 1,556 mg/kg and 186 mg/kg, suggesting F was mainly trapped by clay minerals and carbonates. The bentonites have high F_{car} concentrations, which were controlled by the removal of fluorine from seawater by authigenic carbonates precipitation, suggesting carbonate (e.g., calcite) is an important F sink in bentonite deposits. In addition, the F_{ws} have an average value of 4 mg/kg, which is higher than the corresponding average in soils in Chinese endemic fluorosis-prone areas. The F of bentonites in this study may pose a potential risk to the environment. This study provides an improved understanding of the modes of sediment deposition and environmental conditions at the time of F-rich bentonite deposition.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

YL designed the research and wrote the manuscript. MZ, YZ, and EX discussed the results and commented on the manuscript.

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Conflict of interest

Publisher's note

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