Chemical Weathering of the Southern Tibetan Plateau: Study the Geochemical Weathering Indices in the Top Soils

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Abstract

Continental chemical weathering has been suggested to affect the concentration of atmospheric carbon dioxide that influences global climate change at different time scales. Various indices for chemical weathering have been adopted to investigate past change in chemical weathering intensity and climate change on oceanic and lacustrine sediment archives. The reliability of the chemical weathering indices has been questioned as most sediments likely originate from multiple types of bedrock that may experience various degrees of chemical weathering and can thus be reliably robust indicators of climate and paleoclimate. Here we present Sr-type (e.g. Rb/Sr Sr/Ba) and Na-type (e.g. CIA CIW PIA CPA) chemical weathering indices for top soils across the southern Tibetan Plateau to discuss the chemical weathering characteristic in the Tibetan Plateau and to examine their response to regional climate variation. The results of chemical indices and the A-CN-K ternary plot show that the southern Tibetan Plateau is under the carbonate control of the primary chemical weathering stage with the cold-dry climate. Correlation analyses show that Sr-type indices co-vary with mean annual temperature and annual precipitation while Na-type indices show little consistence with regional climate. The climate condition is the dominant control of Sr-type indices of top soils in the study area and the bedrock may be the dominant control for the Na-type indices. We also compared the corresponding indices at a Holocene lacustrine sediment profile in the Qaidam Basin in the northeast Tibetan Plateau with regional climatic records which strongly supports our observation in the top soils. The results of the study suggest that for the relative cold and dry climate in Tibetan Plateau the Sr-type indices are more sensitive to climate condition than Na-type indices. This suggests that the Sr-type indices are likely more suitable than Na-type indices to reflect the change of climate on the Tibetan Plateau. Caution should be taken for using the Na-type indices for reconstructing the past change in climate for the study area.

1. Introduction

Continental chemical weathering on global scale is suggested to impose a net drawdown of atmospheric CO$_2$ that influences global climate changes (Walker et al. 1981; Berner et al. 1983; Berner and Berner 1997; Ruddiman et al. 1997). The Tibetan Plateau (TP) have been considered as a key region for chemical weathering that has lowered atmospheric CO$_2$ and thus driven global cooling during the Cenozoic (Raymo and Ruddiman 1992; Zachos and Kump 2005). Many investigations have attempted to reconstruct past changes in the intensity of chemical weathering in the TP during the Cenozoic and to examine their relationship between chemical weathering and global climate changes (Yang et al. 2004a; Borges et al. 2008; Clift et al. 2008 2010; Lupker et al. 2013).

Persistent investigations on the controls of chemical weathering have contributed a lot to our understanding on the links between chemical weathering and its controlling factors such as tectonics (geological settings and topographical conditions) provenance climate (temperature precipitation and runoff) vegetation time and even human activities (Qiu et al. 2014). However controversies remain on the controlling mechanisms of chemical weathering. Various indices such as Na-type chemical weathering indices (Buggle et al. 2011) including CIA (Chemical Index of Alteration ) (Nesbitt and Young 1982) CIW(
Chemical Index of Weathering) (Harnois 1988; Cullers 2000) PIA (Plagioclase Index of Alteration) (Fedo et al. 1995) and CPA (Chemical Proxy of Alteration) (Buggle et al. 2011) and Sr-type indices (Buggle et al. 2011) including Rb/Sr and Sr/Ba ratios have been constructed to study changes in chemical weathering intensity climate change and geological events (Nesbitt et al. 1980; Chen et al. 1999; Muhs et al. 2001; Buggle et al. 2011; Velbel 1993; White and Blum 1995; Yang et al. 2004a; Deepthy and Balakrishnan 2005). Applications of the indices well reveal changes in weathering profiles dissolved matters in river water and aeolian sediments. For example Descourvieres et al. (2011) suggested that CIA reflected changes in chemical weathering associated with tectonic activity in Perth Basin in southwest Australia. Chen et al. (1999) showed that the Rb/Sr ratio could be used as an index for chemical weathering associated with past climatic changes at the Luochuan loess-paleosol profile in the central Chinese Loess Plateau. However there is a lack of systematic studies to carefully examine the proxies against regional geochemical background and climate parameters in order to understand their suitability to sediments such as top soils and river sediments that are derived from different rock types and spanning different climatic conditions.

The uplift of the TP and its environmental effects during the Cenozoic have been widely studied since tectonic uplift-weathering hypothesis was proposed by Raymo et al. (1988). Weathering from the river basins on the TP plays a key role in surface processes and geochemical cycles in earth supergene environments including global carbon cycle and chemical composition of the oceans (Berner et al. 1983; Kump et al. 2000). Previous studies have focused on main drainage basins around the TP such as the Yangze River catchment (Yang et al. 2006; Borges et al. 2008) and the Yellow river drainage basin (Li 2003; Yang et al. 2004a; Zhang et al. 1990) and so on. And the results indicate that there is a strong relationship between weathering and the climate change during glacial and interglacial periods (Liu et al. 2004; Yang et al. 2006; Borges et al. 2008). Unfortunately the weathering characteristic of the soils in the TP were discussed rarely. Theoretically the development of top soils by in situ weathering of earthy and rocky materials on direct exposure to atmospheric agents would result in a better preservation of chemical weathering information (Qiu et al. 2014). Top soils on the TP mainly originate from in situ weathering of bedrocks or are transported from nearby high elevation mountains by surface waters (Lin and Feng 2015) which are ideal to investigate the response of various indices to climate change (Qiu et al. 2014). Here we present the geochemical analysis on top soils across the southern TP to 1) investigate the chemical weathering characteristic of top soils; 2) examine the relationship between various chemical weathering indices and regional climate condition (e.g. regional temperature and precipitation). We also compared various indices at a sediment core in Qaidam Basin with Holocene climate records to test our observation in the top soils.

### 2. Geology And Climate

Southern Tibet is situated in a tectonically complex region where the India plate collided with the Eurasian plate about 70 Ma before present (Yin and Harrison 2000). The TP consists of several blocks (Aitchison et al. 2000) including Himalaya Block Lhasa Block and Qiangtang Block separated by east-west trending sutures (Yin and Harrison 2000). The Lhasa block located to the south consists primarily of
continental rocks including Cretaceous-Tertiary granites Tertiary volcanic and other rocks (Sun et al. 2007). The Qiangtang block in the central is characterized by metamorphic rocks and Late Paleozoic (Carboniferous and Permian) shallow marine strata in the west and Triassic-Jurassic shallow marine carbonate rocks interbedded with terrestrial clastic and volcaniclastic strata in the east (Liu 1988). The Himalaya block in the north consists mainly of Precambrian clastic sediments and metasedimentary rocks in the south (Brookfield 1993) late Proterozoic to early Cambrian metasedimentary rocks in the middle (Parrish and Hodges 1996) late Precambrian to early Paleozoic sedimentary and metasedimentary (Yin and Harrison 2000) and thick Permian to Cretaceous continental margin sequences in the north (Brookfield 1993). The sampling sites consists mainly of two east-west-trending structural blocks the Lhasa block to the south and the Qiangtang block to the north.

The climate in the southern TP is generally cold and dry. Monsoon season from June to September is relatively warm and humid and the non-monsoon season from October to May is extremely cold and dry. During the non-monsoon the climate is under the control of westerly winds and dust storms happen frequently in the western TP. During the monsoon season moisture and heat are transported northward to the TP from the south Indian Ocean. The mean annual temperature (MAT) and the annual precipitation (MAP) are relatively high in the southeast area (0°C and 300 mm/year) and lower in the northwest area (-3°C and less than 50 mm/year) (Huang et al. 2008; Li et al. 2009). Thus chemical weathering processes are relatively weak and physical weathering is a dominating process for soil production. For instance glacier activities (e.g. glacial grinding) and frost weathering in high mountains play an important role (Sun et al. 2007).

The climate of the Qaidam Basin is the typical desert climate which is also cold and dry compared to the other area in China. The annual average temperature is ~ 5.33°C with great seasonal difference and the annual precipitation is only 10mm ~ 30 mm. The evaporation could reach up to 3564.4 mm per year. And the climate of Dongtaiji Nuero Lake belongs to the Qaidam Basin desert climate with the MAT of 2.0°C and the MAP less than 25 mm.

3. Samples And Methods

3.1 Top soils on the southern TP

The 114 top soils developed on various rocks and with different climatic zone were collected across the southern TP (Fig. 1 and supplementary Table 1). We collected 0–5 cm soil after removed the visible plants and roots. Each sample was ~ 500 g stored in plastic bags. All soil samples were easily get but far away from human activities and collected at relatively low elevations where the soils mainly originate from in situ weathering or are transported from nearby mountains (Chen et al. 1981; Lin and Feng 2015). Soil samples were collected from different parent rock (Table S1) but all located in Lhasa Block and Qiangtang Block. The geographic coordinate (longitude latitude and altitude) of each sampling sites was given by a handheld GPS device during sampling at the site (Table S1).
3.2 Lacustrine sediment samples from Lake Dongtaiji Nuoer Qaidam Basin

Lake Dongtaiji Nuoer is located in the central Qaidam Basin northeastern TP (Fig. 1). An 11.3-m deep trench was excavated by a local lithium factory. We collected the lake sediment samples at a 10-cm interval and stored in plastic bags.

3.3 Methods

Soil samples were dried in a 50°C oven for more than 24 hours before laboratory analysis. Visible stones and plant residues were picked out before grinding samples using an agate mortar. Then the dry soil samples were passed using a 200 mesh sieve (< 0.074 mm) for laboratory analysis. The lake sediment samples were air-dried at room temperature and grounded using an agate mortar which were passed through using a 200 mesh sieve prior to analysis.

All top soil samples were analysed for geochemical elements of Mo Zr Sr Rb Th Pb Se As Au Zn W Cu Ni Co Cr V Sc S Ba K Fe Mn Ca and Ti during the sampling process in the field using a portable X-ray fluorescence spectrometer (XRF) (Niton XL3t 950). San (2013) presented the complete dataset in her thesis of which only Rb and Sr were presented in this study. We selected 32 soil samples for laboratory analysis in this study in order to investigate the geochemistry characteristic and chemical weathering for the top soils (Table S2). The 32 samples were selected from various types of sampling soils which covers typical climate zones on the TP (Table S2). In the laboratory 32 soil samples were analysed for major elements (SiO₂ Al₂O₃ Na₂O K₂O MgO CaO P₂O₅ TFe₂O₃ TiO₂ and MnO) using X-Ray Fluorescence Spectrometry (XRF) (Rigaku RIX-3000). Trace elements (Rb Sr and Ba) were analysed following nitric-hydrofluoric acid digestion (HNO₃ + HF) using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Replicate samples and reference materials (AGV-2 BHVO-2 BCR-2 and RGM-2) were used for quality control which shows that the standard deviation is less than 6%. Analysis of the soil samples was undertaken at the State Key Laboratory of Geological Processes and Mineral Resources in China University of Geosciences. The concentration of Sr and Rb were highly consistent between laboratory analysis and portable XRF measurements for the 32 samples.

Lake sediment samples were measured for major (Al Na K Mg Ca Fe Ti and Mn) and trace elements (Rb Sr Ba Cr Cu Zn et al.) using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-AES) (Perkin Elmer Optima 5300DV USA) and an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (X-7; Thermo-elemental USA) respectively following nitric-hydrofluoric acid digestion (HNO₃ + HF). The analysis of the lake sediment samples was taken at the key laboratory of Tibetan Environment Change and Land Top Processes in the Institute of Tibetan Plateau Research. The exact analysis process is described by Wu et al. (2008). Replicate samples and reference materials (GSR-1 and GSR-2) were also used for quality control. The analytical precision for both the soil samples and the sediment samples was better than 5%.

3.4 Climate data
In order to examine the relationship between various chemical weathering indices from the top soils and climatic parameters we obtained the MAT and the MAP data for 1992 to 2012 for the 114 sampling sites using the China Meteorological Forcing Dataset (ITPCAS CMFD) (He 2010) (Table S1). The MAP ranged from 69.91 mm to 1073.59 mm and the MAT ranged from −11.14°C to 18.13°C for the study area. From the Fig. 1 and the Table S1 it can be found that there are big differences for the climate conditions for the sampling sites where the MAT is less than 0°C and the MAP is less than 200 mm almost are located in the western Tibet.

4. Results

The concept of geochemical proxies of mineral alteration (e.g. weathering indices) relies on the selective removal of soluble and mobile elements from a weathering profile compared to the relative enrichment for rather immobile and non-soluble elements (Yang et al. 2004b). To transport process the elements of Na Ca and Mg are highly mobile in the weathering environment using as the mobile element and Al is proposed as the immobile counterpart to minimize biases due to variable mineralogical composition of the parent material (Liu et al. 1984; Buggle et al. 2011). We calculated the following some Na-type indices for the study:

\[ \text{CIA} = \frac{\text{Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{CaO}^* + \text{K}_2\text{O}} \times 100 \] (Nesbitt and Young 1982)

\[ \text{CIW} = \frac{\text{Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{CaO}^*} \times 100 \] (Harnois 1988)

\[ \text{PIA} = \frac{(\text{Al}_2\text{O}_3 - \text{K}_2\text{O})}{(\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{CaO}^* - \text{K}_2\text{O})} \times 100 \] (Fedo et al. 1995)

\[ \text{CPA} = \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{Na}_2\text{O})} \times 100 \] (Buggle et al. 2011)

Where CaO* represents silicate CaO. In this study the silicate CaO content was determined on the basis of the molar CaO/Na2O. If CaO/Na2O > 1 the content of Na2O was considered as the content of CaO; if CaO/Na2O < 1 the measured CaO content of the bulk sample was used for the calculation (McLennan 1993).

Only 5 major elements (K Fe Mn Ca Ti) for the 114 soil samples were measured in the field with the using the portable XRF. So we could not calculate the Na-type indices for the all 114 soil samples. We had to use the 32 Na-type indices to discuss the following sections.

The alkali element Sr having a similar ionic radius with Ca and Mg are common in mineral such as plagioclase pyroxene amphibole and biotite which are susceptible to weathering (Nesbitt et al. 1997; Buggle et al. 2011). As the Sr is highly mobile in the weathering environment they appear in several weathering indices like the Sr/Ba and Rb/Sr ratios. Here we also calculated Sr-type indices including Rb/Sr for 114 soil samples and Sr/Ba for collected 32 soil samples because in the field the portable XRF could not analyse Ba for all the 114 soils.
4.1 Na-type indices in the top soils

Figure 2 is a mixing plot of the 32 Na-type indices with the sampling sites for the top soils. CIA ranged from 50 to 68 with an average of 57; CIW ranged from 59 to 79 with an average of 66; PIA ranged from 50 to 74 with an average of 60 and CPA ranged from 73 to 85 with an average of 78 (Fig. 2 and Table S2).

All Na-type indices (CIA CIW PIA and CPA) varied very similar for 32 soil samples which did not show clear spatial distribution pattern on the southern TP (Fig. 2). And the similar value was recorded for the Na-type indices. The lowest values of Na-type indices occurred in samples of TPW-53 (CIA = 50 CIW = 59 PIA = 50 CPA = 71) located in western Tibet and TPW-27 (CIA = 51 CIW = 59 PIA = 51 CPA = 74) (Fig. 2A-D) located in northwestern Tibet. The highest Na-type indices were observed in soil sample YP-7 (CIA = 68) located in the eastern area; however its CIA value was slightly lower than post-Archean Australian average shale’s (PAAS’s) (CIA = 70) (Taylor and McLennan 1985) but higher than Upper Continental Crust’s (UCC’s) (CIA = 48) (Taylor and McLennan 1985). The CIA values of TPW-10 TPW-46 and TPE-3 varied from 64 to 66 were little lower than the highest value of YP-7. Then for the other soils the CIA values had a range at 50–60 varying at a close range. And the CIW PIA and CPA also ranged at a narrow range. All Na-type indices were relatively low for the 32 top soils (Fig. 2 and Table S2) compared to the UCC and PAAS. Relatively lower values of the Na-type indices indicated a weak degree of chemical weathering in the southern TP according to Nesbitt et al. (1997).

4.2 Sr-type indices in the top soils

Rb/Sr ratios varied significantly for the 114 top soils across the southern TP with the highest value observed in YF-3 in the southeastern Tibet and the lowest value in BH-9 in the northwestern Tibet (Fig. 3A and Table S3). The mean Rb/Sr value of the 114 top soils was 0.55 with the range from 0.11 to 4.28. The soils signature YF- and YP- located in the eastern study area always had the relatively big Rb/Sr ratios compared to the other soils (Fig. 3A). And for the BH- samples sited in the western study area they significantly had the lowest Rb/Sr ratio to all the soils and the Rb/Sr ratios in the TPE- and TPW- soils around Lhasa were relatively moderate. It found that with the increasing longitude the tendency of the increasing Rb/Sr ratios was showed significantly. Meanwhile for the collected 32 soil samples measured in the laboratory the Rb/Sr ratios also showed similar distribution pattern (Fig. 3B). The maximum Rb/Sr was recorded in the YF-2 located in the eastern Tibet and the minimum Rb/Sr was recorded in the BH-22 located in the western Tibet. And the other soils had the relatively moderate Rb/Sr value.

For the Sr/Ba ratios we calculated for selected 32 soil samples with the laboratory measurement. The Sr/Ba ratios ranged from 0.32 to 8.34 with the mean value of 1.33 (Fig. 3C). The two highest Sr/Ba ratio were recorded in TPW-43 and BH-22 with the value of 8.35 and 8.00 respectively (Fig. 3C). These two sites were in close all located around Bangong Co in the western Tibet. The lowest Sr/Ba value of 0.32 (Fig. 3C) was recorded in the YF-7 located in the eastern Tibet. It can be found that for the YF- YP- and some TPE- signatured samples located in the western Tibet recorded relatively lower Sr/Ba ratios compared to the BH- and TPW- signatured samples (Fig. 3C). The Sr/Ba ratios were relatively moderate in
the sampling sites almost around Lhasa. From the western to the eastern with the increasing longitude the value of Sr/Ba was increased apparently showing opposite to the Rb/Sr records.

5. Discussions

5.1 Low degree of chemical weathering of the top soils

In rock-forming minerals alkali and alkaline-earth cations such as Na K and Ca form strongly ionic bonds with oxygen that are long and weak. They are thus more easily broken and cations consequently released than transition elements and metalloids forming tighter bonds with more covalent character (Taylor and McLennan 1995). While Ca Na and K are removed from feldspars by aggressive soil solutions the proportion of aluminum to alkali and alkaline-earth metals increases progressively in the products of weathering.

An Al$_2$O$_3$-(CaO*+Na$_2$O)-K$_2$O (A-CN-K) ternary diagram based on the mass balance principle feldspar leaching experiments and the thermodynamic calculation of mineral stability has been used to predict the trend of continental chemical weathering and the alteration of mineralogical or geochemical components (Nesbitt and Young 1982). The extent of conversation of chemical proxies such as CIA which is 50 for unweathered feldspars and varies consequently from 50–65 for low chemical weathering to 65–75 for moderating chemical weathering and to 75–100 for strong chemical weathering (Nesbitt and Young 1982) (Fig. 4). However previous studies of weathering environments based on statistical analyses have suggested that CIA values of 50–65 65–80 and 85–100 indicate cold dry warm-humid and heat-damp conditions respectively (Selvaraj and Chen 2006).

The mean CIA for the top soils in the southern TP was calculated as 57 (mean value) with a range from 50 to 68 which indicated the primary stage of weathering and the chemical weathering environmental was a cold-dry climate with the UCC’s CIA value being 48 and the PAAS’s CIA value being 70 (Fig. 4). The result of low value of CIA is consistent with the results of geochemical investigations of river sediments in the eastern TP (Borges et al. 2008; Yang et al. 2004a). However the CIA value in 32 soil samples clustered in a narrow range with relatively low value mostly higher than the value of the Basalt rock and the Granite (Fig. 4; Buggle et al. 2011).

The distribution of the top soils on a ternary A-CN-K diagram revealed a cluster of points together with a distribution along a line parallel to the A-CN join (Fig. 4) suggesting that the weathering of the soils was close to a non-steady state condition (Nesbitt et al. 1997). The weathering line for the soil samples was very similar and can be drawn back to average UCC composition showing a UCC-like K$_2$O/(CaO*+Na$_2$O) ratio. The data points of the top soils were parallel to the axes of the A-CN line and were located between plagioclase and smectite. Variations in the K-feldspar or mica to plagioclase ration of the unweathered parent material would be revealed by a scatter of data points parallel to the CN-K axis (Buggle et al. 2011). The lower K$_2$O/ (CaO*+Na$_2$O) ratios and the distribution of the data points far away from the Al$_2$O$_3$ in Fig. 4 indicated that the products of weathering were smectite and plagioclase with no kaolinite. A
simple weathering trend was defined in A-CN-K diagram (red line in Fig. 4) which was subparallel to the A-CN boundary primarily because removal rates of Na and Ca from plagioclase generally were greater than the removal rate of K from K-feldspar (Liu et al. 1984; Nesbitt and Young 1984 1989; Nesbitt and Markovics 1997). In terms of the elemental geochemical signature the effect of decalcification and the removal of Na (dissolution of plagioclase) on the top soil was accompanied by the evolution of an Al enrichment. The chemical weathering of the southern TP according to the A-CN-K ternary plot was characterized by the carbonate control of the primary weathering stage under cold-dry climatic conditions and a transition between Ca and/or Na removal. This finding is consistent with the result of Sun et al. (2007) that the chemical weathering processes are relatively weak for the TP. Should the degree of weathering continue the samples are predicted to continue along the A-CN join until it reaches the A apex and Ca Na and K are completely removed.

5.2 Influence of climate on the Sr-type weathering indices for the top soils

According to the ITPCAS CMFD we collected the data of the MAT and MAP for the 114 soil sampling sites (Table S1). The MAP varied with a huge range for the study area. The maximum MAP of 1073.59 mm was recorded in the soil of YF-1 located in the eastern Tibet with the longitude of 97.03° and the latitude of 28.47° (Table S1) while the minimum MAP of 69.91 mm was recorded in the soil of TPW-27 located the South of Bangong Co in the western Tibet (Table S1). Also the MAT ranged in a relatively large range from −11.14°C to 18.13°C. The maximum value of MAT was also recorded in the YF-1 and the minimum value was recorded in BH-15 around Bangong Co in the western Tibet (Table S1). From Fig. 1 and the Table S1 in general the value of the MAT and MAP were all greater in the eastern Tibet than in the western. Mostly the MAP and MAT increased with the increasing longitude.

Sr is common in minerals such as plagioclase pyroxene amphibole and biotite which are susceptible to weathering (Liu et al. 1984; Nesbitt et al. 1980; Reeder et al. 2006). While regarding the choice of the immobile element ions of intermediate ionic potential i.e. ions that tend to from insoluble hydrolysated are generally employed. Rb and Ba can be immobilized by adsorption on clay minerals due to their large ionic radius are often used as immobile references. Therefore under intense weathering conditions the mobility of Sr is greater than Rb and Ba (Chen et al. 1996) and the Rb/Sr should be relatively higher and the Sr/Ba should be relatively lower.

From the distribution characteristics of the Sr-type indices in the top soils (Fig. 3) the relatively high Rb/Sr ratio and low Sr/Ba ratio found in the eastern Tibet suggested that the stronger chemical weathering occurred. And the relatively low Rb/Sr value and high Sr/Ba value in the western Tibet suggested that the relatively weak chemical weathering occurred (Fig. 3). For the soils around Lhasa the Sr-type indices value was relatively moderate indicated the central Tibet suffered the relatively moderate chemical weathering compared to the eastern and western sites. In general the soils in the eastern sites suffered the strongest chemical weathering. The chemical characteristic reflecting by the Sr-type indices looked like similar to the change of the MAT and MAP (Fig. 1) for the study area. Statistical analysis using SPSS
shows that the MAT and MAP were significantly correlated with the Sr-type indices \( r = 0.57 \) for Rb/Sr with \( n = 114 \ p < 0.05 \); \( r = 0.58 \) for Sr/Ba with \( n = 32 \ p < 0.05 \) (Fig. 5) suggesting an important influence of climate parameters on the intensity of chemical weathering. The well correlation suggested that the Sr-type indices could be used as the indicators of climate. Warm temperatures high precipitation as well as dense vegetation cover would result in a more acidified soil and a high content of organic ligands in the soil water (Stumm and Morgan 1996). This would promote removal of Sr from the soil. However Rb-rich minerals such as muscovite biotite and K-feldspar were more chemically stable than Sr-rich minerals such as carbonate plagioclase and amphibole (Goldich and Gast 1966). Therefore the mobility of Sr was greater than for Rb and Ba (Chen et al. 1996). This would explain the higher Rb/Sr and lower Sr/Ba ratios observed in the top soil in the eastern area.

The altitudes of the soil samples obtained in this study ranged from 1503 to 5262 m (Table S1) which showed slightly negative correlation with Rb/Sr ratios of top soils \( r = 0.43 \) (Fig.S1) indicating a moderate influence of altitude on the chemical weathering intensity. However the altitude co-varies with temperature and precipitation vegetation cover which would impose similar influence on the chemical weathering. But the Sr-type indices were more dependent on climate condition than on altitude (the correlation coefficient of altitude with the Sr-type indices was smaller than that of climate condition with the Sr-type indices). The collected top soils were formed in situ or deposit in the low-lying places with the parent materials from surrounding source rocks (Lin and Feng 2015). According to the Table S3 and Table 1 the Rb/Sr and Sr/Ba in soil samples with the different bedrock did have the very similar value under the similar MAT/MAP. For example in the TPW-29 and in TPW-37 with the bedrock of granite and limestone separately under the similar MAP the Sr-type indices had the similar values (Table S2) suggesting the parent rock may has little impact on the Sr-type indices. The value of Rb/Sr ratios were highly correlated between the 32 samples with the size < 200 mm measured by ICP-MS and the 114 bulk samples by portable XRF instrument in the field \( r = 1 \) indicating that for the study top soils the dependence for Sr-type indices on grain size was little.

5.3 Limited Influence Of Climate On The Na-type Indices

We calculated Na-type indices for 32 soils samples. The data of the MAP and the MAT with the 32 soils sites were also listed (Table S2). For the selected 32 soils the MAP ranged from 69.91 mm to 963.45 mm with the mean MAP value of 399.62 mm and the MAT ranged from – 9.02°C to 8.82°C with the MAT value of 1.36°C. The lowest MAP of 69.91 114.44 116.44 and 145.80 were recorded in the sample of TPE-27 TPW-37 TPW-29 and BH-22 located around Bangong Co in the western Tibet. The maximum MAP was recorded in the YF-2 located in the eastern Tibet. Also in the eastern Tibet the MAT value was higher than that in the western Tibet. According to the climate data we discussed in 4.2 the eastern Tibet was much more moisture and warmer than the western Tibet.

However Na-type indices including CIA CIW PIA and CPA clustered apparently in the 32 top soils for the study area (Fig. 2). They all had similar value according to 4.1. In the TP under the more warm and
moisture condition the Na-type indices did not show apparently much higher. There was no significant correlation between the Na-type indices and the MAT and MAP (at the 0.05 level) (Fig. 6) based on the correlation analyses suggesting that influence of climate on the variation of Na-type indices was limited. And therefore the Na-type indices could not be used as the indicators of the climate change for the study area. The limited influence of climate on the Na-type indices is consistent with observations on the bed-load sediments of large rivers originating from the TP (Borges et al. 2008). But the most of the other researches about the chemical weathering with catchment (Li and Yang 2010; Shao and Yang 2012) and top soils (Qiu et al. 2014) in China showed that the Na-type indices usually were controlled by the climate dominantly.

As discussed in 5.1 the distribution of the top soil samples on a ternary A-CN-K diagram (Fig. 4) showed that most soil samples on the southern TP fallen in an early stage of chemical weathering and the carbonate control was the primary weathering stage under cold-dry climatic conditions. As pointed by the investigation chemical weathering like CIA actually reflected the integrated weathering history rather than present weathering intensity (Li and Yang 2010). The carbonate control of the primary weathering stage of the TP led to the Sr and Ca usually bound in carbonates more sensitive to present climate change than Na and K because Na and K generally bound in silicates. This might be caused the poor relationship between the climate condition and the Na-type indices in the 32 sampling sites. This might interpret why Rb/Sr and Sr/Ba may have more positive correlations with temperature and rainfall. It had been suggested that if chemical weathering was limited the weathering products (i.e. the top soils) would inherit the elemental composition of the parent silicate materials according to the CIA and the A-CN-K ternary plot (Tripathi et al. 2007). As we did not collect bedrock for top soils we compiled values of Na$_2$O K$_2$O CaO and Al$_2$O$_3$ for different rocks on the southern TP from publications (Chen et al. 2011; Duan et al. 2005; Fan et al. 2014; Huang et al. 2005; Lai and Liu 2003; Li et al. 2008; Niu et al. 2006; Wang et al. 2013; Zhang et al. 2014; Zhou et al. 2008; Zhu et al. 2009). Then we calculated the Na-type indices for the complied data with the different rock types (Table S4 and Fig. S2). For the results the Na-type indices showed assemble each other with the different rocks for the different sites. Like that in granite rock and basalt rock the Na-type indices varied at the similar range and had the similar value. The variation of the Na-type indices had no significantly different with different rock types for the collected data in the southern TP (Fig. S2). According to the results it meant that for the Na-type indices in the southern TP the influence of the bedrock might be more dominant than the climate condition.

5. 4 Sr- And Na-type Indices At Lake Dongtaiji Nuoer

In order to further investigate whether Sr-type and Na-type indices would reflect climate changes in TP we measured elemental concentration and calculated all indices on a lacustrine sediment profile at Lake Dongtaiji Nuoer in the Qaidam Basin northeastern TP. The climate in the Qaidam Basin has the relatively similar characteristic of cold-dry with the Tibet and the geochemistry of the Qaidam Basin is influenced by the Tibet significantly. Chronological controls on the profile was established based on AMS $^{14}$C ages. The $^{14}$C age at 950 cm depth was 13830+/-50 year (16693 cal yr BP) indicating that most of the
sediment in the profile was accumulated during the Holocene. Since $^{14}$C measurements in saline lakes are affected by the reservoir effect (Hou et al. 2012) our comparison of the results with regional climatic records was tentative. We compared the Sr-type and Na-type indices in the stratigraphic variation with a regional climate record ratio of *Artemisia* to Chenopodiaceae (A/C) at Hurleg Lake in Qaidam Basin that reflects changes in the effective precipitation (Zhao et al. 2009) and the salinity minerals variety reflects the climatic change apparently in Chaka Lake (Liu et al. 2008).

Both Sr-type and Na-type indices exhibited significant variations at Lake Dongtaiji Nuoer (Fig. 7). Higher values of Rb/Sr occurred below 900 cm and above 180 cm and relatively lower Rb/Sr values were observed between 180 cm and 900 cm ($^{14}$C age of 5000–13830 BP) (Fig. 7). The variation of Rb/Sr ratios is generally consistent with A/C records at Hurleg Lake and the salinity minerals records in Chaka Lake. A/C ratios suggest that the climate is relatively dry and variable from 9.5 to 5.5 ka in the Qaidam Basin (Zhao et al. 2009) which was supported by more saline minerals in Chaka Lake during the same period (Liu et al. 2008). Lower Rb/Sr ratios from 9.5 to 5.5 ka at Lake Dongtaiji Nuoer showed relatively weak chemical weathering.

All Na-type indices showed similar variation in the lake sediment profile (Fig. 7). Higher values of the Na-type indices occurred at 0-250 cm (0-5517cal yr BP) and 450-650 cm (6522–7527 cal yr BP). Lower Na-type indices values were observed at 250–450 cm (5517–6522 cal yr BP) and 650–1135 cm (7527–23133 cal yr BP). Only in the upper profile (above 200 cm) were the variations of the Na-type indices consistent with the A/C ratio and the salinity minerals variety which suggested that climate influenced the Na-type indices. But below 200 cm no clear relationship was observed between Na-type indices and A/C records. For the whole sediment profile the consistence of the Na-type indices stratigraphic variation with the climate records did not show apparently.

In general the comparison between the Sr- Na-type indices and climate records in the Qaidam Basin suggested that the records of Sr-type indices would be better reflect the influence of climate change on chemical weathering which is consistent with the observation on the top soils. The Na-type indices probably could not be used as a reliable proxy of instantaneous chemical weathering with climate change (Li and Yang 2010; Shao and Yang 2012) for the sediment profile in Qaidam Basin. Because the Na-type indices usually used for reflecting the integrated chemical weathering processes for sediment (Li and Yang 2010; Shao and Yang 2012). However the difference between the two different chemical weathering indices should be further studied. Clearly therefore caution should be needed when using the Na-type indices as proxies for climate change.

6. Conclusions

We have analysed both Sr-type (Rb/Sr and Sr/Ba) and Na-type (CIA CIW PIA and CPA) indices on the top soils on the southern TP. Based on the results of the chemical indices and the A-CN-K ternary plot the southern TP is under the carbonate control of the primary chemical weathering stage under the cold-dry climate. The statistical analysis results show that the Sr-type indices are more sensitively respond to
mean annual temperature and annual precipitation. This suggests that Sr-type indices (Rb/Sr and Sr/Ba) would better reflect climate changes for the study area. Na-type indices may also reveal intensity of chemical weathering however which seems less sensitive to climate change. The comparison of Holocene records in the Qaidam Basin of Sr- and Na-type indices and climate changes strongly agree with the observation on the top soils. The different performance of the Na-type and Sr-type indices with the climate condition in the TP should also be further studied in the future.

Declarations

Availability of data and materials

All data generated or analysed during this study are included in this published article and its supplementary information files.

Competing interests

The authors declare no competing non-financial/financial interests.

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Authors' contributions

San Feixue sampled the soils and performed the experiment, and also took some analysis of data.

Hou Juzhi helped perform the analysis with constructive discussions and revised the manuscript critically.

Yang Xiaoyan performed the data analyses and wrote the manuscript, and gave final approval of the version to be submitted and any revised version.

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