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## pH: A core node of interaction networks among soil organo-mineral fractions

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### ARTICLE INFO

Handling Editor: Adrian Covaci

#### Keywords:

Alpine ecosystems  
Major metal cations  
Sequential chemical extraction  
Network  
pH  
Precipitation

### ABSTRACT

Mineral-associated organic matter (MAOM) is the largest soil organic carbon (OC) pool with the longest turnover. MAOM is expected to have relatively little sensitivity to climate change due to mineral protection, but its persistence involves several organo-mineral fractions. The uncertainty in the response of specific organo-mineral fractions to climate change hampers the reliability of predictions of MAOM preservation in the future. Here, we applied a sequential chemical fractionation method integrated with network analysis to investigate MAOM stabilization mechanisms across five alpine ecosystems: alpine desert, alpine steppe, alpine meadow, alpine wetland, and alpine forest. Hierarchical cluster analysis revealed grouping of seven extractable OM fractions in MAOM into three OM clusters: a cluster with weak bondings consisting of water-soluble OM (WSOM) and weakly adsorbed fractions (2.1–21.3% of total OC); a cluster with metal-bound complexes comprising Ca-OM complexes and Fe/Al-OM complexes (3.8–12.2% of total OC); and a cluster with strong bonding composed of Al oxyhydroxides, carbonates and Fe oxyhydroxides (12.2–33.5% of total OC). The relative percentages of OM from soils of the five ecosystems in the three clusters exhibited distinct pH dependence patterns. With the increase in pH, the cluster with weak bondings decreased, and that with strong bondings increased, while the one with metal-bound complexes showed a maximum at weakly acidic pH. Organo-mineral fractions and metal cations in MAOM constructed a complex network with pH as the central node. Results suggest that precipitation does not only alter vegetation type and microbial biomass but also regulate soil pH, which is balanced by specific metal cations, thus resulting in particular pH preference of specific OM clusters. These findings demonstrate that soil pH plays a central role in unveiling MAOM dynamics and can serve as a good predictor of soil organo-mineral fractions across alpine ecosystems.

### 1. Introduction

Mineral-associated organic matter (MAOM) is mainly preserved through close association with active minerals and thus has mean residence times on the order of decades to centuries (Lavallee et al., 2020; Lugato et al., 2021; von Lütow et al., 2007). Due to mineral protection, MAOM might also have relatively low vulnerability to environmental disturbance and climate change (Rocci et al., 2021; Tang and Riley,

2015). However, the persistence of MAOM involves multiple organo-mineral fractions, including those that are weakly linked by hydrogen bonding, van der Waals forces, hydrophobic interaction and cation exchange, and strong associations including metal-bound complexes via co-precipitation and organic matter (OM) bound to mineral surfaces via ligand-exchange (Kleber et al., 2015; Singh et al., 2018). Despite these complex organo-mineral fractions, lack of research on the climate sensitivity of different organo-mineral fractions hinders the prediction

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<https://doi.org/10.1016/j.envint.2023.108058>

Received 30 March 2023; Received in revised form 8 June 2023; Accepted 20 June 2023

Available online 25 June 2023

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of MAOM stabilization. Moreover, the relative importance of each organo-mineral fraction to OM persistence by MAOM formation remains unclear (Giannetta et al., 2019; Lopez-Sangil and Rovira, 2013). Inadequate knowledge of the stabilization mechanisms of MAOM limits the accurate implementation of OM sequestration strategies in the future (Bradford et al., 2016; Luo et al., 2016).

The relative importance of different organo-mineral fractions was traditionally thought to depend on soil physicochemical properties such as pH, cation concentrations and soil moisture, which are closely linked to climate, vegetation type and soil weathering degree (Afsar et al., 2020; de Junet et al., 2013; Rowley et al., 2017; Singh et al., 2018). Among these properties, pH, as an index of the overall chemical state of the soil system, exhibits dominant control on the speciation of dissolved metals and the reactivity of mineral-organic molecules (Deng and Dixon, 2002; Rasmussen et al., 2018).

Hence, as an easily measurable and comprehensive indicator reflecting the interactions between inorganic cations, minerals and OM in soils, we hypothesize that pH might serve as a good predictor of the different organo-mineral fractions in MAOM. Different organo-mineral fractions might change nonlinearly with soil pH, showing distinct distribution patterns driven by thresholds in aqueous speciation and mineral stability. To test this hypothesis, soils with a wide pH range across five typical alpine ecosystems on the Tibetan Plateau, i.e., alpine desert (AD), alpine steppe (AS), alpine meadow (AM), alpine wetland (AW) and alpine forest (AF), were selected. As the largest and highest middle-low-latitude alpine region on Earth, the Tibetan Plateau stores a large amount of OM and currently plays an important role in the terrestrial ecosystem carbon cycles (Ding et al., 2017; Ehlers et al., 2022; Zhang et al., 2015; Zhisheng et al., 2001). Moreover, the Tibetan Plateau is more sensitive to climate change than lower elevation regions (Liu and Chen, 2000; Wang et al., 2008), making it highly valuable for studying the response of different organo-mineral fractions in MAOM to climate change.

To examine specific organo-mineral fractions in MAOM across different ecosystems, we applied sequential chemical extraction approaches to (1) quantify the relative importance of different kinds of organo-mineral fractions for MAOM preservation, (2) disentangle the contribution of metal cations to specific organo-mineral fractions, and (3) identify key factors influencing the distribution of organo-mineral fractions.

## 2. Materials and methods

### 2.1. Site description, soil sampling and environmental properties

In this study, five typical alpine ecosystems on the Tibetan Plateau (29°36'N–32°22'N, 80°24'E–94°36'E) along a climatic gradient were compared: alpine desert (AD), alpine steppe (AS), alpine meadow (AM),

alpine wetland (AW) and alpine forest (AF). These locations ranged from 4310 to 4900 m above sea level, with a mean annual temperature (MAT) from −3.0 to 3.7 °C and a mean annual precipitation (MAP) between 134 and 848 mm (Table 1). The typical vegetation includes as major plants in AD *Kobresia humilis* and *Lithospermum erythrorhizon*, in AS *Kobresia macrantha* and *Stipa purpurea*, in AM *Kobresia humilis* and *Stipa capillacea*, in AW *Kobresia tibetica* and *Kobresia pygmaea*, and in AF *Abies georgei*.

According to the World Reference Base for Soil Resources (WRB, 2015), the soil types of AD, AS, AM, AW and AF ecosystem are Arenosols, Calcisols, Cambisols, Gleysols and Luvisols, respectively. For the present study, a set of topsoil samples (0–15 cm) from the five alpine ecosystems were selected. Considering the of spatial heterogeneity of different ecosystems, we adopted inconsistent sampling sizes in different alpine ecosystems. Three replicate 10 × 10 m quadrats and 5 × 5 m quadrats were established at each site in the AF and AD ecosystem, respectively (Chen et al., 2019). And three replicate 1 × 1 m quadrats were established at each site in the other alpine ecosystems. We recorded the density, coverage and height of plant species within each quadrat to estimate the aboveground biomass (AGB). In the AG ecosystem AGB was calculated by establishing the regression models of species biomass and species volume (Wang et al., 2013), while in AF AGB is expressed by the weight of litter per unit area. In each quadrat, five core samples (15 cm length) with a diameter of 5 cm were collected along the two diagonals of the quadrat and then mixed to obtain a composite sample. The soil samples were kept at field moisture in a car refrigerator until taken to the laboratory, then were sieved (2 mm) and divided into two aliquots: one part was air-dried for the following sequential chemical extraction experiment and physicochemical analysis, and the other part was stored at −80 °C for future soil microbial analysis.

### 2.2. Measurement of soil environmental properties

Soil moisture was calculated by weight loss after heating 5 g fresh soil samples at 105 °C in an oven for 12 h. Soil pH was measured in a 1:2.5 mixture of fully air-dried soil and deionized water by a Sartorius PB-10 digital pH meter. Microbial phospholipid fatty acids (PLFA) as obtained by a modified Bligh-Dyer method was used to measure microbial biomass (Hill et al., 2000). Organic carbon (OC) was quantified using a total organic carbon (TOC) analyser (TOC-VCPH, Shimadzu, Japan), and total nitrogen (TN) was determined using a modified Kjeldahl method (Bremner, 1960).

### 2.3. Sequential chemical extraction of soils

The separation of different MAOM fractions was based on the sequential chemical extraction introduced by Lopez-Sangil and Rovira

**Table 1**

Characteristics of the study sites in the five alpine ecosystems on the Tibetan Plateau and basic soil physicochemical properties. Different lowercase letters (a, b and c) indicate significant differences ( $P < 0.05$ ) of soil physicochemical properties in different ecosystems based on ANOVA analysis.

Ecosystem	Location	Altitude (m)	MAT (°C)	MAP (mm)	Soil Moisture (%)	pH	AGB (g/m <sup>2</sup> (-))	PLFA (nmol/g)	OC(%)	TN(%)	C/N ratio
Alpine desert (AD)	32°22'N, 80°24'E	4532	−2.95	134	1.99 ± 0.27c	8.32 ± 0.12 a	44.91 ± 7.68b	11.35 ± 6.33b	0.97 ± 0.12b	0.09 ± 0.02b	11.25 ± 0.73b
Alpine steppe (AS)	30°46'N, 90°59'E	4400	3.7	227	6.83 ± 4.35 bc	6.91 ± 0.45 ab	114.15 ± 8.93 ab	28.34 ± 7.94 ab	2.37 ± 0.73 ab	0.22 ± 0.05 ab	10.27 ± 1.08b
Alpine wetland (AW)	30°34'N, 91°06'E	4500	3.26	211	86.68 ± 12.81 a	7.18 ± 0.36 ab	397.07 ± 52.84 ab	70.14 ± 16.41 ab	8.37 ± 1.89 a	0.58 ± 0.14 a	14.74 ± 1.28b
Alpine meadow (AM)	30°31'N, 91°03'E	4900	0.3	434	18.61 ± 1.80 bc	5.35 ± 0.10 ab	216.67 ± 54.70 ab	105.20 ± 12.76 ab	4.51 ± 0.16 ab	0.33 ± 0.02 ab	13.84 ± 0.96b
Alpine forest (AF)	29°36'N, 94°36'E	4310	−0.09	848	39.82 ± 1.23b	4.03 ± 0.03b	586.30 ± 52.33* a	129.61 ± 13.14 a	10.73 ± 0.29 a	0.27 ± 0.01 ab	40.75 ± 2.59 a

Note. MAT, mean annual air temperature; MAP, mean annual precipitation; AGB, aboveground biomass; PLFA, Phospholipid fatty acids, as microbial biomass index; OC, organic carbon; TN, total nitrogen; C/N, ratio of organic carbon to total nitrogen.

\*Litter.

(2013) and was combined with the method of (Cui et al., 2014; Lopez-Sangil and Rovira, 2013). The fractionation scheme of soil organic matter (SOM) is depicted in Fig. 1 and included the fractions:

**Water-soluble OM (WSOM):** Deionized water ( $H_2O$ ) was used to extract water-soluble organic compounds, which are readily accessible for microbial decomposition.

**Weakly adsorbed OM:** 0.1 M sodium tetraborate ( $Na_2B_4O_7$ ) buffer at pH 9.7 was used to extract organic compounds adsorbed to mineral surfaces by weak bonds such as van der Waals interaction or outer-sphere complexation (Bruckert, 1979; Greenland, 1971).

**Ca-OM complexes:** 0.5 M sodium sulfate ( $Na_2SO_4$ ) buffer at pH 7 was used to extract organic compounds that co-precipitated with Ca and Mg cations (Jones and Willett, 2006; Xu and Yuan, 1993).

**Fe/Al-OM complexes:** 0.1 M sodium pyrophosphate ( $Na_2P_2O_7$ ) buffer at pH 10.2 was used to extract organic compounds that were co-precipitated with Fe and Al cations. Sodium pyrophosphate extraction is quite specific because it does not affect amorphous or crystalline Fe and Al oxyhydroxides (McKeague, 1967).

**Residual particulate organic matter (POM):** Residues that were isolated by flotation in sodium iodide (NaI) solution ( $\rho = 1.6 \text{ g cm}^{-3}$ ). The residual heavy fraction ( $\rho > 1.6 \text{ g cm}^{-3}$ ) was used for subsequent extraction.

**Al oxyhydroxides-stabilized OM:** 0.1 M sodium hydroxide (NaOH) buffer at pH 12.0 was used to extract organic compounds strongly linked to Al oxyhydroxides. Traditional extraction with sodium hydroxide was considered given its powerful extractive properties. The large amount of  $Al^{3+}$  extracted in this fraction may be due to the high dissolution of Al

oxyhydroxides caused by NaOH (Heckman et al., 2018; Yvanes-Giuliani et al., 2014).

**Carbonate-occluded OM:** 0.1 M hydrochloric acid (HCl) and further extraction with 0.1 M NaOH were used to extract organic compounds that is occluded by carbonate coatings in calcareous soils (Hass and Fine, 2010). However, in acid soils lacking carbonates, the implementation of this step (low and high pH) may cause more mobilization of amorphous Fe and Al oxyhydroxides (Coward et al., 2017; Yvanes-Giuliani et al., 2014).

**Fe oxyhydroxides-stabilized OM:** 0.1 M sodium dithionite ( $Na_2S_2O_4$ ) buffer at pH 8.0 and further extraction with 0.1 M NaOH were used to extract organic molecules stabilized by Fe oxyhydroxides. Sodium dithionite as well-known reagent for reducing Fe in both amorphous and crystalline oxyhydroxides, hence can solubilise the organic compounds stabilized by them (Coward et al., 2017; Zou et al., 2018).

**Residual OM:** OM remaining after all previous steps was dried and burned in a muffle oven at  $550 \text{ }^\circ\text{C}$  for 4 h (Heiri et al., 2001), followed by extraction with 0.1 M hydrochloric acid to extract the released metal cations (Ruttenberg et al., 2009). Its strong insolubility maybe due to be bound in interlayers of clay minerals (Giannetta et al., 2019).

As compared to previous studies, we performed some modifications on the sequence extraction steps and reagents. The reagents containing organic compounds (e.g., oxalate and citrate) used to release metal cations from soil are not appropriate for measuring the OC liberated after mineral dissolution (Heckman et al., 2018). For the extraction of carbonate, we used 0.1 M hydrochloric acid instead of acetate, sulfuric acid to minimize the damage to other minerals (von Lützow et al., 2007).

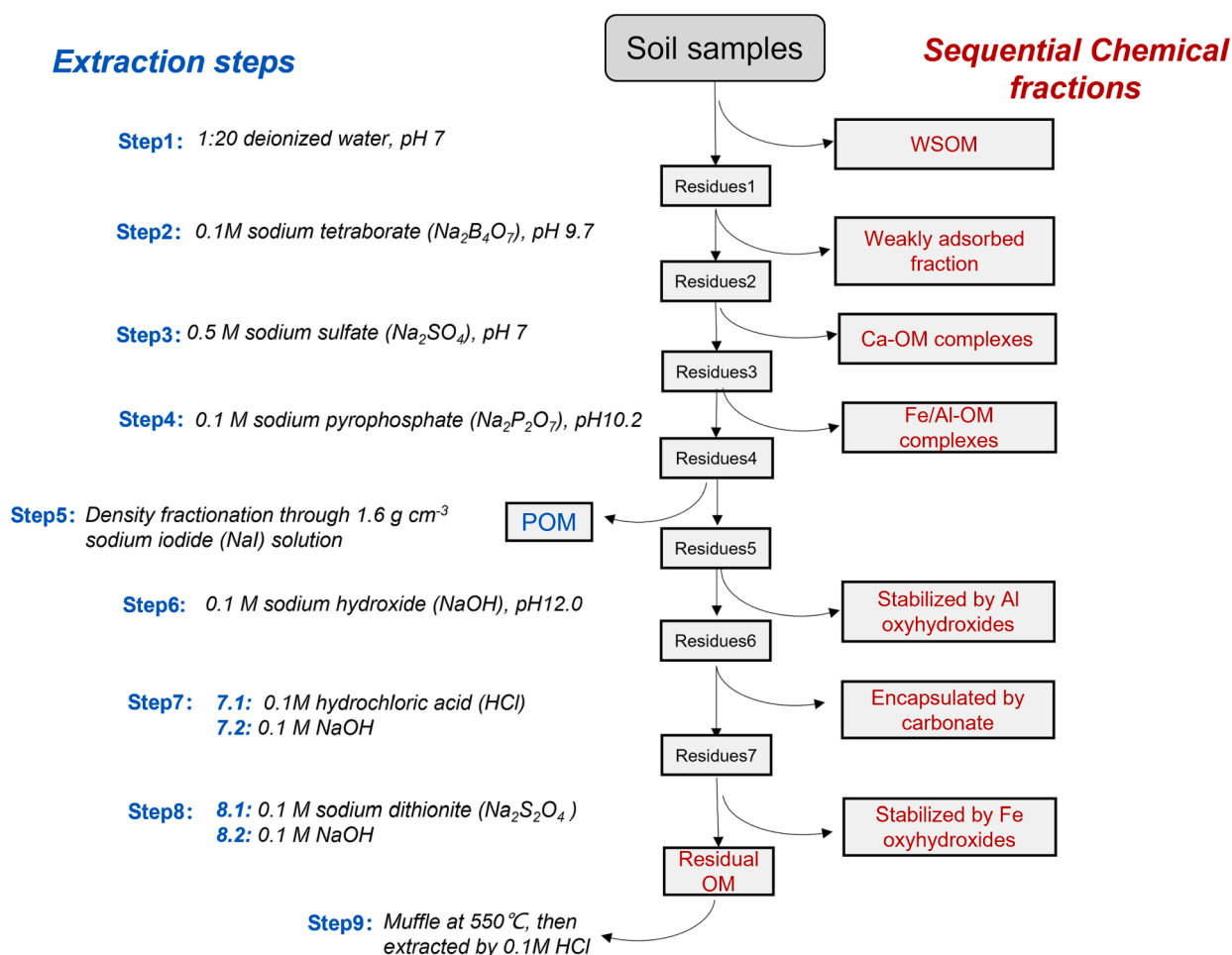


Fig. 1. Flow diagram of the soil organic matter (SOM) fractionation method. The sequential extraction was modified based on Lopez-Sangil's method (Lopez-Sangil and Rovira, 2013).

Hence, we selectively used inorganic reagents to conduct sequential chemical extraction. Previous studies have shown that alpine ecosystem soils contain a large proportion of particulate organic matter (POM) fractions, which are composed of partially or completely humified plant and fungal hyphal residues (Alvarez et al., 1998; Budge et al., 2011; Chen et al., 2019). The fractionation of POM was implemented in step 5 instead of step 1 to reduce the extraction error of the NaI solution for the water-soluble, weakly adsorbed OM and organic-metal complex fractions (Plaza et al., 2019). In contrast to previous methods, we added steps for the extraction of the WSOM and OM associated with Ca complexes (Jones and Willett, 2006; Xu and Yuan, 1993). Ca-OM complexes was added to distinguish the roles of Ca and of Fe and Al in metal-bound OM complexes, especially for soils rich in carbonates.

The extraction process to receive the eight fractions was as follows: four g of sample was placed in a 50 mL centrifuge tube, and chemical reagent (soil-reagent ratio 1:10) was added. Then, the 50 mL centrifuge tubes were placed on a horizontal shaker (160 rpm) for 16 h (overnight). The tubes were placed in a centrifuge (3300g for 15 min), and the supernatant was transferred into new 200 mL vials. This cycle was repeated two or three times, with only one hour of shaking instead of overnight shaking. Each extraction step was repeated two to three times, and then the sample was washed with deionized water until the solution was colourless. To minimize organic matter and metal cation loss during extraction, the supernatants and wash solution were combined and fixed to an exact volume (usually 150 mL, according to the number of extractions). Finally, the extraction solutions were stored in a 4 °C refrigerator for subsequent analysis.

#### 2.4. Analysis of organic C in chemical fractions

The dissolved OC obtained by sequential chemical extraction was analysed through colorimetry at 585 nm by dichromate oxidation (Nelson and Sommers, 1996), in which 20 mL of extract, 5 mL of 0.27 M potassium dichromate, 0.1 g of mercuric sulfate and 5 mL of sulfuric acid were successively added to a digestion tube and digested at 180 °C for 10 min. The digested samples were treated with sodium salicylate and sodium dichloroisocyanurate and were then measured using ultraviolet spectrophotometry. The OC of the extract in step 7 (hydrochloric acid)

and step 8 (sodium dithionite) was analysed by a liquid total organic carbon (TOC) analyser (TOC-VCPH, Shimadzu, Japan) because hydrochloric acid and dithionite might interfere with dichromate oxidation. In each of the steps 7–8, two consecutive extracts were obtained, and OC were measured separately for each extract. Here we considered both extracts together, for it is the sum of both extracts what covers the whole OC, which became soluble after the dissolution of sorption partners (carbonates, Fe oxyhydroxides) by pre-treatment (Fig. 2) (Giannetta et al., 2019).

#### 2.5. Cation contents within chemical fractions

The concentrations of cations (including Ca, Mg, Fe, and Al) of all sequential chemical extracts were measured by inductively coupled plasma optical emission spectroscopy (ICP–OES, Thermo Fisher Scientific, iCAP 7200, Waltham, USA). Before measurement, 15 mL of each extract was digested at 95 °C with 1 mL of 65% nitric acid and 3 mL of 30% hydrogen peroxide to oxidize the OM in the extracts (completion of the reaction was indicated by the extract becoming colourless). The cation concentrations of all extracts were presented in mol/g soil dry weight (dw) (Fig. S1).

#### 2.6. Statistical analysis

One-way analysis of variance (ANOVA) was used to assess the differences of soil physicochemical properties in different ecosystems. Principal coordinate analysis (pCoA) was used to compare the composition of metal cations in the sequentially chemically extracted fractions from the five alpine ecosystems through R package ‘vegan’. Spearman’s correlation and hierarchical cluster analyses were performed to study the interactions among chemical OM fractions and the correlations among environmental variables through R package ‘Corrplot’ and ‘factextra’, respectively. The Mantel test was performed to show the relationship between MAOM fractions and environmental variables through R package ‘linkET’. Linear and quadratic regression analyses were conducted to determine the relationship between specific OM clusters and pH through R package ‘ggplot2’. Ternary plots of all alpine ecosystems based on the three specific OM clusters were prepared to

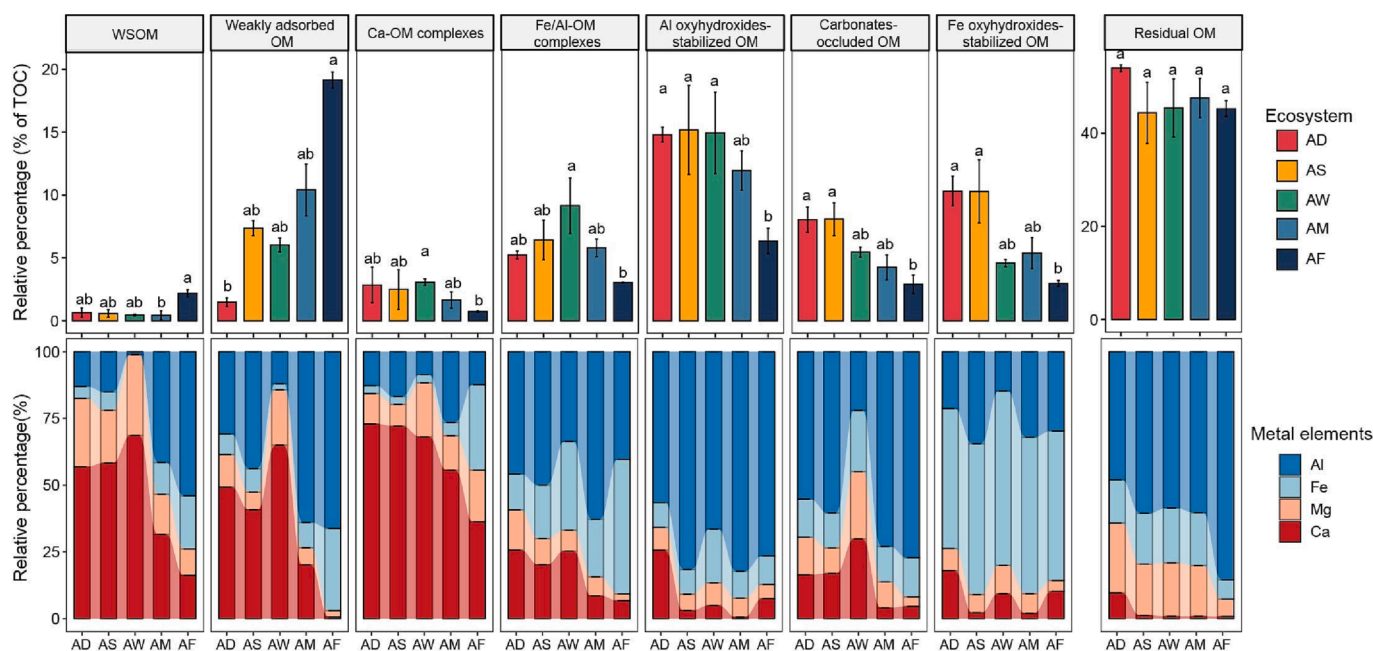


Fig. 2. Relative percentage of total organic carbon (TOC) and major metals (Ca, Mg, Fe, Al) recovered by sequential chemical extractions of soil organic matter (SOM) in different alpine ecosystems. AD, alpine desert; AS, alpine steppe; AW, alpine wetland; AM, alpine meadow; AF, alpine forest; WSOM, water-soluble organic matter. Different lowercase letters (a and b) indicate significant differences ( $P < 0.05$ ) of OC in different ecosystems based on ANOVA analysis.

represent the pH preferences of the OM clusters through R package 'ggtern'. Network analyses based on correlation coefficients were used to investigate the statistical relationships between the chemical fractions to verify the physical relationships among them through R package 'igraph' (Barberan et al., 2012; Delgado-Baquerizo et al., 2018). All analyses were carried out in R software 4.2.0.

### 3. Results

#### 3.1. Distribution of OC and main metal cations in the sequential extracts

The environmental properties of the different alpine ecosystems are summarized in Table 1. Soil moisture content gradually increased from AD (2%) to AF (40%), except AW which had the highest moisture content (87%) in mid-August. The pH values in the five alpine ecosystem soils spanned a wide range. Soils at AF and AM were acidic with pH values of 4.03 and 5.35, respectively, soils at AS and AW had nearly neutral pH values of 6.91 and 7.30, respectively, and AD had alkaline pH values of 8.32. Soil OC contents basically followed an increasing trend from AD (9.7 mg g<sup>-1</sup> soil dw) to AF (107.3 mg g<sup>-1</sup> soil dw), while AW also had high OC contents (83.7 mg g<sup>-1</sup> soil dw). Soils at AW had the highest TN content (5.8 mg g<sup>-1</sup> soil dw) and at AD had the lowest (9.0 mg g<sup>-1</sup> soil dw). The C/N ratio of the AF soil was significantly higher than that of the other alpine ecosystem soils.

The relative OC contents of the different chemical fractions in MAOM is shown in Fig. 2. Residual OM represented the highest proportion of OC (44.4–53.9%). The weakly adsorbed OM and Al oxyhydroxides-stabilized OM accounted for a substantial proportion of OC (1.5–19.2% and 6.3–15.2% of OC, respectively). Fe oxyhydroxides-stabilized OM, carbonates-occluded OM and Fe/Al-OM complexes also occupied a certain proportion of OC (3.0–10.3%, 2.9–8.1% 3.0–9.1% of OC, respectively). And the relative proportion of Ca-OM complexes and WSOM was the lowest (0.7–3.1% and 0.4–2.2% of OC, respectively). When comparing the distribution patterns of OM fractions across different alpine ecosystems, we found that the OC proportions of WSOM and weakly adsorbed OM were higher in acidic soils than in the others. In contrast, the OC proportions associated with Al oxyhydroxides, Fe oxyhydroxides and carbonates increased with pH, showing 33.2–33.5% of OC in alkaline soils as compared to 12.2–21.6% of OC in acidic soils. The percentage of OC in Fe/Al-OM complexes and Ca-OM complexes was lower in acidic and alkaline soils than in neutral soils, and the

proportion of OC in residual OM was slightly higher in alkaline soils than in neutral and acidic soils.

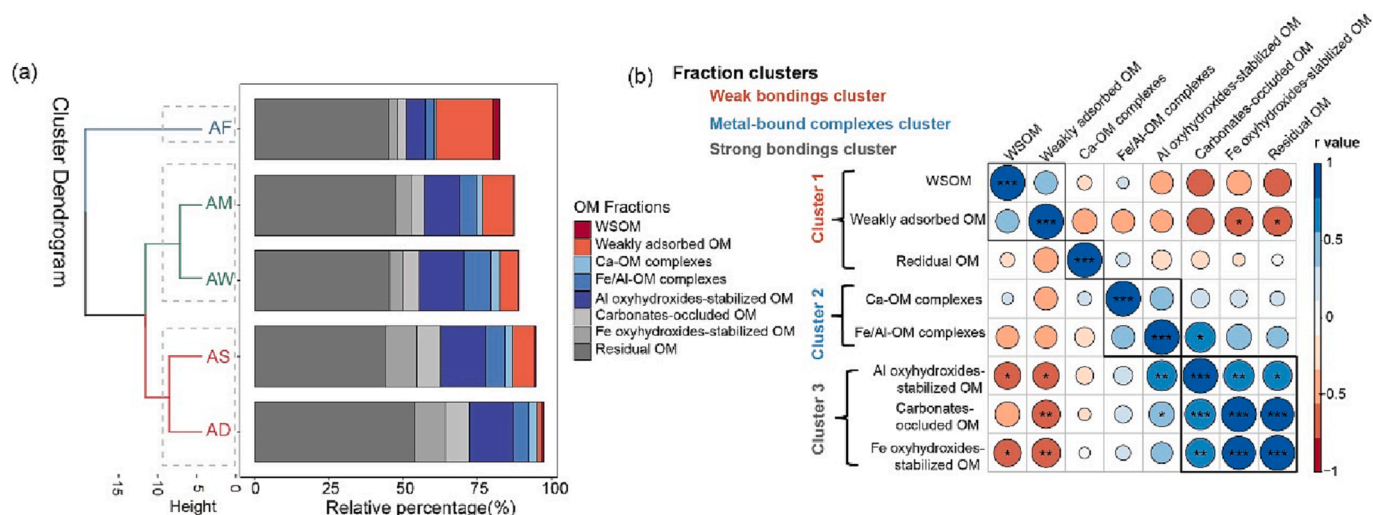
Concerning the major metal cations released upon the sequential chemical extraction, we found the metal assemblages of WSOM and weakly adsorbed fractions exhibited opposite patterns in soils with different pH values (Fig. 2). The proportion of Ca and Mg was higher in alkaline and neutral AD, AS and AW soils (47.4–98.8%), but in contrast Fe and Al accounted for the largest proportion in the acidic AM and AF soil, (53.4–97.0%). In terms of fractions, Ca and Mg played dominant roles in the fraction with Ca-OM complexes of all soils (79.3–88.4%). While in the other fractions, Fe and Al accounted for the highest proportion. Specifically, the proportion of Fe and Al was highest in the Fe/Al-OM complexes, (59.3–90.7%). In the fraction with Al oxyhydroxides, Al had the highest proportion (65.8–92.3%). In the fraction occluded by carbonates, Fe and Al had high proportion in all soils (44.8–91.9%). With respect to the fraction with Fe oxyhydroxides, Fe contributed the most in all soils (52.4–65.3%). Among the elements released during the burning of the residual OM, Al occupied the highest proportion in all soils (48.0–85.5%).

#### 3.2. Characteristics and relationships of OM in chemical fractions

To differentiate OM fractions among alpine ecosystems, hierarchical cluster analysis was conducted (Fig. 3a). The composition of OM fractions in different ecosystems followed the three pH groups; alkaline and neutral soils represented by AD and AS ecosystems, neutral and slightly acidic soils including AW and AM ecosystems, and acidic soils from the AF ecosystem. A hierarchical cluster analysis on the relationships among different OM fractions revealed that the OM fractions can be clustered into three groups (Fig. 3b). The first group defines OM with weakly associated metal phases represented by WSOM and weakly adsorbed OM, the second group is characterized by metal-bound OM complexes including the Ca-OM and Fe/Al-OM complexes, while the third group defines OM stabilized by Al oxyhydroxides, carbonates, and Fe oxyhydroxides.

#### 3.3. Characteristics of metal cations in chemical fractions

To further explore the relationship between the main metal cations and specific OM fractions, pCoA was used to show the characteristics of metal cations in different chemical fractions and ecosystems. First, the



**Fig. 3.** (a) Cluster diagram of the five alpine ecosystem soils based on a hierarchical cluster analysis of the results of the sequential OM extraction. (b) Cluster analysis of different MAOM fractions based on Spearman's correlation of MAOM fractions AD, alpine desert; AS, alpine steppe; AW, alpine wetland; AM, alpine meadow; and AF, alpine forest; WSOM, water-soluble organic matter. Classification of acidity and alkalinity of soils was represented by different colours, red indicate alkaline soils, green indicate neutral-acidic soils, blue indicate acidic soils. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

difference in the composition of major metal cations among alpine ecosystems was compared (Fig. 4a). The first two principal component axes explained 78.67% (PC1 62.28%, PC2 14.39%) of the variability in the metal composition among the alpine ecosystems, and the metal cation composition in different alpine ecosystem soils was distinctly separated from each other. Second, we compared the differences in metal cations in the chemical fractions (Fig. 4b). The first two principal component axes explained 83.15% (PC1 57.81%, PC2 25.34%) of the variability in the metal composition in the chemical fractions. The metal cation composition in most OM fractions was also significantly separated from each other, except that strongly adsorbed fraction and residual OM were indistinguishable, and WSOM and weakly adsorbed fraction were similar.

### 3.4. Relationship between OM in chemical fractions and environmental properties

We identified key factors that influenced the distribution of specific OM fractions. The Mantel test indicated that OC release from the different chemical fractions was most strongly correlated with pH, MAP, AGB and PLFA ( $p < 0.01$ ), and soil pH was negatively correlated with MAP, AGB and PLFA ( $p < 0.001$ , Fig. 5a). A ternary plot of all alpine ecosystems plotted based on the three main MAOM clusters showed that the cluster with weak linkages was relatively enriched in acidic AF soils, while the cluster of metal-bound complexes was relatively enriched in neutral AW soils, and the cluster with strong linkages with minerals was more obvious in AD and AS soils (Fig. 5b). Consequently, the response pattern of the main OM clusters along the pH gradient further revealed that the cluster with weak bondings decreased with increasing pH, the cluster with strong bondings increased, while the one with metal-bound complexes showed a maximum at weakly acidic pH (Fig. 5c).

## 4. Discussion

### 4.1. The roles of metal cations in specific OM clusters

Multivalent metal cations such as Ca, Mg, Fe and Al can enhance OM stabilization through adsorption of OM to mineral surfaces or co-precipitation by forming insoluble complexes with OM (Rasmussen et al., 2018; Rowley et al., 2017). In the WSOM and weakly adsorbed fraction, the highest proportion of  $\text{Ca}^{2+}$  in the AD, AS and AW soils

(Fig. 2) indicate in neutral to alkaline soils, high  $\text{Ca}^{2+}$  concentrations might react with negatively charged OM (Barreto et al., 2021; Rowley et al., 2017). In acidic soils, rather dissolved  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  (depending on redox potential and pH) enter the soil solution and may react with OM (Kleber et al., 2015; Rasmussen et al., 2018; Singh et al., 2018). For the metal-bound OM complexes, the metal cations in Ca-OM complexes extracted by sodium sulfate were mainly dominated by  $\text{Ca}^{2+}$  in all ecosystem soils, while  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  played a major role in Fe/Al-OM complexes, and the OM extracted by sodium hydroxide (NaOH), showed a close relationship with Al (Fig. 2).

Organic matter extracted by NaOH might be closely related to amorphous Al oxyhydroxides (Ross et al., 2008; Skyllberg, 1999). For the OM occluded by carbonate coatings (Lopez-Sangil and Rovira, 2013), our data showed that  $\text{Ca}^{2+}$  in this fraction was higher in alkaline to neutral soils than in acidic soils, suggesting that this extract can partly represent OM protected by carbonates in alkaline to neutral soils (Fig. 2). Moreover, in all ecosystems, especially in the forest soils,  $\text{Al}^{3+}$  contributed the most to this fraction. A previous sequential extraction experiment proved that HCl can destroy amorphous Fe and Al oxides (Coward et al., 2017; Fox et al., 2017; Hass and Fine, 2010), implying that the OM released in the fraction belong to the OM protected by amorphous Fe and Al oxides in acidic soils.

The high percentage of Fe in the dithionite extract in all ecosystem soils demonstrated that indeed crystalline Fe oxyhydroxides played a key role in this fraction, but their contribution to SOM in acidic AF soils was low due to their relatively low specific surface area (Heckman et al., 2018). Finally, we found that Al occupied the highest proportion in the residual OM, implying that clay minerals related to Al are important for the preservation of the residual OM (Singh et al., 2018).

### 4.2. Specific OM clusters and their environmental preferences

Mantel analysis between OM and relevant environmental properties showed that the MAOM composition in alpine ecosystems was most significantly related to pH ( $p < 0.01$ , Fig. 5a), implying that pH might be a significant predictor of organo-mineral fractions in MAOM. Based on the hierarchical cluster analysis of OM fractions (Fig. 3a). A ternary plot of the five ecosystem soils based on the three OM clusters indicated that specific OM clusters were closely associated with pH (Fig. 5b). Specifically, we found that the OM cluster with weak bondings showed a preference to acidic soils, the OM cluster with metal-bound complexes

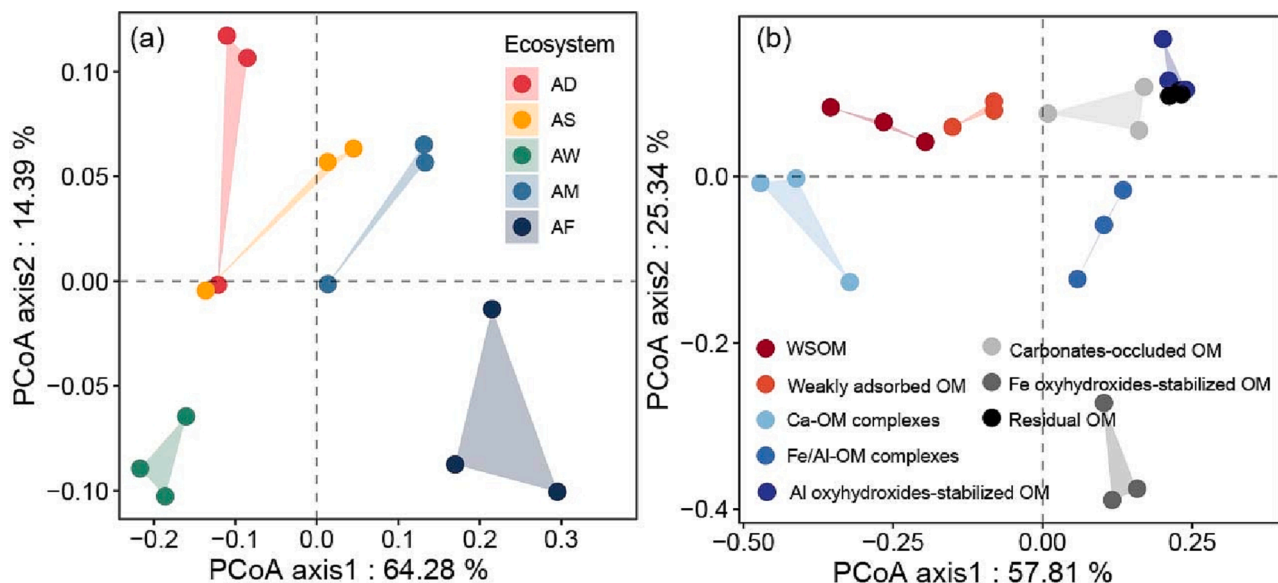
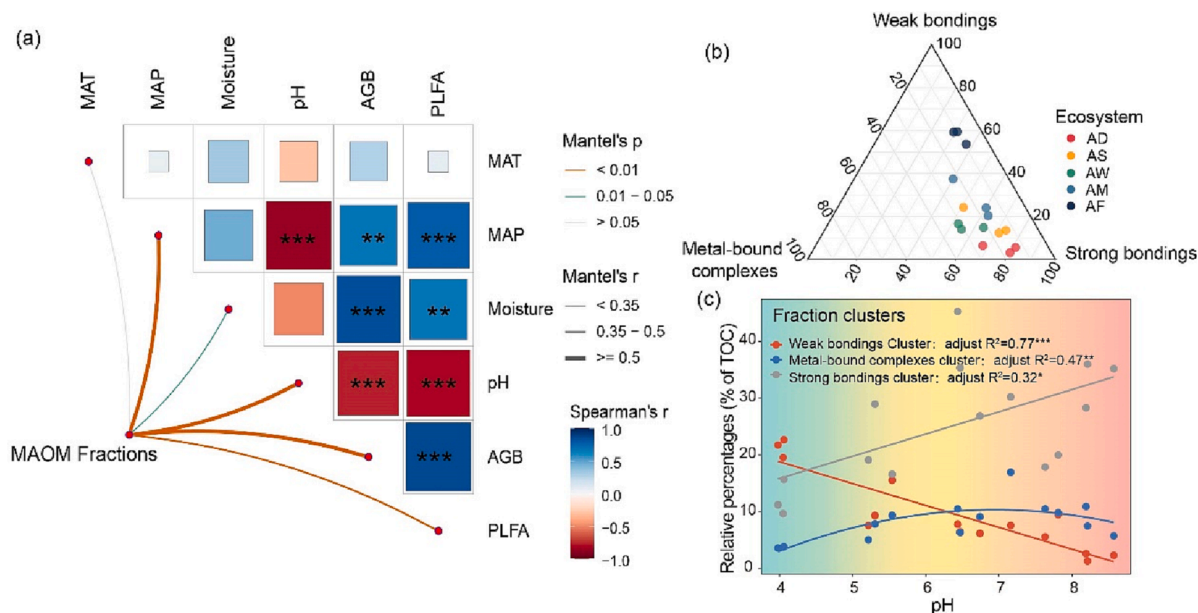


Fig. 4. Principal coordinate analysis (PCoA) plot of the main metal cation composition in the five alpine ecosystem soils (a) and in the different OM fractions (b). AD, alpine desert; AS, alpine steppe; AW, alpine wetland; AM, alpine meadow; and AF, alpine forest.



**Fig. 5.** (a) Pairwise comparisons of environmental factors with a colour gradient denoting Spearman's correlation coefficient. The OM fraction composition was mainly related to pH, MAP, AGB and PLFA by Mantel tests. The edge width corresponds to Mantel's  $r$  statistic for the corresponding distance correlations, and the edge colour denotes the statistical significance. (b) Ternary plot of all alpine ecosystems (across a wide pH gradient) plotted based on the three main OM clusters (Weak linkages, Complexes-Strong linkages, and Mineral cluster). (c) Response patterns of the main OM clusters along the pH gradient. MAT, mean annual air temperature; MAP, mean annual precipitation; AGB, aboveground biomass; PLFA, phospholipid fatty acids, as a microbial biomass index.

showed a preference to rather neutral soils, and the OM cluster with strong bondings showed a preference to alkaline soils. These results suggest that the dominant OM fractions can be clustered into predictable ecological groups that share similar pH preferences.

Overall, interactions among organic molecules with metal cations or minerals stabilize SOM. First, dissolved polyvalent metal cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  are balanced through mineral dissolution or precipitation, metal-bound complexes and surface exchangeable cations. Acting as important pH buffers in different soil pH ranges, carbonates and Fe and Al oxyhydroxides release the cations  $\text{Ca}^{2+}$ ,  $\text{Al}(\text{OH})_n^{(3-n)+}$  and  $\text{Fe}(\text{OH})_n^{(3-n)+}$  into solution, and are stabilizing the tertiary structure of SOM (Clarholm and Skjellberg, 2013). Second, soil organic molecules, especially low-molecular-weight functional groups, compete for long-term preservation through bonding such as surface absorption, polyvalent metal cations and association with Fe and Al oxyhydroxides (Clarholm et al., 2015). The position of hydroxyl groups relative to carboxyl groups or phenol groups also affects the chelation strength of metal-bound complexes (Tam and McColl, 1990). Third, polyvalent metal cations hold organic functional groups together as soil organic supramolecules via noncovalent bonds such as van der Waals forces and hydrogen bonds or outersphere complexation (Singh et al., 2018). Specifically,  $\text{Al}^{3+}$  stabilizes SOM much more frequently in the most acidic soils, especially at pH 3.0–4.8, compared with neutral and alkaline soils, where  $\text{Ca}^{2+}$  bridging predominates (Ross et al., 2008). The relative amount of metal-bound complexes formed by  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  bridging depends both on the absolute amounts and the relative strength of metal cations in binding organic compounds, which largely depend on the ion charge and radius (Deng and Dixon, 2002; Kleber et al., 2015). Cation speciation and exchangeable cation content and composition might also impact competition among polyvalent metal cations for organic molecules (Rowley et al., 2020). Thus, interactions among organic molecules, cations and minerals form a complex network.

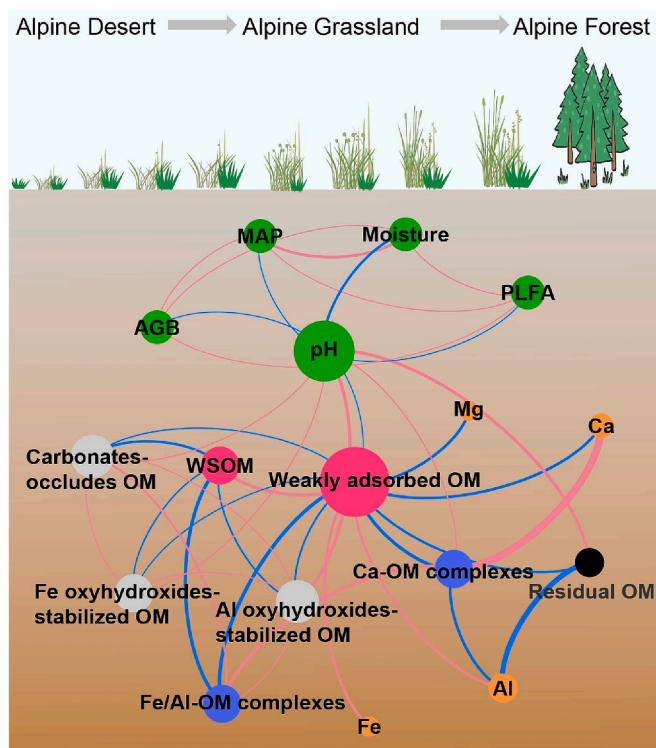
To cross-validate the specific OM clusters, we used interaction network analyses to investigate whether specific OM fractions sharing similar pH preferences tended to co-occur (Fig. 6). Our results showed that pH played a core role in the organic–inorganic interaction network. Taken together, our network analyses indicated that the contribution of

metal cations to organo-mineral stabilization in MAOM depends on the mutual balance of Ca with Fe and Al, which is closely related to soil pH. pH is the major driver for the two processes of release of metal cations into solution and formation of secondary minerals, both of which are decisive for the formation of different MAOM fractions.

Here, we propose that the main organo-mineral bonding mechanism varies as a function of pH (Fig. 5c). Hence, our results demonstrated that pH can serve as a predictor of organo-mineral fractions in MAOM across ecosystems. According to existing soil data products (HWSD, Harmonized World Soil Database), global soil pH grid data may provide the most direct and easily processed variables for assessing different stabilization mechanisms in MAOM. Moreover, we found that soil pH was closely linked to MAP, AGB and microbial biomass (measured through PLFA, Fig. 5a, 6). At constant parent geogenic material, climate (temperature and precipitation) is decisive for the pH development in soil (Slessarev et al., 2016).

## 5. Conclusions

In this study, we revealed different MAOM stabilization mechanisms across different ecosystems by using a series of chemical extractions. The extractable chemical organic matter (OM) fractions in MAOM can be grouped into three clusters: a cluster with weak bondings, a cluster with metal-bound complexes and a cluster with strong bondings. Specific OM clusters exhibited particular pH preferences and distribution patterns: the cluster with weak bondings, the cluster with metal-bound complexes and the cluster with strong bondings showed monotonically decreasing, hump-shaped and monotonically increasing patterns, respectively. These results indicate that pH might serve as a predictor of organo-mineral fractions in MAOM across ecosystems. In addition, we found that interactions among organic molecules, cations and minerals formed a complex network in which pH played a core role. More interestingly, our results further showed that precipitation not only altered the vegetation type and microbial biomass but also regulated soil pH, which is balanced by specific metal cations, thus resulting in a particular pH preference of specific OM clusters.



**Fig. 6.** Interaction network analysis of mineral-associated organic matter (MAOM) and their response to climate change. Precipitation did not only alter vegetation type and microbial biomass but also regulated soil pH, thus resulting in a particular pH preference of specific OM clusters. Purple lines indicate a positive relationship, and blue lines indicate a negative relationship. The line width represents the correlation coefficient. The colour of the circles shows different OM clusters and environmental variables: purple circles indicate the cluster with weak linkages, blue circles indicate the cluster with complexes-strong linkages, and grey circles indicate the mineral cluster, orange circles indicate major metal cations, green circles represent environmental variables. MAP, mean annual precipitation; AGB, aboveground biomass; PLFA, phospholipid fatty acids, as a microbial biomass index. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

#### CRedit authorship contribution statement

**Bin Niu:** Conceptualization, Investigation, Validation, Writing – original draft, Writing – review & editing. **Tianzhu Lei:** Resources, Writing – review & editing. **Qiuyu Chen:** Investigation, Writing – review & editing. **Ming Shao:** Writing – review & editing. **Xiaoqin Yang:** Writing – review & editing. **Hongzhe Jiao:** Writing – review & editing. **Yibo Yang:** Writing – review & editing. **Georg Guggenberger:** Supervision, Writing – review & editing. **Gengxin Zhang:** Supervision, Resources, Funding acquisition, Conceptualization, Validation, Writing – review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

#### Acknowledgements

This research was supported by grants from the Second Tibetan Plateau Scientific Expedition and Research Program (STEP) (2019QZKK0503) and the National Natural Science Foundation of China (41871066, 41471055). We also thank the Naqu Alpine Grassland Ecosystem National Field Scientific Observation and Research Station; the Motuo Observation and Research Center for Earth Landscape and Earth System, Chinese Academy of Sciences; and the Southeast Tibet Observation and Research Station for the Alpine Environment, Chinese Academy of Sciences (SETORS), for field sampling.

#### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envint.2023.108058>.

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