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***Redox control of chromium in the red soils from China
evidenced by Cr stable isotopes***

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Highlights

- Cr isotope data in soil FMNs is reported for the first time.
- FMNs/Fe oxides capture isotopically heavy Cr (VI).
- Redox and not land use drives Fe oxide formation and FMNs, affecting Cr mobility.
- Cr in red soil profiles mainly results from colluvium mineral weathering.

Abstract

With chromium isotopes, we study the intricate dynamics of adsorption and redox processes in soil ecosystems, focusing on chromium's behaviour, in red soil profiles enriched with iron-manganese nodules (FMNs) in South China. Key findings reveal that the primary geological source of chromium in the red soil profiles is the weathering of colluvium parent minerals. FMNs have higher chromium concentrations (325-1,451 µg/g) compared to surrounding soils (95-247 µg/g) and display stable $\delta^{53}\text{Cr}$ values ($0.78 \pm 0.17\text{‰}$), indicating their role as stable chromium repositories, reflecting historical processes. Furthermore, by isolating chromium associated with iron oxides (FeO) and silicate minerals (ReS) within FMNs and surrounding soils using CBD extractions, we show that FeO predominantly carry chromium, particularly in FMNs. The $\delta^{53}\text{Cr}$ values of FeO fractions consistently exhibit heavier

signatures than ReS fractions, suggesting the sequestration of isotopically heavy chromium (VI) during Fe oxide precipitation. Fluctuations in soil's redox, rather than land use, play a pivotal role in controlling the precipitation of Fe oxides in surrounding soils and the formation of FMNs, thus influencing chromium mobility. This highlights the significance of these factors when utilizing chromium isotopic techniques for source tracking in soil systems, contributing to our understanding of chromium's behaviour in soil environments.

Keywords

Chromium hazard, Chromium isotopes, red soil, iron-manganese nodules, soil redox, Iron oxides

1. Introduction

In soils, stable Cr is found as trivalent (III) and hexavalent (VI) species with low concentrations (15-100 µg/g) in general (Shahid et al., 2017). However, high Cr levels (180-60,000 µg/g) can be measured in soils developed over mafic and ultramafic rocks like serpentinite or basalt (Fandeur et al., 2009; Paulukat et al., 2015; Sun et al., 2022). Anthropogenic activities, such as mining, smelting, paper and leather manufacturing, result in $\sim 2.3 \text{ Mg} \cdot \text{yr}^{-1}$ of chromium flux into soils and are the major contributors to soil chromium contamination (Rauch and Pacyna, 2009). Therefore, soil Cr contamination is becoming a widespread concern due to its impact on the human food chain (Ao et al., 2022a; Shahid et al., 2017).

Cr is a redox-sensitive element, and manganese oxides are its main natural oxidant in soil. The transformation from rock-derived chromium (III) to more mobile and hazardous hexavalent Cr (CrO_4^{2-} , HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$) has been documented in natural systems like groundwaters (Qin and Wang, 2017). Negatively charged Cr (VI) can be sorbed onto iron oxides or clay minerals, reducing its mobility and risk (Covelo et al., 2008; Dimos et al., 2012; Johnston and Chrysochoou, 2014; Yu et al., 2020a; Zhang et al., 2022). However, Cr (VI) interactions with clay minerals are weak and can be easily disrupted through ion exchange (Covelo et al., 2008; Frank et al., 2019; Rosales-Landeros et al., 2013). Soil organic matter, sulfides, and Fe (II) can convert Cr (VI) to Cr (III), which can then bind to iron oxides or co-precipitate. Soil components like oxides, clay minerals, organic matter, collectively influence the geochemical behavior of Cr in soil systems, with oxides, particularly Fe and Mn oxides, playing a

dominant role. The bacterial activity, experimented using soil incubations have shown that weakly crystalline or amorphous Fe oxides can be reduced, leading to the release of associated metals, including Cr (Quantin et al., 2002).

Tropical and subtropical climates, characterized by heavy rainfall and high temperatures, result in extensive soil weathering and leaching, causing the formation of "red soils" with phyllosilicates and iron, aluminum, and manganese accumulated as oxides (Berger and Frei, 2014; He et al., 2004). Iron and Mn oxides continually dissolve and precipitate, forming iron-manganese nodules (FMNs), which act as important scavengers of soil pollutants, including Cr. FMNs were found to influence the oxidation of Cr (III) to Cr (VI) (Hai et al., 2020), and field studies indicated that Fe and Mn oxides promoted the migration and transformation of chromium in basalt-derived soils (Ao et al., 2022b; Sun et al., 2022; Wille et al., 2018; Zhang et al., 2023). In naturally Cr-enriched soils, such as those found in the ultramafic areas in Brazil and New Caledonia, Cr primarily associates with well-crystallized Fe oxides or chromite, indicating the predominance of stable trivalent chromium. However, notable amounts of hexavalent chromium (plant-available, up to 1,000 mg/kg) have been detected. This occurrence may be linked to the oxidation of Cr (III) by Mn oxides (Becquer et al., 2003; Fandeur et al., 2009; Garnier et al., 2013, 2006), influenced by the use of fertilizers, as Cr (VI) can exchange with phosphates (Becquer et al., 2003), or associated with microbial weathering (Quantin et al., 2002). In floodplain soil profiles, prolonged flooding increases chromium mobility, while chromium solubility is higher below the water table, highlighting the role of soil hydrology in chromium dissolution and migration (Shaheen and Rinklebe, 2014). A gap remains between controlled lab experiments and field studies with more variables impacting chromium dynamics.

Non-traditional isotope techniques have emerged to understand metals and metalloid cycles in modern or paleoenvironments. In red soils, significant isotope fractionation, like that of Cd and Mg isotopes, reveals formation processes linked to FMNs, originating from soil water or granite weathering (Gao et al., 2021, 2018). Redox activity dictates Cr mobility, highlighting the chromium isotope system as a valuable proxy for understanding red soil formation and Cr fate. Recent findings emphasize that redox reactions, particularly the reduction of hexavalent chromium to trivalent chromium, are primary contributors to chromium isotope variability in surface environments (Qin and

Wang, 2017; Wang et al., 2021). Studies have evaluated the effect of single or multiple environmental components on chromium redox and isotopic fractionation. Biotic or abiotic reduction of Cr (VI) to Cr (III) results in enrichment in light isotopes of Cr (III) ($\Delta^{53}\text{Cr} = \delta^{53}\text{Cr}_{\text{product}} - \delta^{53}\text{Cr}_{\text{reactant}}$, varying between -7.6‰ and -0.4‰), whereas oxidation of Cr (III) results in a variable $\Delta^{53}\text{Cr}$ (from -2.5‰ to +1‰) (Qin and Wang, 2017). However, the understanding of isotopic fractionation during Cr (III) oxidation is hampered by limited experimental investigations and an incomplete understanding of the underlying mechanisms.

Cr isotope records in current soil profiles are limited compared to extensive research on ancient paleosols indicating atmospheric oxygenation (Babechuk et al., 2019; Colwyn et al., 2019; Mänd et al., 2022). Berger and Frei (2014) have characterized Cr behavior in Malagasy Madagascar's laterite soil, revealing increased Cr concentration in the uppermost portions of the soil profile, accompanied by a decrease in $\delta^{53}\text{Cr}$ values, which is interpreted by a partial immobilization (e.g., by adsorption or co-precipitation of Fe oxides) occurring during the upward migration of mobile Cr (III) from deeper parts of the weathering profile. Co-variation of chromium isotopes with silicon isotopes and iron content, along with significant chromium enrichment and silicon loss found in laterite profile by Wille et al. (2018), underscores the impact of Fe oxides on chromium mobility. In laterite profiles, different $\delta^{53}\text{Cr}$ value distribution is linked to parent rock stratification and groundwater levels fluctuations (Paulukat et al., 2015). The migration of weathering fluids in porous layered rocks can lead to uneven chromium loss and fractionation. Additionally, changes in groundwater levels introduce heterogeneity in the Cr isotopic composition and soil organic matter may contributed to chromium fractionation through its ability to reduce isotopically heavy Cr (VI) to Cr (III).

Our study investigates chromium distribution in soil profiles from South China, focusing on paddy and non-paddy soils. These regions are paramount to China's food security strategy, especially in rice cultivation. However, persistent food security challenges have emerged in recent years due to toxic metal contaminants in rice (Huang et al., 2019; Ren et al., 2022). These challenges stem from two primary sources: the naturally elevated geological background, as reported in the karst region of Guangxi (Yang et al., 2021), and anthropogenic activities, notably observed in Hunan Province (Wang et al., 2016). Our research aims to utilize a combination of chemical extraction and chromium stable

isotope techniques to understand differences in Cr partitioning between FMNs and surrounding soils. We seek to identify potential chromium sources and explore key factors influencing chromium cycling in red soil systems with abundant FMNs, thereby enhancing our understanding of chromium behavior. This study provides a scientific basis for assessing soil chromium pollution and food safety in the region. Additionally, it offers insights into the applicability of chromium isotope techniques in natural soil systems.

2. Material and methods

2.1 Study area and sampling

The study was carried out in Wangling Town (109°01'07"E, 23°11'01"N) and Litang Town (109°05'49"E, 23°11'38"N), in Binyang County, Guangxi Zhuang Autonomous Region, in South China. About 8 km separate the two locations. The subtropical monsoon controls the climate here, resulting in an annual precipitation of ~1,491 mm, with a wet season from April to September, accounting for about 78% of the annual precipitation, and a mean annual temperature of 21°C. Carbonated bedrock dominates the region, but red soils are mostly developed from quaternary colluvium deposited over carbonates (Wei et al., 2014). At each site, two soil profiles were sampled: a paddy (rice culture) and a non-paddy soil profile (vegetable culture). The land use has not been modified from at least 40 years. Based on soil texture and color, soil profiles were separated at both sites into several horizons; see details in Table S1. Contrary to the three other profiles, the Litang paddy soil profile is drained at a depth of 40 cm, the outlet water being exported and collected in an artificial cemented reservoir, where rainfall and drained waters are stored and used for irrigation.

For each horizon, approximately 50 kg of bulk soil samples were collected, air-dried, and separated into two parts in the laboratory: FMNs (> 1 mm) and surrounding soil (< 1 mm). The separated FMNs were washed gently with Milli-Q water, dried, and then sieved into three size classes: 1-2 mm, 2-5 mm, and > 5 mm. The nodule proportions of each horizon were determined by weighing each FMN class. Finally, 5-10 g of each sub-sample (FMNs and surrounding soil) were ground in an agate mortar, passed through 0.15 mm sieves, and stored in sealed bags for further analysis. Additionally, to constrain natural and anthropogenic inputs in soils, three samples of bare calcareous

rocks, and seven samples of fertilizers used by local farmers, as well as two samples of irrigation water at the sampling sites of both locations were collected (Table 2). Rocks and fertilizers were ground, dissolved. Water samples (~12 L) were filtered *in situ* through 0.22 µm polyethersulfone membranes (Jinteng, China) and acidified with distilled 16 M HNO₃.

2.2 Physico-chemical properties of soils

All chemicals used in this study were at least analytic grade from Merck company and acids were double-distilled for enhanced purity. Soil properties were determined using bulk soil except for XRD analysis. Soil pH was measured potentiometrically in a soil/water (1:2.5) mixture with a PHS-3C pH meter (Leici, China) (Thomas, 2018). The cation exchange capacity (CEC) was determined by the ammonium acetate saturation technique combined with the titration method (Gillman et al., 1983). Wet sieving in conjunction with the hydrometer technique was used to determine soil texture (Gee and Bauder, 2018). Soil bulk density was estimated by weighing and calculating the dry weight of soil per volume unit (Grossman and Reinsch, 2018). Soil organic matter (SOM) content was evaluated using an oil bath-K₂Cr₂O₇ titration method (Nelson and Sommers, 2015). The mineralogical composition of FMNs and surrounding soil (< 0.15 mm fraction) was measured by X-ray diffraction (XRD) analysis using a PANalytical diffractometer with Ni-filtered Cu Kα radiation (at 45 kV and 40 mA) scanning from 5° to 75° 2θ with a scan step of 0.01° at RX platform of Université Paris Cité. The minerals were then identified using X'Pert HighScore Plus software (PANalytical, Almelo, The Netherlands) and quantified using the MAUD program (Material Analysis Using Diffraction) based mainly on the Rietveld refinement method (Lutterotti et al., 1999). Element content was measured by inductively coupled plasma mass spectrometry (ICP-QMS 7900, Agilent) at PARI Analytical Platform of IPGP-Université Paris Cité (hereafter referred to as PARI-IPGP) after HCl-HF-HNO₃ digestion. The USGS geological standards BHVO-2, BCR-2, and Nod-P-1 were used for quality control of sample digestion and elemental analysis. In most cases, the measurement deviation does not exceed 10% of the reference value, and the standard deviation is below 5%.

2.3 Fe oxide extraction using the citrate-bicarbonate-dithionite (CBD) method

161 Fe oxides were extracted to examine their impact on Cr isotope signatures due to the affinity of
162 Cr towards Fe oxides. A modification of the citrate-bicarbonate-dithionite (CBD) deferrification
163 method from Holmgren (1967) was used to quantify Cr associated with Fe-oxides. One hundred mg
164 of sample was mixed with 40 mL of 0.3 M sodium citrate, 5 mL of 1 M sodium bicarbonate, and 1 g
165 of sodium dithionite, then heated at 80°C for 4 h with manual shaking every 30 min. After centrifugation,
166 the supernatant was removed while the solid residue was kept. The extraction was repeated 3-10 times
167 to ensure that all Fe oxides had been removed. Finally, the residue was rinsed several times with Mill-
168 Q water and dried at 40°C before being weighed, ground, and stored before elemental and isotope
169 analyses.

170 2.4 Cr purification and isotope analysis

171 The chromium purification was achieved by a 2-step column chemistry with cation exchange
172 resin (AG®50W-X8, 200-400 mesh, Bio-Rad) using the procedure modified from Larsen et al. (2016)
173 in a Class 1000 cleanroom (PARI-IPGP). Since Cr isotope fractionation can occur during the chemical
174 separation through chromatographic columns and the final purification yields rarely exceed 70-80%,
175 we used a double spike technique following the protocol detailed in Sossi et al. (2018).

176 First, samples containing 1 µg Cr were spiked with an appropriate ⁵⁰Cr-⁵⁴Cr double spike solution
177 volume to achieve a Cr_{spike}/Cr_{sample} ratio of ~0.28. The spiked samples were heated in 6 M HCl at 100°C
178 for 24 h to facilitate homogenization and promote the formation of Cr-Cl complexes. Then, cold Milli-
179 Q water (4 L) was added to dilute the HCl concentration to 1 M. Sample was loaded into a pre-cleaned
180 and conditioned column of 1 mL resin, and Cr was collected immediately. Further elution of Cr was
181 carried out in 5 mL of 1 M HCl, and both eluates were evaporated together. The resin was washed with
182 10 mL of 6 M HCl and 5 mL of Mill-Q water. After that, the Cr fractions were exposed to 0.5 M HNO₃
183 and 0.8% H₂O₂ at room temperature for at least 48 h to facilitate the conversion of all Cr species to
184 Cr³⁺. The remaining major elements (e.g., Al) as well as interferents (Ti, V, and Fe) were removed by
185 loading the sample onto the pre-conditioned AG®50W-X8 resin followed by elution with 5 mL of 0.5
186 M HF and 22 mL of 1 M HCl. Finally, Cr was eluted with 10 mL of 2 M HCl, evaporated, and the Cr
187 concentration was adjusted to ~100 µg/L with 2% HNO₃ for isotope measurement.

188 The Cr isotope compositions were measured on a Neptune Plus MC-ICP-MS (ThermoScientific)
 189 equipped with a PFA μ Flow nebulizer (100 μ L/min), an Apex HF desolvation introduction system
 190 (Elemental Scientific) and eight Faraday collectors that allowed for simultaneous collection of ^{50}Cr ,
 191 ^{52}Cr , ^{53}Cr , ^{54}Cr together with ^{49}Ti , ^{51}V and ^{56}Fe , to correct the isobaric interferences of ^{50}Ti , ^{50}V , and
 192 ^{54}Fe on ^{50}Cr and ^{54}Cr , respectively. In the medium resolution mode, a 4-8 V sensitivity on ^{52}Cr was
 193 obtained for a 100 $\mu\text{g/L}$ Cr solution using Jet sample and H skimmer cones. The purification yield of
 194 our method ($\sim 80\%$) is in line with previous studies (Zhu et al., 2018, 2019). The procedural blanks of
 195 0.2-11 ng ($n = 7$), are negligible compared to the loaded sample mass (1000 ng). Isotope results are
 196 reported as $\delta^{53}\text{Cr}$ and normalized to the certified Cr isotopic standard NIST SRM 979 as Eq. (1):

$$197 \quad \delta^{53}\text{Cr}(\text{‰}) = \left(\frac{(^{53}\text{Cr}/^{52}\text{Cr})_{\text{sample}}}{(^{53}\text{Cr}/^{52}\text{Cr})_{\text{NIST SRM 979}}} - 1 \right) \times 1000 \quad (1)$$

198 Reproducibility and accuracy of isotope measurements were checked using the NIST SRM 3112a
 199 and USGS BHVO-2 reference materials, resulting in $\delta^{53}\text{Cr}$ of $-0.09 \pm 0.03\text{‰}$ (2SD, $n = 9$) and $-0.14 \pm$
 200 0.05‰ (2SD, $n = 27$), respectively, which agreed with reported values in the literature (Liu et al., 2019;
 201 Wu et al., 2020).

202 3. Results

203 3.1 Soil physicochemical properties

204 The key physicochemical properties of the soils are listed in Table 1. Neutral pH values ($7.2 \pm$
 205 0.13) are found in most soil horizons except for the non-paddy soil profile in Wangling (pH ~ 4.8) and
 206 the topsoil horizon of the two paddy soil profiles in Wangling (pH 6.2) and Litang site (pH 6.5). The
 207 difference in soil pH may be attributed the different crops and the recycling of organic material, which
 208 tends to acidify soil (Butterly et al., 2013; Wei et al., 2006). The SOM content is higher in the surface
 209 horizon and decreases with depth. Overall, paddy soils have more SOM than non-paddy soils because
 210 a small portion of above-ground rice stalks and underground roots remains in the field after rice harvest,
 211 where intermittent reducing conditions promote their decomposition. The soil density ranges from 0.9
 212 to 2.3 g/cm^3 , with the minimum and maximum values observed in the Litang paddy soil profile.
 213 Additionally, there is a gradual increase in soil density with depth within this profile, finally reaching
 214 approximately twice the value of the bottom horizon in the Wangling paddy soil profile. Soil CEC and

215 clay content increase with depth, ranging from 11.8 to 24.1 cmol/kg and 16 to 40%, respectively.

216 3.2 Distribution and mineralogy of FMNs and surrounding soils

217 In all soil profiles, except with of the Litang paddy soil profile, FMNs content in each size class
218 and across each soil profile exhibits relatively low variability (Table 1). In particular, both non-paddy
219 soil profiles have a dominant FMNs content (61-76% of the total) over the surrounding soil, while the
220 paddy soil profile at Wangling has a lower FMNs content (37-51%). On the other hand, the Litang
221 paddy soil profile shows a gradually increase in the total FMNs content with depth, ranging from ~5%
222 in the top to 45% in the bottom horizon. This increase affects each FMNs size class. In soil profiles,
223 most FMNs are found in the 2-5 mm class (~66%), followed by the > 5 mm class (~23%), and the 1-
224 2 mm class (~10%).

225 Mineral compositions of FMNs are generally similar independently of size or soil horizon (Fig.
226 S1, Table S2); we now discuss these FMNs as a whole compared with the surrounding soils, as depicted
227 in Fig. 1. In both non-paddy and paddy soil profiles of Wangling, the mineralogy remains constant
228 with depth irrespective of fraction (surrounding soils and FMNs, Figs. 1a and 1c, Table S2).
229 Specifically, the surrounding soil at Wangling is primarily composed of ca. 35-40% kaolinite, 30-35%
230 quartz, 10-15% gibbsite, and 10-15% goethite, whereas the FMNs encompass 60-65% goethite, 15-
231 20% gibbsite, and 10-15% kaolinite. However, distinctions in mineralogical composition are
232 noticeable between non-paddy and paddy soil profiles in Litang. In the Litang non-paddy soil profile,
233 from top to bottom, the surrounding soil is affected by a decrease in quartz (55 to 35 %) and microcline
234 (10 % to traces) and a rise in kaolinite (35 to 65%) proportions (Fig. 1b). A similar vertical evolution
235 of the quartz-kaolinite couple is also observed in the surrounding soil of Litang paddy soil profile (Fig.
236 1d). The 15 % of illite found in the upper horizons are progressively replaced by microcline at
237 intermediate depth. The deepest sample is almost exclusively composed of kaolinite and quartz. FMNs
238 in both profiles are primarily constituted of 60-80 % iron oxides (mostly goethite) and 10% quartz
239 (Fig.1b and 1d). Kaolinite represents 10-30 % of the nodules, except in the waterlogged horizon (Brg,
240 45-70 cm) in the Litang paddy soil profile where it is almost absent. Mn-rich phases (e.g., birnessite)
241 have not been observed in either FMNs or surrounding soil samples, primarily due to their low

242 abundance or to the presence of Mn as impurities in other minerals like iron oxides (Wang et al., 2023).

243 3.3 Vertical distribution of elements in soil profiles

244 The concentrations of Cr and other key elements are listed in Table S3 and plotted in Fig. S2.
245 High Mn concentrations (up to 24 g/kg) are only found in the largest FMNs of two horizons of the
246 non-paddy Litang profiles, showing that overall FMNs should be better defined as iron nodules only.
247 Compared to the surrounding soils, FMNs contain higher redox-sensitive trace elements such as V, Cr,
248 and Fe. Conversely, higher concentrations of immobile elements (e.g., Ti) or major and soluble
249 elements (e.g., Mg) are reported in the surrounding soils. In the surrounding soils, Cr concentrations
250 are higher in Wangling (223-247 µg/g) than those in Litang (95-180 µg/g) and relatively independent
251 of the cultivation mode (paddy vs. non-paddy). Across all soil profiles, Cr content is higher in the
252 smallest FMNs (822-1,451 µg/g) than in the largest ones (325-693 µg/g).

253 To evaluate the potential accumulation or depletion of elements throughout the soil profile, the
254 mass balance coefficient (τ) was applied (Braun et al., 1993) according to Eq. (2):

$$255 \tau_{X,Nb} = \frac{(C_X/C_{Nb})_{sample}}{(C_X/C_{Nb})_{parent}} - 1 \quad (2)$$

256 where C_X and C_{Nb} are the concentrations of element X and niobium in soil samples or parent materials,
257 respectively. The corresponding values in the deep Quaternary red earth reported by Yang (2006) were
258 used as those in the parent materials, since our soil profiles were developed from quaternary colluvium.
259 Niobium was selected as an immobile element due to its stability during advanced weathering
260 processes (Guinoiseau et al., 2021). As indicated in Fig. 2, the τ values of immobile elements (Al and
261 Ti) remain constant across all soil profiles, suggesting a similar conservative behavior of Nb. The
262 major and soluble element (Mg) shows a slight depletion. The reactive element (Mn) behavior is
263 comparable to that of Mg in the Wangling soil profiles. In contrast, in Litang soil profiles, Mn displays
264 either pronounced depletion (in the paddy soil profile) or enrichment (in the non-paddy soil profile).
265 The redox-active elements (Cr, V, Fe) show strong enrichment, particularly in the non-paddy soil
266 profiles. Significant enrichment of redox-active elements is observed mainly in the Brg horizon (45-
267 70 cm) downwards in the paddy soil profile of Litang, which contrasts with the trend observed in
268 Wangling.

269 To assess the extent of soil weathered erosion throughout the soil profile, we applied the soil-
270 weathered erosion coefficient (ba), using the content of the following oxides, as described by Zhang
271 et al. (2004):

$$272 \quad ba = \frac{(Na_2O + MgO + K_2O + CaO)}{Al_2O_3} \quad (3)$$

273 This coefficient indicates the degree of leaching of soil base ions. Al_2O_3 is more stable and less
274 susceptible to washing away during soil formation than Na_2O , MgO , K_2O , and CaO . Thus, the greater
275 the leaching effect of soil weathering, the lower the ba value. As shown in Table 1, the ba values are
276 generally low (≤ 0.07), except in the Litang paddy profile where ba values are notably higher, peaking
277 at 0.19 at the surface but gradually decreasing with depth to 0.09 at the bottom. This indicates that the
278 Litang paddy profile experiences weaker and more variable soil-weathered leaching compared to the
279 other profiles.

280 3.4 Effect of Fe oxides on element partitioning via CBD extraction

281 For comparison, the CBD extraction was conducted on the two soil profiles from Litang, to
282 determine: 1) the main carrier of Cr both in FMNs and surrounding soils, 2) the respective Cr isotope
283 signatures of the oxides (FeO hereafter, extracted fraction) and silicate phases (ReS hereafter, residual
284 fraction), and 3) whether the observed $\delta^{53}Cr$ values shape in the Litang paddy soil profile is associated
285 with Fe oxide or silicate phases. The paddy soil profile has a heterogeneous elemental distribution
286 (Table S3 and Fig. S2) and the lowest and the most variable FMNs content (Table 1) with depth. In
287 contrast, the non-paddy soil profile is characterized by a homogeneous elemental distribution and a
288 higher and more stable FMNs content with depth. In addition to the surrounding soil fraction, the
289 medium-sized FMNs (2-5 mm) were also included since this fraction represents 58-71% of the total
290 FMNs mass in these profiles. The results are reported in Fig. 3 and Table S4. Specifically, the ReS
291 fraction of the surrounding soil and FMNs has similar low Cr concentrations (60-130 mg/kg, Fig. 3a)
292 in non-paddy and paddy soils. The FeO fraction of the FMNs contains the highest Cr concentrations
293 (800-1000 mg/kg), while Cr concentrations in the FeO fraction of the surrounding soil are intermediate
294 (200-400 mg/kg). Additionally, in the 2-5 mm FMNs, the CBD extraction removed almost all Fe, Mn,
295 and Cr ($> 90\%$), indicating that Cr is almost entirely carried by Fe and Mn oxides in FMNs. In the

surrounding soils, however, the extraction yield of Cr (50-75%) is lower than for Fe and Mn (80-95%), demonstrating that Cr is carried by oxides and silicates (illite, kaolinite or microcline, cf. Fig. 1). Further, although the Fe extraction yield is almost constant in the Litang paddy soil profile (80-85%), the Cr and Mn extraction yields appear to be at their maximum in the waterlogged horizon (Brg, 45-70 cm). This may imply that the waterlogged conditions in this horizon strongly influences the behavior of Cr and Mn.

3.5 Cr isotope signature in soil profiles

Chromium isotope signatures of FMNs and soil samples are reported in Fig. 4 and Table S3. Heavier Cr isotope signatures are observed in FMNs compared with the surrounding soils (Figs. 4a, 4b, 4d and 4e). Between the different FMNs size classes, Cr isotope signature does not vary much, with a mean value of $0.78 \pm 0.17\text{‰}$ ($n = 45$), which is not correlated with the enrichment of Cr in the smallest FMNs (Table S3 and Fig. S2). Regarding the surrounding soils, $\delta^{53}\text{Cr}$ values are constant and cluster around $0.32 \pm 0.07\text{‰}$ across all soil profiles except for the Litang paddy soil profile. Conversely, the surrounding soils of Litang paddy soil profile demonstrate a clear increase in $\delta^{53}\text{Cr}$ values with depth, ranging from $0.02 \pm 0.05\text{‰}$ in the topsoil to a maximum of $0.38 \pm 0.06\text{‰}$ in the waterlogged horizon (Brg horizon, 45-70 cm), and decreasing to $0.19 \pm 0.03\text{‰}$ in the bottom horizon (Fig. 4e and Table S3).

The chromium isotope signatures of the two fractions isolated by CBD extraction differ significantly (Table S4 and Figs. 4c, 4f). Because of the high Na concentration in the FeO extract, the analysis of chromium isotope signatures associated with iron oxides cannot be performed directly. Therefore, to determine the $\delta^{53}\text{Cr}_{\text{FeO}}$, we calculated the extracted mass of iron oxides (Mass_{FeO}) and its element content (X_{FeO}), assuming that Nb is resistant to CBD extraction and is concentrated in the residue:

$$Nb_{\text{Res}} \times (\text{Mass}_{\text{total}} - \text{Mass}_{\text{FeO}}) = Nb_{\text{total}} \times \text{Mass}_{\text{total}} \quad (4)$$

then the extracted ratio and X_{FeO} were calculated according to:

$$\text{Mass}_{\text{FeO}} / \text{Mass}_{\text{total}} = 1 - Nb_{\text{total}} / Nb_{\text{Res}} \quad (5)$$

$$X_{\text{FeO}} = (X_{\text{total}} - X_{\text{Res}}) \times \text{Mass}_{\text{total}} / \text{Mass}_{\text{FeO}} + X_{\text{Res}} \quad (6)$$

and by combining the known Cr concentration and isotope composition in the total material and in the ReS fraction, we determined the $\delta^{53}\text{Cr}_{\text{FeO}}$ according to Eq. (7):

$$\delta^{53}\text{Cr}_{\text{FeO}} = \frac{(Nb_{\text{ReS}} \times Cr_{\text{total}} \times \delta^{53}\text{Cr}_{\text{total}} - Nb_{\text{total}} \times Cr_{\text{ReS}} \times \delta^{53}\text{Cr}_{\text{ReS}})}{(Nb_{\text{ReS}} \times Cr_{\text{total}} - Cr_{\text{ReS}} \times Nb_{\text{total}})} \quad (7)$$

As shown in Fig. 4c, in the non-paddy soil profile of Litang, the $\delta^{53}\text{Cr}$ values are not only constant with depth but also quite similar for ReS (mean: $0.23 \pm 0.06\text{‰}$), for FeO fractions (mean: $0.33 \pm 0.11\text{‰}$) of the surrounding soils and for ReS fraction extracted from the FMNs (mean: $0.36 \pm 0.10\text{‰}$). However, the FeO fraction of the FMNs has a higher $\delta^{53}\text{Cr}$ signature ($0.76 \pm 0.10\text{‰}$), showing a likely isotope fractionation before or during Cr incorporation within Fe oxides. Litang paddy soil profile, however, presents a quite different picture (Fig. 4f). In this profile, the $\delta^{53}\text{Cr}$ values for the FeO fraction are always heavier than the ReS fraction in the FMNs and the surrounding soil, and the $\delta^{53}\text{Cr}$ values for the ReS fraction in FMNs and surrounding soils are stable with depth but with a heavier signature in the former ($\Delta^{53}\text{Cr}_{\text{ReS_FMN-ReS_Soil}}$ of 0.53‰). While the gap between FeO and ReS' $\delta^{53}\text{Cr}$ is constant within the FMNs and close to the one measured in the Litang non-paddy soil profile ($\Delta^{53}\text{Cr}_{\text{FeO-ReS}}$ of $0.35 \pm 0.18\text{‰}$), significant variations are noticed within the surrounding soil. A maximum value of $\Delta^{53}\text{Cr}_{\text{FeO-ReS}}$ is being observed in the waterlogged horizon (Brg, 45-70 cm), suggesting that Cr redistribution through redox processes and/or its coprecipitation within Fe oxides or FMNs may be the main drivers of the observed $\delta^{53}\text{Cr}$ changes.

3.6 Water, rock and fertilizer samples

The chromium isotope compositions and the element contents of these samples are listed in Table 2. Irrigation waters from Wangling and Litang have low chromium contents of 0.07 and 0.28 $\mu\text{g/L}$, respectively. Calcareous rocks exhibit high calcium contents of up to 40% (consistent with their mineral composition of > 90% dolomite or calcite) and chromium contents of 4 mg/kg. The N-P-K compound fertilizers typically contain 10-20% phosphorus and potassium, with potassium primarily being in the form of potassium chloride, except for F3. The chromium content of the fertilizer ranges from 16 to 26 mg/kg. At the same time F3 where potassium is predominantly in the form of potassium sulfate derived from the dichlorination of potassium chloride, has a lower chromium content of 9 mg/kg, likely due to chromium loss during dechlorination.

Wangling and Litang irrigation waters have very different $\delta^{53}\text{Cr}$ values, $1.47 \pm 0.06\text{‰}$ and $0.16 \pm 0.02\text{‰}$, respectively (Table 2). The irrigation water in Wangling originates from a natural stream, and therefore its $\delta^{53}\text{Cr}$ value and Cr/Ca ratio are similar to those of calcareous rocks. In contrast, the irrigation water in Litang is stored in an artificial cemented reservoir, which primarily serves to collect rainwater during rainfall events and functions as a drainage pond for paddy fields. Consequently, its $\delta^{53}\text{Cr}$ value is similar to the surrounding soils in paddy fields. Calcareous rock samples have generally high $\delta^{53}\text{Cr}$ values (mean $1.01 \pm 0.58\text{‰}$, $n = 3$), while fertilizer samples have $\delta^{53}\text{Cr}$ values ranging from 0.1‰ to 0.5‰ , except for F3 ($1.49 \pm 0.12\text{‰}$). The high $\delta^{53}\text{Cr}$ value of F3 can be attributed to the preferential loss of light chromium isotopes during its dechlorination.

4. Discussion

4.1 Origin of chromium in red soils: a source effect?

Soil profiles have consistent chromium isotopic signatures for FMNs and most of surrounding soils, except for the Litang paddy soil profile, which shows variability. To identify if a source effect can explain the variations observed in these red soils, we need to assess input and output fluxes and compare them to the average Cr concentrations.

As a first step, the average Cr concentration and soil density of soil profiles can be used to calculate soil Cr stocks in the cultivated soil horizon in 0.3 m^3 box (Fig. 5) according to Eq. (8):

$$\text{Soil Cr stock (g)} = \text{Soil density (g/cm}^3\text{)} \times \text{Cr (mg/kg)} \quad (8)$$

Comparing Cr stock, external inputs (fertilizer, rainfall, and irrigation water) and outputs (harvesting, drainage), per unit area reveals significant differences. As shown in Fig. 5, Wangling non-paddy and paddy soil profiles hold $259 \text{ g}/0.3 \text{ m}^3$ and $176 \text{ g}/0.3 \text{ m}^3$ of Cr, while Litang has $220 \text{ g}/0.3 \text{ m}^3$ and $43 \text{ g}/0.3 \text{ m}^3$, respectively. Before to analyse Cr cycle in a whole, we assess the "active" Cr stock, i.e. reactive to current pedological conditions by evaluating in details the mineralogical composition and the primary Cr carriers. In red soils, surrounding soils must be decoupled from FMNs story. Indeed, a significant difference has been measured for the residual $\delta^{53}\text{Cr}$ signature after CBD extraction in the surrounding soil ($\delta^{53}\text{Cr} = -0.02 \pm 0.10 \text{‰}$) and the FMNs ($0.51 \pm 0.09 \text{‰}$) of the Litang paddy soil profile (Fig. 4f), despite a similar mineralogy (abundant kaolinite and quartz, Fig. 1d) and Cr

377 concentrations (Fig. 3a).

378 The most plausible explanation is that these two components, surrounding soils and FMNs, are at
379 different formation stages, with FMNs serving as ancient archives that persist. This aligns with findings
380 in the literature, where evidences like old ^{14}C formation ages for FMNs (Pai et al., 2003) and insights
381 from 3-D microstructure analysis (Yu et al., 2020b) support this view. Therefore, FMNs should be seen
382 as historical and chemically stable archives unaffected by current pedological conditions, rather than
383 as recent and reactive mineral phases. In surrounding soils, Cr can be associated with primary minerals
384 like illite/microcline or secondary products such as kaolinite and gibbsite in Wangling. Despite no iron
385 oxides has been detected by XRD analysis, amorphous phases like ferrihydrite can constitute a notable
386 portion (10-30 wt%) based on Fe concentrations in bulk samples (3.8-9.4 wt%, Table S3) and the
387 effectiveness of Fe removal by CBD extraction reported for Litang profiles (80-95%, Fig. 3b). The
388 high percentage (50-75 wt%) of chromium removed by CBD extraction in surrounding soils suggests
389 that these amorphous iron oxides are a major carrier of Cr in this fraction (200-400 $\mu\text{gCr/g}$, Fig. 3a
390 and Table S4). The Cr concentration in the ReS fraction (60-80 $\mu\text{gCr/g}$) and the prevalence of quartz
391 and kaolinite indicate the latter as a significant Cr-carrying phase in red soils. A simple mass balance
392 gives a 120-350 $\mu\text{gCr/g}$ kaolinite, larger than the UCC value (92 $\mu\text{g/g}$, Rudnick and Gao (2014)), but
393 in line with the immobile behaviour of Cr during chemical weathering. Thus, if the surrounding soil is
394 considered as the Cr source available for chemical weathering (formation of kaolinite/gibbsite) or
395 oxidative dissolution (iron oxide precipitation), this “active” Cr stock amounts to 22 and 32 $\text{g}/0.3 \text{ m}^3$
396 in the Litang non-paddy and paddy soil profiles, respectively (Fig. 5).

397 Regarding the input, atmospheric deposition, including rainwater and dust, can be a significant
398 source of soil metal contamination (Fu et al., 2021). Rainwater in the area has low Cr levels (≤ 1 ppb)
399 and with an annual rainfall of $\sim 1,491$ mm (Gao et al., 2021), the maximum rainwater Cr flux of 1.5
400 $\text{mg}/\text{m}^2/\text{yr}$ (F_{rain} , Fig. 5). Human-made dust deposition is negligible due to the absence of factories.
401 Natural dust deposition, following Kok et al. (2021), ranges from 1 to 3 $\text{g}/\text{m}^2/\text{yr}$, giving a Cr flux of
402 0.09 to 0.28 $\text{mg}/\text{m}^2/\text{yr}$ (F_{dust} , Fig. 5), about ten times lower than rainwater input.

403 Irrigation water, as a Cr source in soil, differs between Wangling and Litang. In Wangling, river-
404 based irrigation with low Cr content (0.07 $\mu\text{g/L}$) yields a Cr flux (F_{irw} , Fig. 5) of 0.1 $\text{mg}/\text{m}^2/\text{yr}$. In

405 Litang, water reservoirs receive rainwater and drained water, resulting in a higher Cr concentration
406 (0.28 $\mu\text{g/L}$) due to soil interactions, leading to a Cr flux of 0.2 $\text{mg/m}^2/\text{yr}$ for non-paddy fields. However,
407 for the Litang paddy soil profile, this water cannot be considered an external input as most of the Cr
408 originates from drainage within the soil.

409 Fertilizers impact soil Cr levels. We analyzed seven local fertilizers (Table 2) used for rice and
410 vegetable cultivation. On average, 1,500 kg/ha/yr of fertilizer is applied in paddy fields, and 1,500-
411 3,000 kg/ha/yr in non-paddy fields. With fertilizers containing 20 mg/kg Cr, estimated Cr flux is 3-6
412 $\text{mg/m}^2/\text{yr}$ (F_{fer} , Fig. 5). Notably, widespread fertilizer uses in China began after 1980. Over 40 years,
413 it contributes about 0.12-0.24 gCr/m^2 , less than 1.1% of the soil's "active" Cr stock. Fertilizers are not
414 the primary Cr source in the soil.

415 Cr outputs from soil profiles are limited to crop uptake and runoff. Crop uptake comprises
416 vegetables and rice for non-paddy and paddy soil profiles. In Guangxi Zhuang Autonomous Region,
417 vegetable yield averages 2.2 $\text{kg/m}^2/\text{yr}$ (Ministry of Agriculture, 2016), with a Cr concentration of 0.3
418 mg/kg , resulting in a Cr output of about 0.7 $\text{mg/m}^2/\text{yr}$ (F_{veg} , Fig. 5). For Cr export through rice
419 harvesting, most of the Cr remains in rice roots after harvest. With a Cr concentration of 0.2 mg/kg in
420 rice grains (Xiao et al., 2018) and an aboveground plant biomass of 1.2 kg/m^2 for rice (Roy et al.,
421 2012), the estimated Cr export from rice cultivation is approximately 0.5 $\text{mg/m}^2/\text{yr}$ (F_{rice} , Fig. 5).

422 Estimating Cr runoff is challenging. In Litang, due to the absence of major water bodies, it is
423 likely negligible. In Wangling, the river draining the fields shows low Cr levels and isotope features
424 aligned with calcareous formations within the basin, suggesting a negligible Cr flux outside the field
425 area.

426 Input and output fluxes are depicted in Fig. 5. Fertilizers' impact over 40 years is negligible at the
427 soil formation scale. The net Cr enrichment in soils ranges from 1.0 to 1.4 $\text{mg/m}^2/\text{yr}$ based on long-
428 term inputs and outputs. This rate would require 15,700 to 32,000 years to build the "reactive" Cr pool
429 in surrounding soils, inconsistent with its recent nature. Hence, the primary Cr source in soils is likely
430 the chemical weathering of colluvium parent minerals, influenced by changes in redox conditions.

431 4.2 Land use or hydrological control on elemental distribution in soils

432 Distinct land use may play on soil hydrology, which could influence Cr mobility or distribution
433 within paddy and non-paddy soils. Mineralogically, all soil profiles comprise FMNs rich in goethite
434 (60-85%, Fig. 1) and some accessory minerals (quartz, kaolinite, and gibbsite). The FMNs are more
435 abundant in non-paddy soil profiles than in paddy ones, and only the Litang paddy soil profile shows
436 a variability of FMNs content with an increase in depth. The surrounding soils are mostly an
437 assemblage of quartz and kaolinite, but gibbsite and iron oxides can be found at Wangling sites (Figs.
438 1 and S1). At Litang, illite or microcline are found in the top horizons, while amorphous iron oxides,
439 not detected by XRD analysis, can reach 10-30 % (see section 4.1). In modern soils, illite is frequently
440 found under moderate weathering intensity compared with gibbsite and kaolinite, typical of intense
441 chemical weathering, such as faced red soils (Churchman et al., 2012). Gibbsite typically occurs in
442 soils with insufficient Si supplies under intense leaching, while kaolinite forms in soils with weak
443 leaching and high Si availability (Berger and Frei, 2014; Churchman et al., 2012). Our data suggest
444 that soils in Wangling are facing more extreme chemical weathering than in Litang, as confirmed by
445 the lower ba values observed in Wangling. Therefore, the location (Wangling vs. Litang) rather than
446 the land use (vegetable vs. rice culture) seems to dictate the soil hydrology that will condition the
447 mineralogy and the distribution of elements throughout the soil profile. The lower elevation at
448 Wangling (94 m, Table S1) than at Litang (101 m) may result in a shallower groundwater level,
449 subjecting the entire soil profile to long-term fluctuations in groundwater and consequently enhancing
450 soil leaching intensity. In contrast, in Litang, prominent gleying features are observed within the Brg
451 horizon (45-70 cm) of the paddy soil profile, resulting from localized waterlogging. The soil density
452 can be a controlling factor here since its values at the bottom of the Litang paddy soil profile are
453 approximately twice that of Wangling. Consequently, the compactness of the soil at the bottom of the
454 Litang paddy soil profile acts as a barrier, restricting or slowing down the downward movement of
455 water. This restricted permeability contrasts to the porous and permeable nature of the loose soil in the
456 bottom horizon of the Wangling paddy soil profile. Another controlling factor may be the water
457 drainage at 40 cm in the Litang paddy soil profile. Adjacent to this profile lies a cemented water
458 reservoir, and a drainage pipe is connected to the Litang soil profile, positioned approximately 40 cm
459 below the ground, to collect drainage from it. As a result, the upper 40 cm of this profile, including the

Ap1, Ap2, and AB horizons, remain consistently dry during periods of non-rice cultivation, in stark contrast to the horizons below, which exhibit gleying features. Therefore, hydrological conditions are a key driver shaping the red soil profiles. By noticing the distinct behaviour of the Litang paddy soil profile, it is also clear that local change in hydrological conditions influences the soil redox conditions and thus plays on the distribution of redox-sensitive elements such as Cr. The principal component analysis (PCA, Fig. S3) based on element concentrations of soil profiles confirms that redox-sensitive elements (Fe, Cr, As, and V) behave similarly, as already observed in other studies (Aide, 2005; Ettler et al., 2017), and consistent with a redox control. Based on the reactivity of Cr isotopes to redox changes (e.g., Wei et al. (2020)), such a redox control should be seen in our soil Cr isotope signatures.

4.3 Highlighting the effect of redox cycling on Cr mobility using Cr isotopes (Litang soils)

The link between redox conditions and Cr isotope variations has been reported in numerous studies on paleosols and laterites (i.e., red soils). A typical negative $\delta^{53}\text{Cr}$ values is due to the loss of Cr through oxidative weathering (Berger and Frei, 2014; Crowe et al., 2013). This is attributed to the preferential oxidation of the heavy isotopes of Cr during the conversion of Cr (III)-bearing minerals to more soluble and mobile Cr (VI), leading to residual materials enriched in light isotopes. Meanwhile, the positively fractionated mobile pool of Cr (VI) may be transported via runoff to water bodies, as supported by the isotopically heavier $\delta^{53}\text{Cr}$ values of rivers and oceans (D'Arcy et al., 2016; Sun et al., 2019). However, positive $\delta^{53}\text{Cr}$ values and Cr enrichment have also been observed in some weathering profiles, which have been explained as the re-deposition of the isotopically heavy fraction of Cr (VI) (Berger and Frei, 2014; Crowe et al., 2013).

Taken as a bulk, our red soil profiles all exhibit more positive $\delta^{53}\text{Cr}$ values (bulk samples all cluster around 0.7‰, except for the mildly positive values (~0.3‰) in the upper part of the Litang paddy soil profile, Fig. 4) than the $\delta^{53}\text{Cr}$ reported for soils from different geobackgrounds (as summarized in Table S5). Remarkably, all FMNs have a constant enrichment in Cr, Fe, and Mn as well as a similar heavy $\delta^{53}\text{Cr}$ signature, but clear correlations between $\delta^{53}\text{Cr}$ values and the inverse of Cr or Fe concentration exist (*Pearson coefficients* $r = -0.91$ and -0.93 , respectively), and are mostly driven by the soil samples from the Litang paddy soil profile (Fig. 6). A robust correlation between Cr and Fe

enrichments has been identified in other weathered soil profiles, where Fe oxides (e.g. goethite, hematite) serve as the primary Cr-bearing minerals, exerting control over the mobility and redistribution of chromium (Becquer et al., 2003; Garnier et al., 2013, 2006; Sun et al., 2022). The weaker correlation between $\delta^{53}\text{Cr}$ values and the inverse of Mn concentration (*Pearson coefficients* $r = -0.74$, Fig. S4) can be attributed to the fact that Mn is likely driving the release of Cr, from minerals through the oxidation, inducing a decoupling of Cr and Mn concentrations. Reversely, Fe serves as a key driver for the sequestration of Cr, effectively immobilizing the released Cr within Fe oxides. This statement is validated by the CBD extraction performed on both surrounding soils and FMNs of the Litang soil profiles, where the Cr concentration in the FeO fraction is much higher than that in the ReS (Fig. 3a), indicating that the majority of Cr is carried by Fe oxides. It is particularly valid in FMNs, where almost all Cr is bound or within goethite, while in the surrounding soils, Cr is significantly associated to silicate minerals like kaolinite (Figs. 1 and 3b). The isotope signatures of the two Cr pools (ReS and FeO) indicates a systematic enrichment in heavy isotopes in the FeO fraction for both surrounding soils and FMNs (Figs. 4c and 4f). In the section 4.1, we have concluded that Cr sequestered in Fe oxides is mostly resulting from ancient (in FMNs), or recent (in surrounding soils) parent material weathering. We thus propose that the enrichment in heavy isotopes in iron oxides is directly linked with a pool of heavy Cr (VI) mobilized by oxidative weathering in our red soil profiles, and which is largely coprecipitated, as other researchers have speculated (Berger and Frei, 2014; Crowe et al., 2013). However, the magnitude of the Cr isotope fractionation between FeO and ReS is less variable for FMNs throughout the profile ($\Delta^{53}\text{Cr}_{\text{FeO-ReS}}$ of ca. 0.35‰) than for the surrounding soils ($\Delta^{53}\text{Cr}_{\text{FeO-ReS}}$ ranging from 0.0 to 0.6‰). Based on the distinct history of FMNs and surrounding soils (see section 4.1), it points towards different scenarios of Cr precipitation within Fe oxide phases.

Firstly, FMNs are initially formed as pore fillings in soils (Yu et al., 2020b), and consist of Fe from the surrounding soil matrix and the Fe oxides newly formed through the oxidation and precipitation of Fe^{2+} in the soil solution revealed by Fe isotopes (Feng et al., 2018; Sipos et al., 2023). As a result, FMNs may encapsulate Cr from the soil matrix and adsorb/co-precipitate Cr from the solution (mainly as Cr (VI) species like CrO_4^{2-} , HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$) during Fe oxide formation. Numerous studies have shown that significant amounts of Cr (VI) can be adsorbed and incorporated into the

515 structure during the formation and transformation of Fe oxides, and the presence of organic matter and
516 Mn (II) can enhance the adsorption (Liang et al., 2021a; Yu et al., 2020a). Adsorption of Cr (VI) by
517 goethite does not cause significant isotope fractionation according to Ellis et al. (2004), thus Cr (VI)
518 is quantitatively sequestered without isotopic fractionation in the FMNs. These findings indicate that
519 the isotopically heavy Cr (VI) from the soil solution is the most likely source of the Fe oxide-associated
520 Cr in these FMNs. This also explains why FMNs of varying sizes have similar Cr isotopic
521 characteristics despite differences in Cr content. We first hypothesized that the larger surface area of
522 smaller FMNs might lead to an increase of chromium absorption compared to larger nodules. However,
523 scanning electron microscopy pictures (unpublished data) revealed an absence of circular or ring-like
524 structures within the FMNs, and the external layers displayed no noticeable chromium enrichment.
525 FMNs probably formed in one step rather than gradually evolving from smaller to larger sizes. This
526 suggests that higher chromium concentrations might have been found in the soil solutions during the
527 genesis of the smaller FMNs, thereby facilitating chromium accumulation. To validate this hypothesis,
528 further experiments such as CBD extraction from FMNs of varying sizes and the application of
529 methodologies like C^{14} are essential. Regarding the FMNs stability with time, Cornu et al. (2009)
530 showed that Fe oxides in FMNs were not dissolved by redox shifts. Additionally, Quantin et al. (2002)
531 demonstrated that well-crystalline Fe oxides resist to bacterial reduction and reducing conditions,
532 while amorphous and poorly crystalline Fe oxides do not. Given that Cr in our FMNs is mostly carried
533 by crystalline Fe oxides (i.e. goethite, Fig. S1), the FMNs may be stable against soil redox oscillation
534 at later stages, thus minimizing the risk of Cr release. However, further dissolution experiments are
535 needed to confirm this hypothesis, as FMNs from different soils or regions display distinct features
536 and may exhibit variations in their dissolution behavior.

537 Secondly, for the surrounding soils, where iron oxides are amorphous or weakly crystalline, the
538 $\Delta^{53}\text{Cr}_{\text{FeO-ReS}}$ is almost null in the non-paddy soil profile while it is variable and maximal in the
539 waterlogged horizon (Brg) in the paddy soil profile. This limited $\Delta^{53}\text{Cr}_{\text{FeO-ReS}}$ could potentially be
540 attributed to fractionation caused by preferential uptake of Cr (VI) by surface vegetation. This uptake
541 may occur through phosphate or sulfate carriers due to the structural resemblances they share with Cr
542 (VI) (Ao et al., 2022a), finally leaving behind Cr (III) enriched in lighter isotopes in the soil. However,

this hypothesis fails to elucidate the observed variations in $\delta^{53}\text{Cr}$ values within non-cultivated horizons, where the penetration of plant roots is restricted. Moreover, as discussed earlier, we have demonstrated that the Cr output flux caused by plant uptake does not have a significant impact on soil Cr stock and, thus, should have a limited influence on the soil chromium isotope signatures.

Alternatively, the presence of more soluble Cr (III) species, such as organic-Cr (III) complexes, in the surrounding soils might also contribute to the limited $\Delta^{53}\text{Cr}_{\text{FeO-ReS}}$. Previous researches have demonstrated that soil acidity and organic matter facilitate the dissolution of Cr (III)-bearing minerals (Li et al., 2022; Sun et al., 2022).

For the Litang paddy soil profile, the limited $\Delta^{53}\text{Cr}_{\text{FeO-ReS}}$ of the surrounding soils in the upper part may be attributed to the unique drainage characteristics of this profile, as discussed in the section 4.2. This specific drainage system could have led to the removal of a portion of isotopically heavy Cr (VI) from the soil solution in the upper part of the profile through drainage. Consequently, the soil iron oxides in this region are unable to capture this portion of Cr, resulting in lighter $\delta^{53}\text{Cr}$ values and lower Cr concentrations (Fig. 3a) compared to the Brg horizon. Furthermore, Bonneville et al. (2009) and Quantin et al. (2002) established that amorphous and weakly crystalline forms of iron oxides exhibit greater solubility compared to their crystalline counterparts. Soil incubation experiments have demonstrated that during anaerobic phases, the reduction of Fe (III) oxides not only releases structurally bound chromium but also induces the breakdown of soil aggregates and the dissolution of organic matter. This process indirectly mobilizes chromium (Zhang et al., 2023). Conversely, in aerobic conditions, the oxidation of Fe (II) to form Fe (III) oxides, followed by subsequent recrystallization, initiates the reaggregation of soil colloids, leading to the incorporation of chromium. Therefore, the variability of $\delta^{53}\text{Cr}$ within the FeO fraction of the surrounding soils in this profile may also be directly linked with the dynamics of redox conditions. Based on their lower crystallinity (as evidenced by the absence of iron oxide minerals detected by XRD, Fig. 1) than in FMNs (Cornu et al., 2009), the Fe oxides within the surrounding soils are expected to exhibit higher solubility and reactivity, potentially leading to variations in $\delta^{53}\text{Cr}$ values. The highest $\delta^{53}\text{Cr}$ value and CBD-extractability of Fe, Mn, and Cr measured in the waterlogged horizon (Brg, 45-70 cm) imply repetitive cycles of iron oxide dissolution, Cr oxidation by Mn oxides and subsequent sequestration on Fe oxides, resulting in

elevated $\delta^{53}\text{Cr}$ values. Indeed, it has become clear that Cr (III) oxidation is constrained by its inability to diffuse and be sorbed onto the surface of Mn oxides (Liang et al., 2021b). The waterlogged conditions in this region may facilitate such diffusion and promote the sorption of Cr (III) onto Mn oxides. Meanwhile, the neutral pH conditions prevalent in this area contribute to a negatively charged surface of Mn oxides, enhancing the adsorption of trivalent Cr (e.g., Cr^{3+} , $[\text{CrOH}]^{2+}$), thus the possibility for Cr (III) to be oxidized. However, in Ferralsols derived from ultramafic rocks in Brazil, it has been shown that the Cr (VI) generated through the oxidation of Mn oxides may subsequently adsorb onto the soil matrix (i.e. Fe oxides) and be chemically extractable by KH_2PO_4 . Therefore, this portion of highly mobile Cr (VI), associated with fine Fe oxide particles, may be transported via post-rainfall runoff, potentially causing harmful environmental effects (Garnier et al., 2013). Such a process cannot be ruled out in our surrounding soils giving the instability of Fe oxides, coupled with the reactivity of Mn oxides. Thus, the toxicity and mobility of Cr (VI) underscore potential environmental threats, particularly concerning groundwater. Therefore, further studies, including KH_2PO_4 extraction of Cr (VI), dissolution studies of FMNs vs. surrounding soils, and particularly those employing synchrotron XAS (X-ray absorption spectroscopy) to examine the speciation of Cr, Mn, and Fe, will provide more precise information regarding valence, or speciation. This will greatly enhance our understanding and interpretation of Cr isotope variations and the cycling of chromium within the soil profile.

5. Conclusions

This study represents the first integration of CBD extraction experiments and chromium isotope techniques to investigate the dynamics, redistribution, and chromium isotopic fractionation within FMNs-rich red soil profiles in southwest China, including non-paddy and paddy soil profiles. The chromium isotope characteristics of soil nodules, a distinctive soil fraction, are also presented for the first time. Our results show that Cr in the red soils is primarily of geogenic origin, deriving from the weathering of the colluvium parent minerals. The effect of land use (non-paddy vs. paddy) is modest on the distribution and/or mobility of Cr within the red soils. FMNs of varying sizes consistently exhibit higher Cr concentrations compared to the surrounding soils, along with more positive $\delta^{53}\text{Cr}$ values and are considered as pedological archives not reactive to current physicochemical conditions.

Iron oxide extraction technique shows that both FMNs and surrounding soils consistently exhibit heavier signatures in the oxide than in the residual fraction. It suggests the significant capture of isotopically heavy Cr (VI) from soil solution by Fe oxides. Additional variability of $\delta^{53}\text{Cr}$ observed in the amorphous iron oxides recently precipitated in an active paddy soil demonstrates the dominant control of soil hydrology on driving the soil redox conditions and thus Cr other redox-sensitive element dynamics. Contrary to FMNs, which are supposed relatively stable under current physicochemical conditions, the long-term persistence of amorphous iron phases in red soils is more questionable. These findings underscore the potential of chromium isotopes as a tool for tracing chromium dynamics within natural soil systems, particularly those abundant in redox features. However, they also indicate that considerable variations in chromium isotope features resulting from these redox processes might obscure information regarding chromium pollution sources. Nonetheless, conducting further investigations, encompassing dissolution experiments, chromium speciation in soil solutions, analysis of chromium isotope characteristics, and acquiring in-situ data on chromium and iron speciation using synchrotron analysis, will significantly enhance our understanding of soil chromium stability and dynamics. Addressing the absence of chromium content and isotope characteristics in vegetation, especially in crops like rice plants, emerges as a crucial avenue for future investigation. Overcoming this limitation will significantly bolster our ability to provide a more direct and comprehensive response to regional food security concerns related to chromium. To achieve this, forthcoming studies could focus on extensive sampling and analysis of chromium content and isotopic signatures in various plant species, particularly those prevalent in regions with heightened chromium exposure. Additionally, conducting controlled greenhouse experiments or field studies aimed at elucidating chromium uptake, translocation, and accumulation mechanisms within plant tissues will be pivotal. These future endeavors hold the promise of shedding light on the role of vegetation as a potential indicator and reservoir of chromium contamination, thereby contributing significantly to strategies aimed at mitigating environmental and agricultural implications linked to chromium pollution.

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1 Table 1

2 Soil key physicochemical properties.

Profile	Horizon	pH	SOM	Density	CEC	Clay	Slit	Sand	FMNs distribution				ba*
									> 5 mm	2-5 mm	1-2 mm	Total	
									g/kg bulk				
			g/kg	g/cm ³	cmol/kg	%							
Wangling Non-paddy	A	4.9	30.9	1.5	12.4	37.5	23.2	39.3	177	500	82	759	0.02
	B	4.7	19.8	1.7	17.8	40.0	22.5	37.5	87	613	55	755	0.02
Wangling Paddy	Ap1	6.2	49.7	1.3	15.0	34.0	32.4	33.6	81	262	61	404	0.05
	Ap2	7.3	37.9	1.6	14.9	23.0	39.9	37.1	108	310	45	463	0.05
	AB	7.3	16.9	1.7	11.8	23.0	31.4	45.6	124	334	47	506	0.04
	Br1	7.4	12.0	1.5	21.1	33.0	27.9	39.1	59	264	53	376	0.04
	Br2	7.2	8.4	1.2	20.1	37.0	27.4	35.6	42	231	101	374	0.04
Litang Non-paddy	A	7.0	25.7	1.4	12.0	16.0	33.9	50.1	124	411	75	610	0.07
	AB	7.1	26.5	2.0	15.5	39.0	27.2	33.8	274	421	26	721	0.05
	B	7.4	15.4	1.7	16.5	36.0	27.5	36.5	254	403	25	681	0.06
Litang Paddy	Ap1	6.5	50.3	0.9	15.3	28.0	51.0	21.0	15	36	3	55	0.19
	Ap2	7.3	31.1	1.5	15.9	25.0	51.9	23.1	11	28	5	44	0.19
	AB	7.4	16.6	1.8	20.5	35.0	41.7	23.3	10	33	4	47	0.16
	Brg	7.1	12.7	1.7	23.4	39.0	38.4	22.6	35	107	17	158	0.12
	Br	7.2	6.7	2.3	24.1	39.0	24.4	36.6	124	291	36	451	0.09

3 *ba: the soil-weathered eluviation coefficient. FMNs: iron-manganese nodules.

4

5 Table 2

6 Element and Cr isotope compositions of irrigation waters, rocks, and fertilizers.

Element		Irrigation water		Rock			Fertilizer						
		Wangling	Litang	Carbonate1	Carbonate2	Calcite	F0 (NPK 45%, 15-15-15)	F1 (NPK 51%, 17-17-17)	F2 (NPK 45%, 15-15-15)	F3 (NPK 45%, 15-15-15)	F4 (NPK 45%, 15-15-15)	F5 (NPK 45%, 15-15-15)	F6 (NPK 30%, 18-5-7)
$\delta^{53}\text{Cr} \pm 2\text{SD}$	‰	1.47 ± 0.06	0.16 ± 0.02	1.30 ± 0.07	0.72 ± 0.04	1.01 ± 0.03	0.34 ± 0.01	0.33 ± 0.07	0.36 ± 0.04	1.49 ± 0.12	0.44 ± 0.04	0.11 ± 0.03	0.45 ± 0.04
P	g/kg	bdl	0.001	bdl	bdl	0.002	66.9	72.4	62.5	75.5	62.6	70.1	18.2
K		0.004	0.02	0.003	0.01	0.01	127.7	139.0	133.0	118.9	128.0	117.2	55.9
Ca		0.06	0.06	395.9	395.3	209.5	7.6	8.7	8.8	1.8	9.3	11.4	8.9
Mn		bdl	0.001	2.7	2.7	16.2	724.1	400.7	574.2	88.1	421.0	162.4	100.6
Fe		bdl	0.002	46.8	45.2	175.6	7026.5	4149.2	5323.7	796.8	4353.3	2121.4	2238.3
Cr	µg/kg (ug/L for water samples)	0.07	0.28	3876.8	3836.2	4037.6	19980.5	22300.5	21552.7	8862.1	23074.1	16408.4	25792.8

7 bdl=blow detection limit.

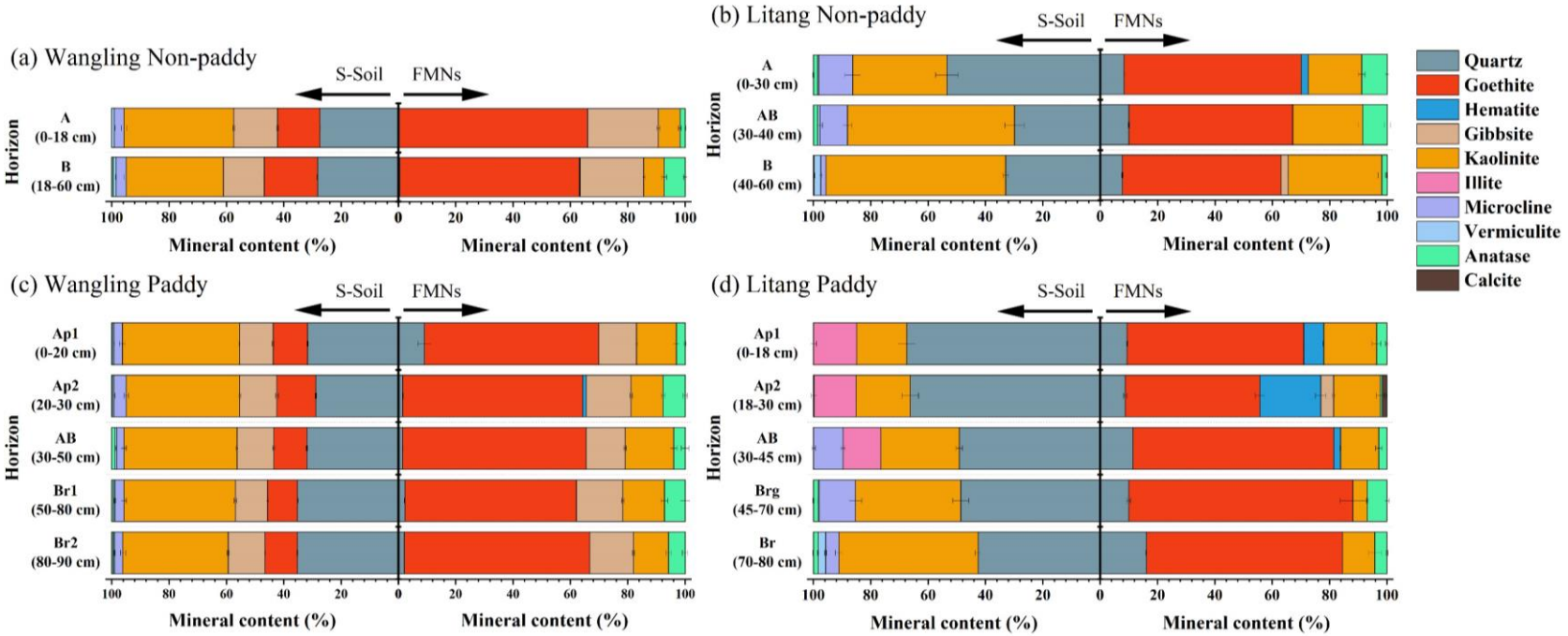


Fig. 1. Variations in mineral content obtained by XRD analysis of the surrounding soils and FMNs (bulk of all sizes) in non-paddy and paddy profiles of Wangling and Litang. S-Soil: surrounding soil, FMNs: iron-manganese nodules.

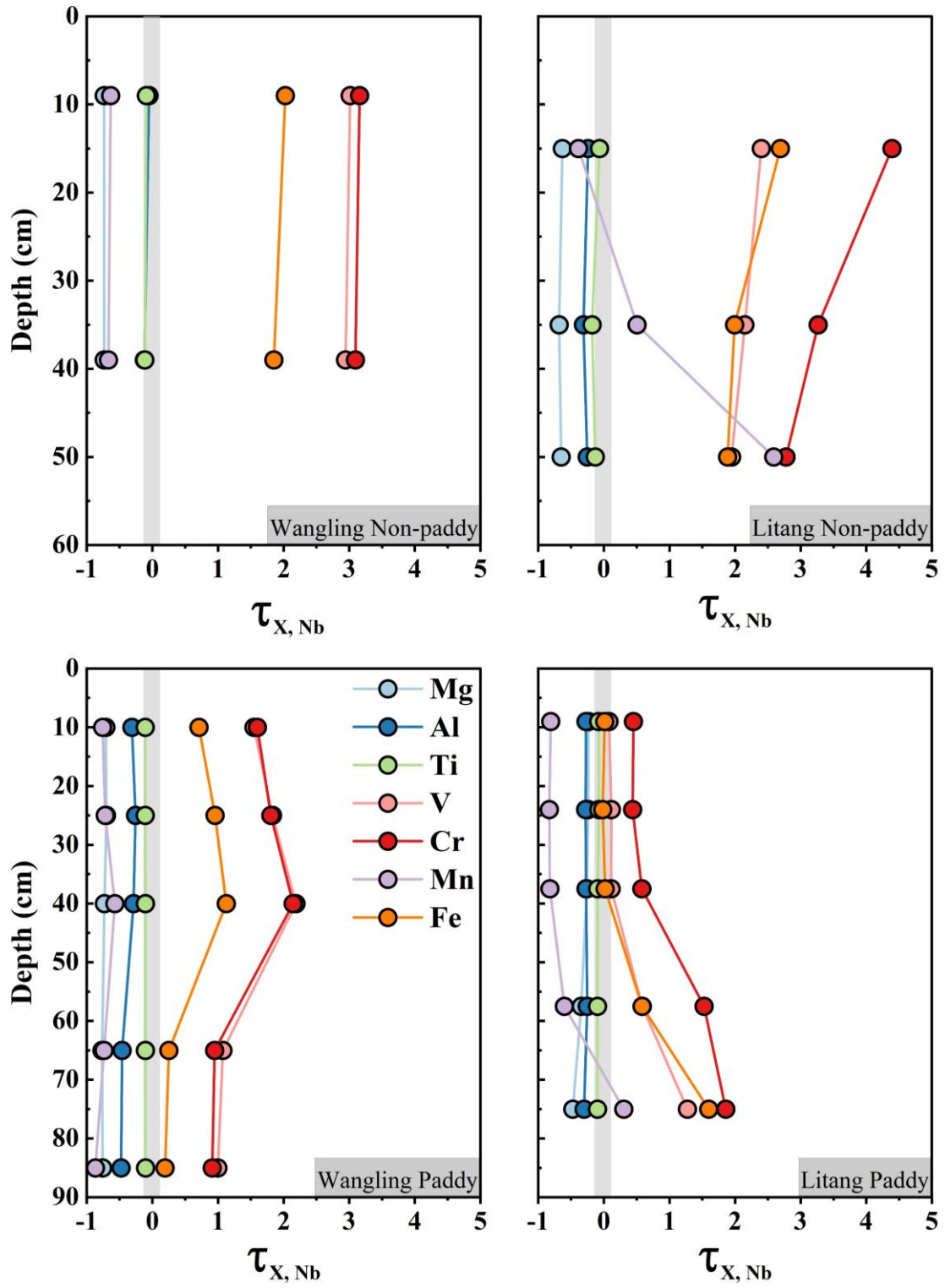
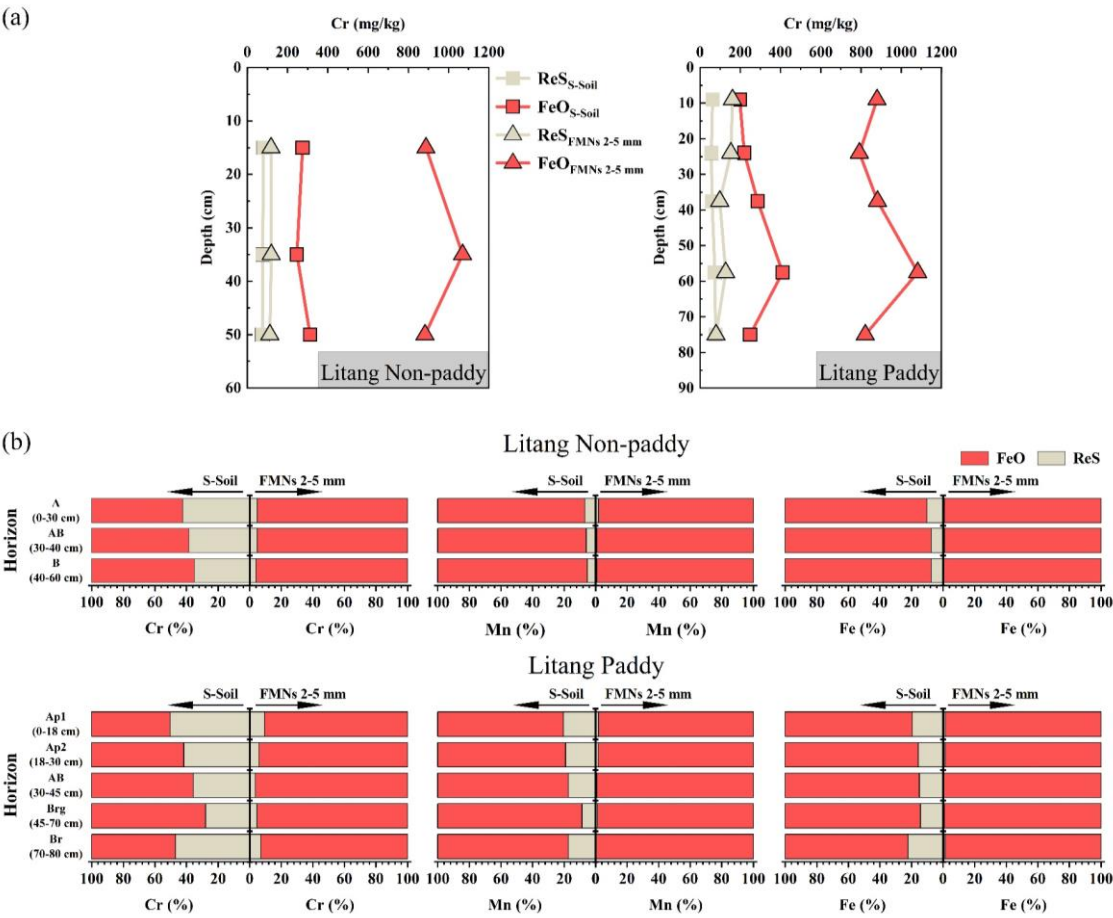


Fig. 2. Key element mass balance coefficients ($\tau_{X, Nb}$) in the non-paddy and paddy soil profiles of Wangling and Litang.



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Fig. 3. CBD extraction results of (a) Cr concentrations of residue (ReS) and extract (FeO). (b) Relative distributions of Cr, Mn, and Fe between ReS and FeO in the surrounding soils and FMNs 2-5 mm in Litang soil profiles. S-Soil: surrounding soil, FMNs: iron-manganese nodules.

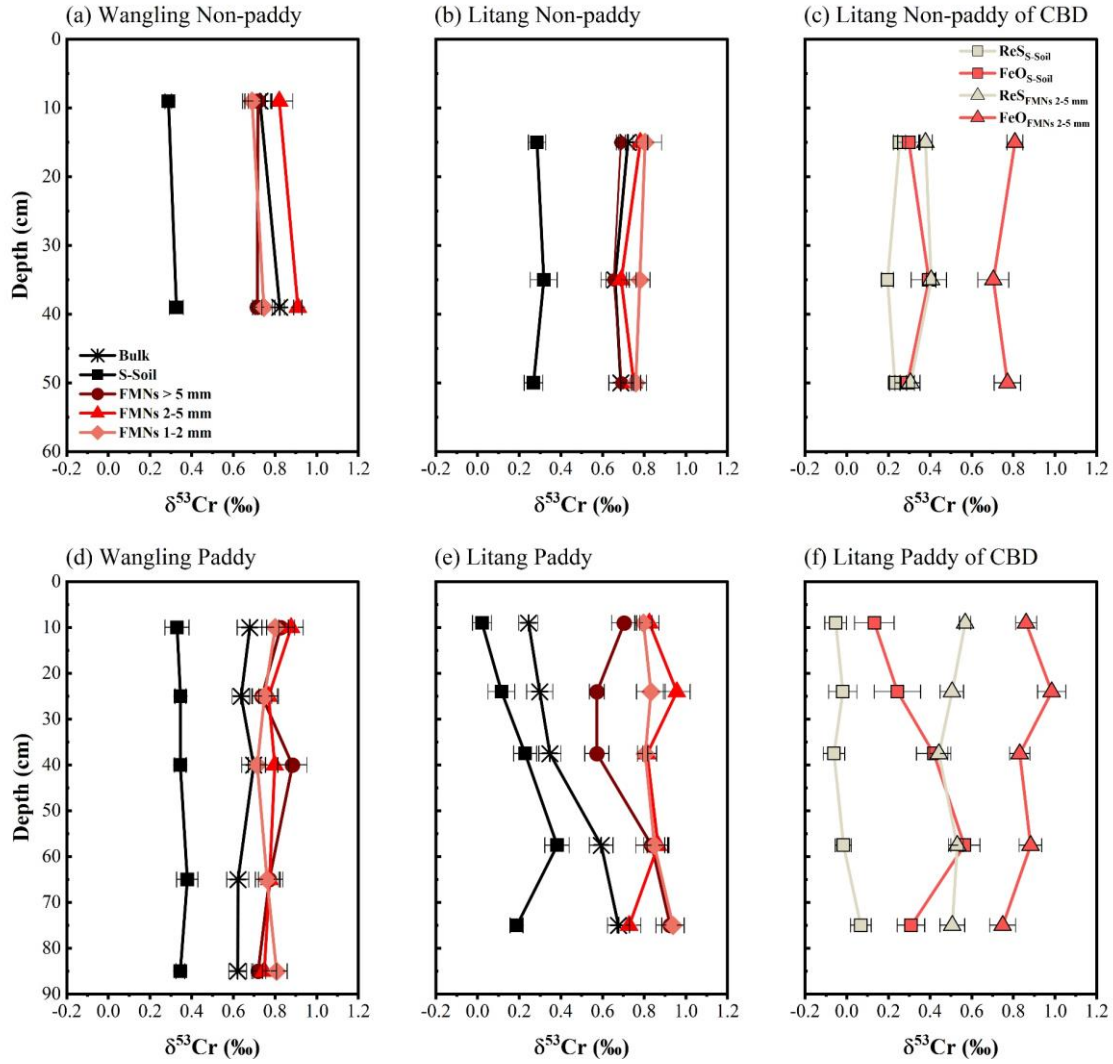


Fig. 4. Chromium isotope composition of samples in non-paddy and paddy profiles of Wangling, Litang before and after CBD extraction. Bulk: the bulk soil containing FMNs and surrounding soil, S-Soil: surrounding soil, FMNs: iron-manganese nodules, ReS and FeO: the residue and extract of CBD extraction, respectively. The error bars show the 2SD uncertainty derived from repeat measurements.

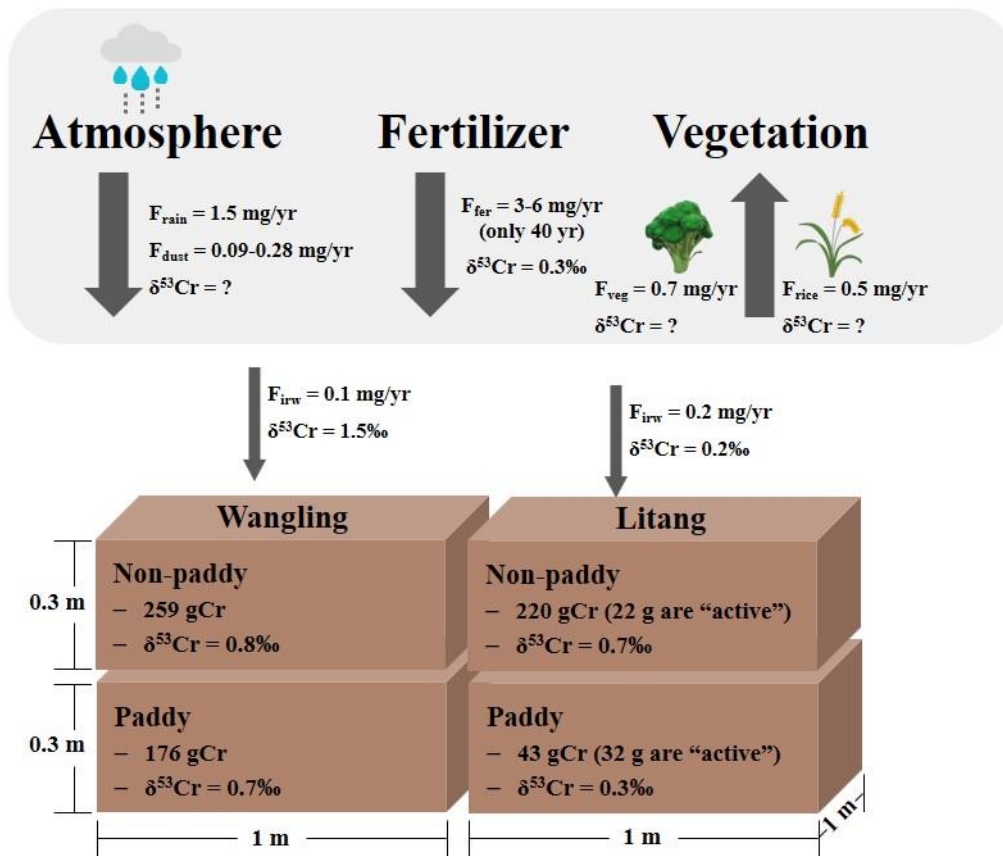


Fig. 5. Fluxes and stocks of Cr in the soil profiles of cultivated soil horizon in 0.3 m³ box at Wangling and Litang. F_{rain} : rainwater Cr flux, F_{dust} : human-derived dust Cr flux, F_{fer} : fertilizer Cr flux, F_{veg} : vegetable Cr flux in non-paddy field, F_{rice} : rice Cr flux in paddy field, F_{irw} : irrigation water Cr flux.

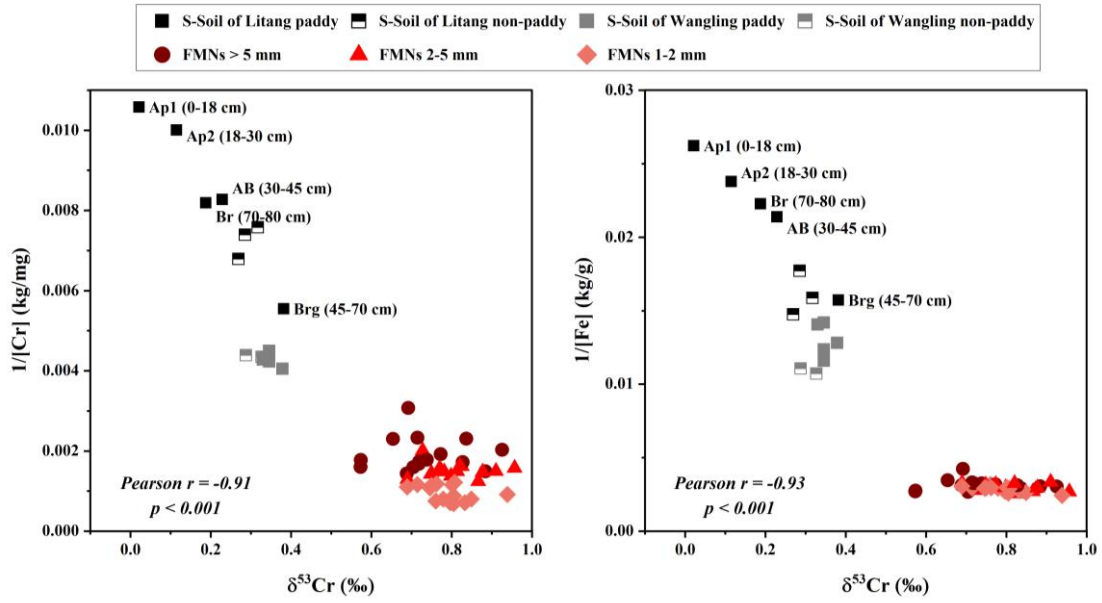
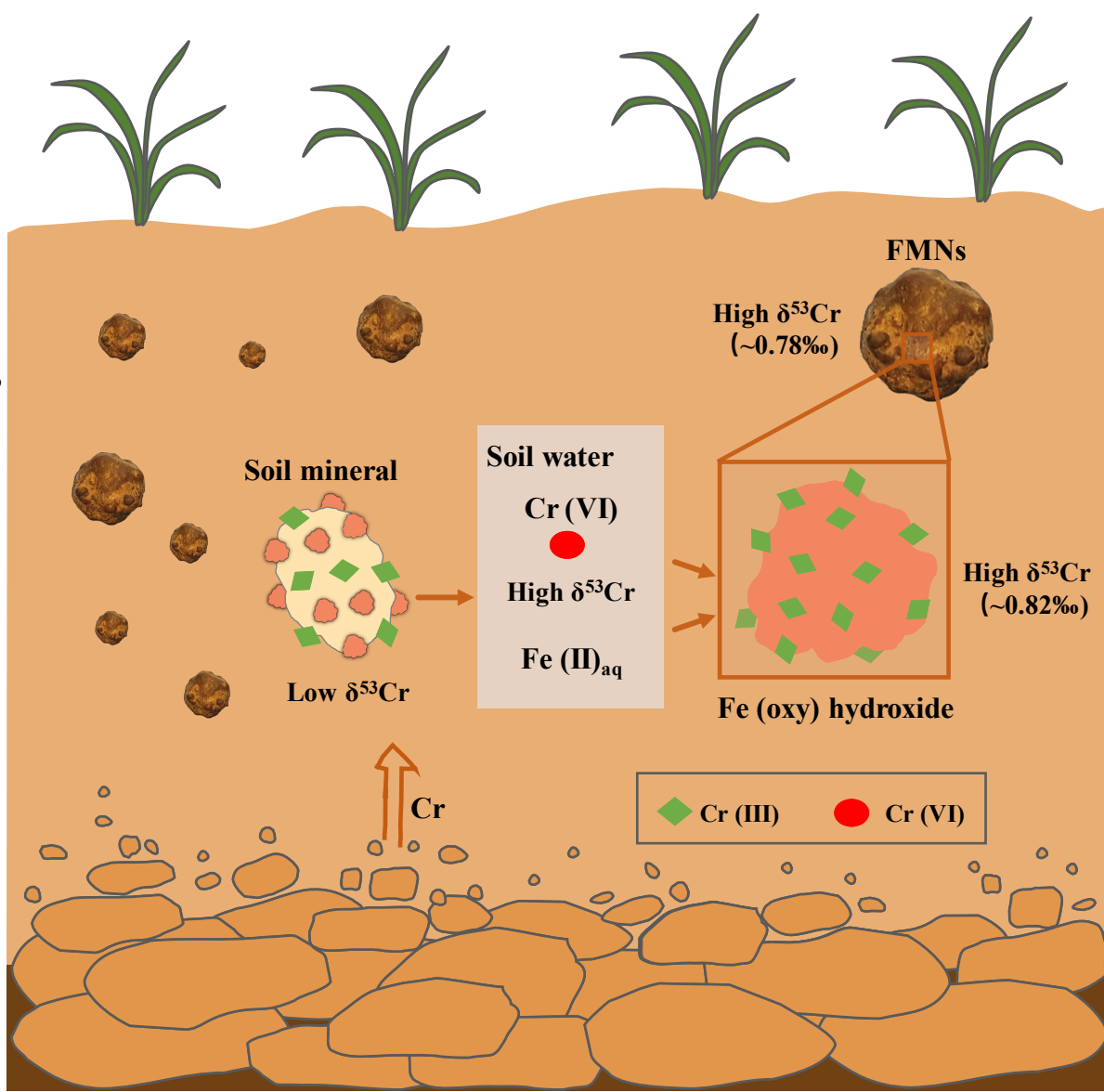


Fig. 6. $\delta^{53}\text{Cr}$ values vs $1/[\text{Cr}]$ and $1/[\text{Fe}]$ of the surrounding soils and FMNs of different sizes in Wangling and Litang. S-Soil: surrounding soil, FMNs: iron-manganese nodules.

Environmental Implication

The existence of iron-manganese nodules (FMNs) in soil plays a crucial role in addressing soil pollution, especially when it comes to heavy metals. Our research demonstrates that FMNs found in red soils effectively capture and secure substantial quantities of the more easily movable and harmful form of chromium called Cr (VI), which also happens to be heavier in terms of its isotopic properties. This mainly happens because of the dominant presence of iron oxide in FMNs. This process significantly lowers the risk of chromium contamination in the red soils of the area we studied. Nevertheless, it's essential to stress the importance of further investigation into how stable these non-crystalline forms of iron oxide-bound chromium are in the surrounding soils over a long period.

S-Soil
 $\delta^{53}\text{Cr}$: 0.02-0.38‰



Colluvium parent
materials

Highlights

- Cr isotope data in soil FMNs is reported for the first time.
- FMNs/Fe oxides capture isotopically heavy Cr (VI).
- Redox and not land use drives Fe oxide formation and FMNs, affecting Cr mobility.
- Cr in red soil profiles mainly results from colluvium mineral weathering.