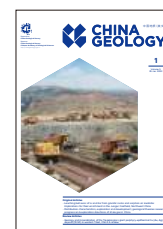




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## Effects and mechanism of igneous rock on selenium in the tropical soil-rice system in Hainan Province, South China

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### ABSTRACT

To illuminate the migration and transformation of selenium (Se) in the igneous rock-soil-rice system, 285 pairs of rhizosphere soil and rice samples were collected from the granitoid and basalt areas in Hainan Province, South China. The contents of Se in soils derived from granitoid and basalt are, respectively,  $0.19 \pm 0.12$  mg/kg and  $0.34 \pm 0.39$  mg/kg, which are much higher than Se contents in granitoid and basalt. Selenium shows remarkable enrichment from granitoid and basalt to soils. The mobile fraction of Se in soils derived from granitoid is  $0.0100 \pm 0.0034$  mg/kg, which is significantly higher than that of basalt ( $0.0058 \pm 0.0039$  mg/kg). Although soil derived from basalt shows higher Se contents, Se contents in rice samples, mobile fractions of Se in soils, and biological concentration factor (BCF) is similar or even lower than that from granitoid. Basalt consist of calcic plagioclase and pyroxene, and are much richer in Fe, Al, and Ca than granitoid. Correspondingly, the basalt-derived soils have higher goethite, hematite, kaolinite, cation exchange capacity (CEC) content, and higher pH than the granitoid-derived soils, which result in higher adsorption capacity for Se and relatively lower Se bioavailability. Soils derived from granitoid and basalt in tropical regions are beneficial to produce Se-rich rice.

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## 1. Introduction

Selenium is an essential nutrient for human health in trace amounts. In organisms, Se serves as an antioxidant preventing the damage caused by reactive oxygen species and plays a crucial role in reducing the incidence of cancer and cardiovascular disease (Navarro-Alarcón M and López-Martínez MC, 2000; Rayman MP, 2012). The selenium-rich (Se-rich) crops, such as rice, wheat, and corn, are an effective approach for Se intake. The 1 : 250000 geochemical survey on national land quality has found about 298000 km<sup>2</sup> Se-rich land, and the exploitation and utilization are energetically promoted. However, there is generally some inconsistency between the occurrence of Se-rich soil and Se-rich crops. For example, the proportion of Se-rich soil was up to 75%, while

the proportion of Se-rich rice was only 24% in shale and carbonate areas in Sichuan Province (Liu XJ et al., 2020). Contrasting results have been reported for granitoid and basalt areas in Hainan Province, where Se-rich soil accounts for 29%, and the proportion of Se-rich rice reaches up to 82% (Li Z et al., 2016). Therefore, the migration and transformation of selenium in the soil-rice system has become a research topic and has an important significance on the exploitation of Se-rich agricultural products.

It is well known that the parent rocks play crucial roles in the Se concentration of soils. Organic-rich sedimentary rocks, such as shales, coals, and mudstones, are commonly rich in Se (Zhu JM et al., 2014; Tian XL et al., 2017). As a consequence, soils derived from these rocks also have high Se concentrations, which could be observed in many countries including China (particularly in Enshi and Ziyang cities), Australia, India (particularly in the Punjab region), Ireland, and the USA (Dhillon KS and Dhillon SK, 2003, 2014; Zhu J et al., 2008; Eiche E et al., 2015; Tian H et al., 2016; Chang CY et al., 2019). Igneous rocks commonly have low Se

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concentration (Wells N, 1967; Xia WP and Tan JA, 1990; Fan HF et al., 2008), therefore, the Se content in corresponding soils is also relatively low (Wu J, 2018). However, the effects and mechanism of igneous rocks on Se content and bioavailability of soils are still unclear. In South China, Mesozoic and Cenozoic granitoid and basalt are widespread (Sun T, 2006; Gong JF, 2012; Chen XY, 2014; Shu XJ, 2014), and the humid tropical condition are favorable for chemical weathering of granitoid and basalt to soil (Huh Y, 2003; Liu ZF et al., 2012).

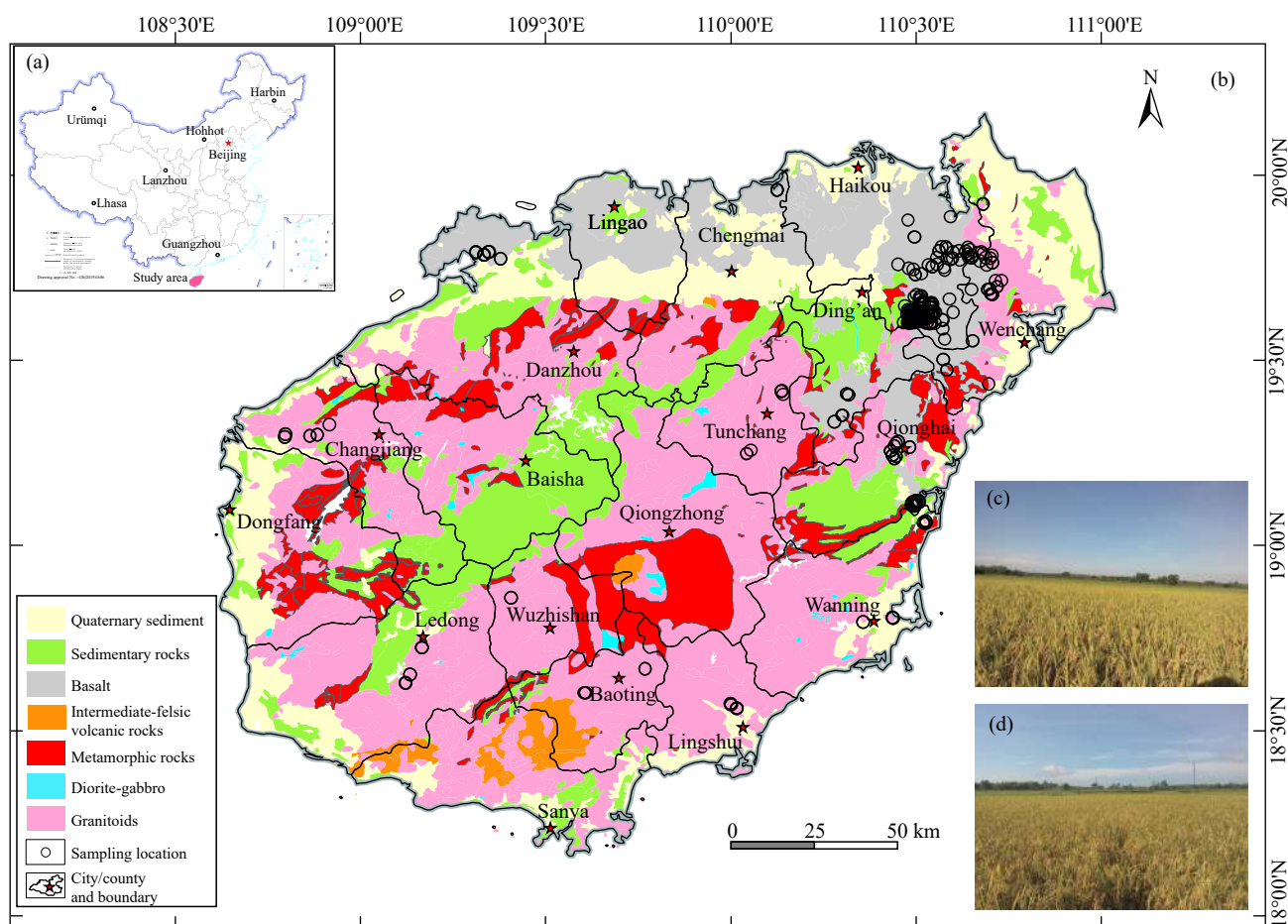
In Hainan Province, granitoid and basalt were pervasively distributed, and the exposed area of which account for 40% and 14% of the land surface, respectively (Yang ZF et al., 2012; Wen SN, 2013). Rice is the main grain crop and staple food in Hainan Province. Previous studies have reported Se contents in soils or crops, especially paddy rice in local areas in Hainan Province (Geng JM et al., 2012; Yang ZF et al., 2012; Wang DF et al., 2014; Zhang DM et al., 2017; Hao Z et al., 2018; Xu WQ et al., 2018), and preliminarily discussed effects of pH, organic matter or cation exchange capacity (CEC) on Se contents in soils (Geng JM, 2010; Yang ZF et al., 2012; Li Z et al., 2017; Qin HB et al., 2017). However, few studies have focused on the difference of Se content and bioavailability in soils between granitoid and basalt area, as well as the effect and mechanism of igneous parent rocks on distribution features of Se in rhizosphere soil-rice system.

In this study, 285 pairs of rhizosphere soil and rice samples in Hainan Province were investigated to illuminate the distribution characteristics of selenium content and bioavailability in soils derived from different parent rocks. The authors further discuss the control of mineral and geochemical features of parent rocks on Se content and biological concentration factor (BCF) in soil-rice systems.

## 2. Geological background

Hainan Province is located in the southernmost of South China (Fig. 1a), between 18°10'N–20°10'N and 108°37'E–111°03' E. The area is characterized by a tropical monsoon climate and has an average annual precipitation of 1639 mm and an average annual temperature of 23–26°C. From the center to the periphery, the landscape changes from mountains to hilly areas, plateaus, and floodplains, forming an annular stratiform landform.

Permian–Late Cretaceous granitoid and Pleistocene basalt are the most common igneous rocks in Hainan Province (Fig. 1b). The granitoid consists of granite, monzonitic granite, and granodiorite, which are mainly composed of quartz, sodium plagioclase, and alkali feldspar, and contain minor biotite and hornblende (Ge XY, 2003). The basalt is predominantly tholeiitic basalt and trachybasalt, which contain pyroxene, calcic plagioclase with minor alkali feldspar, and olivine (Mei



**Fig. 1.** a–Location of Hainan Island; b–geological map showing the distribution of rocks and sample locations; c–photos of rice grown in granitoid-derived soils; d–photos of rice grown in basalt-derived soils.

SW, 2018).

The soils derived from granitoid and basalt area have generally been used for growing rice (Fig. 1c and 1d), which is a major land use in Hainan Province.

### 3. Materials and methods

#### 3.1. Sampling

The rhizosphere soil and rice grain samples were collected from rice paddy fields in the northeastern part of Hainan Island (Fig. 1). The rice grain was washed with tap water and then rinsed with deionized water more than three times, put into a carnelian mortar after being dried, and ground to 0.149 mm for analyzing total Se content. The soil samples were collected from the root zone of the rice samples, air-dried and homogenized, and then crushed before passing through a 2 mm sieve for pH analysis and a 100-mesh sieve for other physicochemical analyses, total and available content of Se.

#### 3.2. Analytical methods

The 285 sets of soil and rice samples were analyzed for Se content and soil pH, and then 25 soil samples were selected to measure available Se content and other physicochemical properties.

The sample preparation, chemical treatment, and analysis were conducted in Hebei Geological Experiment and Testing Center. The soil pH was measured with deionized water (1 : 2.5, w/v) using a pH meter. Soil organic matter was measured with potassium dichromate sulfuric acid titration. CEC was determined by the method of ammonium acetate exchange. Soil particle distribution was obtained by a laser particle size analyzer.

To measure the chemical composition and the total amount of Se in soil, samples were digested in a mixture of concentrated  $\text{HNO}_3$ ,  $\text{HClO}_4$ , and  $\text{HF}$  ( $V_1 : V_2 : V_3 = 8 : 1 : 8$ ) in an electrothermal furnace at  $180^\circ\text{C}$  until the resulting solution volume was  $<1$  mL. The residue was transferred to a 25 mL test tube and diluted with deionized water. The contents of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ , and  $\text{Na}_2\text{O}$  were determined by inductively coupled plasma optical emission spectrometry (Agilent 725). The content of Se was analyzed by Atomic Fluorescence Spectroscopy (AFS-3000).

The mobile Se fractions were analyzed by the sequential extraction method. 2.5 g soil sample and 25 mL extracting agent were shaken for 30 mins at  $25^\circ\text{C}$ , and then centrifuged at 4000 rpm for 20 mins and filtered. The extracting agents and their operationally defined fractions are presented in Table 1. The Se contents of geochemical fraction were

analyzed by Atomic Fluorescence Spectroscopy (AFS-3000). The detection limits of soluble, ion exchangeable and carbonate-bound Se fraction are 0.005 mg/kg, 0.010 mg/kg and 0.005 mg/kg, respectively.

The rice samples were digested using a mixture of 4 mL nitric acid ( $\text{HNO}_3$ ) and 2 mL hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and the digestion tubes were kept overnight at room temperature ( $25^\circ\text{C}$ ). Acid digestion was conducted at  $190^\circ\text{C}$  in an automatic temperature control furnace until the digestion solution became clear. After acid digestion, sample solutions were cooled and transferred into a 30 mL volumetric flask with deionized water. The Se content of rice samples was analyzed by an inductively coupled plasma mass spectrometer (Agilent 7700x).

#### 3.3. Analytical quality control

To ensure the accuracy and precision of analytical results, internal and external controls were implemented during routine analysis. The reagent blanks, duplicated samples, and national standard reference materials (GBW07410 for soil and GBW10010 for rice grain) were analyzed with samples simultaneously for internal control. Good agreement was achieved between the certified values and the measured values for national standard reference materials. The relative standard deviation in duplicated samples is less than 5%. Blind reference materials were inserted in cipher and analyzed simultaneously with samples for external control. All the analysis of the cipher samples obtains satisfactory results.

#### 3.4. Statistical analyses

The median and standard deviation of the experimental data were calculated using Excel 2010 software, and statistical analyses and *t*-test were processed using the SPSS software. For the datasets, the Se content and bioavailability of soil were regarded as the dependent variable, respectively, and the other parameters were considered as independent variables (including contents of Fe and Al oxides, the content of clay minerals, CEC, pH, total soil S and Se content).

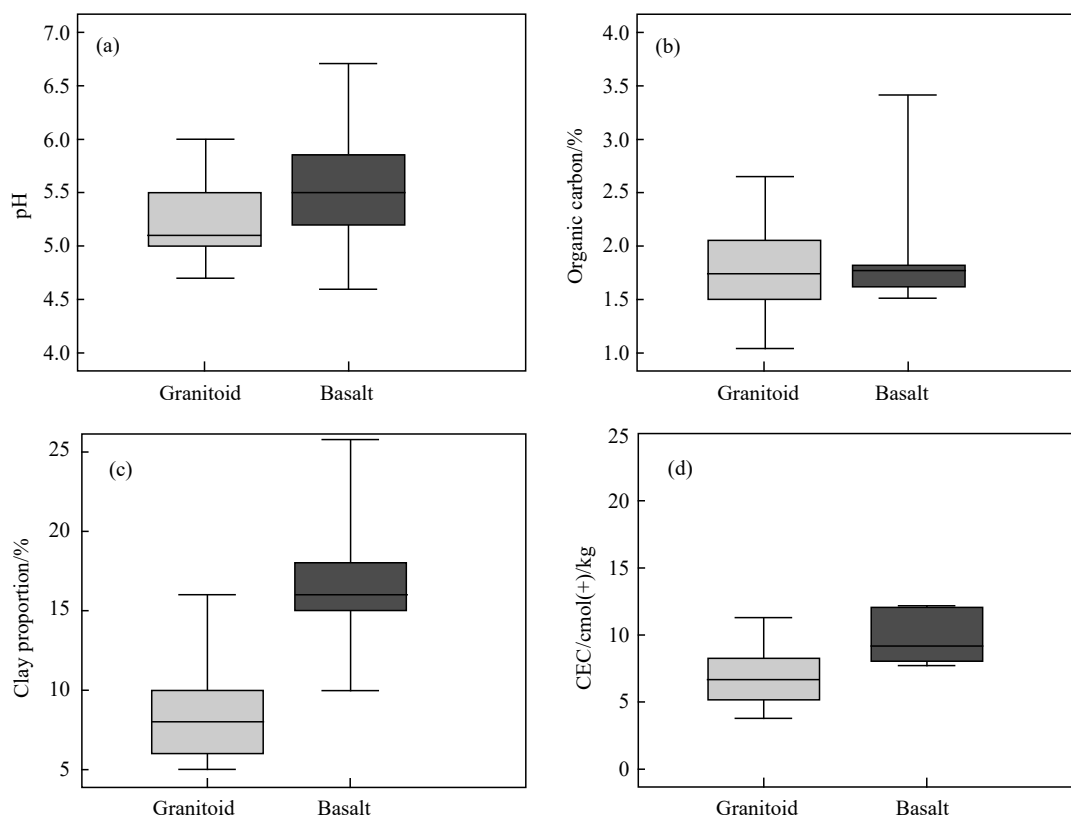
## 4. Results

#### 4.1. Soil properties and chemical composition

The physicochemical properties of the soils derived from granitoid and basalt in Hainan Province are shown in Fig. 2. The pH, organic carbon content, soil clay proportion, and CEC in soils derived from granitoid are 5.04–6.03, 1.04%–2.95%, 4.70%–16.50%, and 3.78–11.30 mol/kg, respectively. The pH, organic carbon content, soil clay

**Table 1.** Sequential metals geochemical fraction procedures and targeted metal forms.

Fraction	Targeted forms	Extractants	Equilibration
F1	Soluble fraction	Distilled water (pH 7.0)	25 mL, shaking for two hours at room temperature
F2	Ion exchangeable fraction	1M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (pH 7.0)	25 mL, shaking for two hours at room temperature
F3	Carbonate fraction	1M NaAc-Hac (pH 5.0)	25 mL, shaking for five hours at room temperature



**Fig. 2.** Tukey boxplots of pH (a), organic carbon (b), clay proportion (c), and CEC (d) in soils derived from granitoid and basalt.

proportion, and CEC in soils derived from basalt vary between 5.27–6.70, 1.51%–3.42%, 10.50%–25.90%, and 7.70–24.90 mol/kg, respectively. The *t*-test results show that pH, clay minerals, and CEC in soils derived from granitoid are significantly lower than that from basalt, while organic carbon content shows an insignificant difference between granitoid and basalt areas (Fig. 2).

The chemical composition of soils derived from granitoid and basalt are shown in Table 2. These soils are predominantly composed of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, with a small amount of TFe<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O, and minor amounts of MgO, CaO, and Na<sub>2</sub>O. In granitoid area, contents of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and TFe<sub>2</sub>O<sub>3</sub> in soils are 59.92%–77.33%, 8.57%–19.92%, and 1.74%–6.31%, respectively. In basalt area, soils have much lower SiO<sub>2</sub> (39.25%–59.18%) and higher Al<sub>2</sub>O<sub>3</sub> (12.91%–19.76%) and TFe<sub>2</sub>O<sub>3</sub> (8.95%–17.63%) contents.

The XRD analytical result shows that the clay minerals in both soils are mainly kaolinite, illite, and minor chlorite. The illite and chlorite contents of the soils were similar, but the granitoid-derived soils had lower kaolinite content than the basalt-derived soils (Table 3).

#### 4.2. Se content in rhizosphere soil-rice system

Se contents and BCF in rhizosphere soil-rice systems from different parent rocks are shown in Fig. 3 and Fig. 4. In the granitoid area, the soils have Se content ranging from 0.04 mg/kg to 0.72 mg/kg and a median content of 0.19 mg/kg (SD=0.12). According to the technical standard of “Delimitation and the logo for natural selenium-enriched

**Table 2.** Statistical summary of the chemical composition of rhizosphere soil in granitoid and basalt from Hainan Province, China.

Parent rocks	Oxides	Max/%	Min/%	Median/%	Mean/%	Standard deviation (SD)
Granitoid area	SiO <sub>2</sub>	77.33	59.92	73.79	70.21	6.04
	Al <sub>2</sub> O <sub>3</sub>	19.92	8.57	12.96	13.18	3.27
	TFe <sub>2</sub> O <sub>3</sub>	6.31	1.74	3.26	4.01	1.66
	FeO	2.95	0.87	1.57	1.67	0.54
	MgO	0.36	0.07	0.21	0.20	0.08
	CaO	0.33	0.09	0.16	0.19	0.06
	Na <sub>2</sub> O	0.30	0.04	0.14	0.15	0.07
	K <sub>2</sub> O	2.94	0.35	1.98	1.78	0.76
Basalt area	SiO <sub>2</sub>	59.18	39.25	51.13	51.05	7.86
	Al <sub>2</sub> O <sub>3</sub>	19.76	12.91	15.20	15.77	2.54
	TFe <sub>2</sub> O <sub>3</sub>	17.63	8.95	15.50	13.66	3.87
	FeO	6.94	2.00	5.70	4.80	2.08
	MgO	1.11	0.27	0.45	0.53	0.34
	CaO	1.47	0.18	0.25	0.48	0.55
	Na <sub>2</sub> O	1.42	0.06	0.18	0.39	0.58
	K <sub>2</sub> O	2.25	0.16	0.34	0.81	0.88

land” (DD 2019-10), the proportion of Se-rich soil is 10.97%. The rice samples have Se content ranging from 0.001 mg/kg to 0.21 mg/kg, and a median content of 0.07 mg/kg (SD=0.04), and a Se-rich proportion of 65.16%, which is according to the National Standard of “Rich selenium paddy” (GB/T 22499—2008). The BCF of Se in the soil-rice systems



**Table 3.** Statistical summary of clay minerals content of rhizosphere soil in granitoid and basalt from Hainan Province, China.

Parent rocks	Statistical value	Clay mineral content/%			Sample quantity
		Kaolinite	Illite	Chlorite	
Granitoid	Range	1–8	3–10	1–4	17
	Median	3	6	1	
	Mean	3	6	2	
Basalt	Range	1–8	5–14	1–6	16
	Median	5	8	2	
	Mean	5	9	3	

varies from 0.01 to 1.27 and had a median of 0.29 (SD=0.22).

The soils from the basalt area have Se contents between 0.01 mg/kg and 1.25 mg/kg with a median content of 0.34 mg/kg (SD=0.39), and a Se-rich proportion of 42.11%. The rice samples have Se contents varying from 0.001 mg/kg to 0.18 mg/kg with a median content of 0.06 mg/kg (SD=0.05), and Se-rich rice accounts for 71.05%. The BCF of Se in the soil-rice systems varies from 0.07 to 3.25, with a median value of 0.16 (SD=0.41).

The rhizosphere soil and rice samples in igneous areas are characterized by relatively low Se content in soil and high Se content in rice (Figs. 3, 4). The *t*-test results show that the Se content in the granitoid-derived soils was significantly lower than that in the basalt-derived soils, and that the BCF of Se in the granitoid area was significantly higher than that in the basalt area. The Se content in rice samples exhibit insignificant difference between the granitoid and basalt areas (Fig. 3). Fig. 4 also suggests that the granitoid-derived soils frequently have a lower Se content than the basalt-derived soils, whereas the Se content of the rice samples from the granitoid-derived soils was similar to or higher than that from the basalt-derived soils (Fig. 4).

#### 4.3. Mobile fractions of Se in rhizosphere soils

The soluble, exchangeable, and carbonate-bound Se contents in soils derived from granitoid are 0.0022–0.0114 mg/kg, 0.0004–0.0051 mg/kg and 0.0015–0.0038 mg/kg, respectively, while 0.0009–0.0034 mg/kg, 0.0004–0.0048

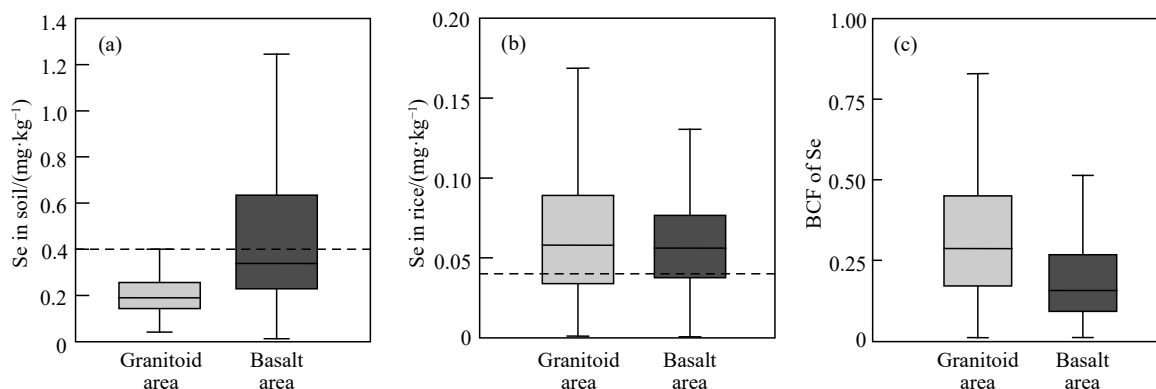
mg/kg and 0.0002–0.0031 mg/kg in the basalt-derived soils (Table 4). The *t*-test results indicate that the soluble, carbonate-bound, and mobile Se fractions in soils derived from granitoid are significantly higher than those from the basalt area. There is no significant difference in the ion exchangeable Se fraction and Se bioavailability between the granitoid- and basalt-derived soils.

### 5. Effects of parent rocks on selenium in rhizosphere soil-rice systems

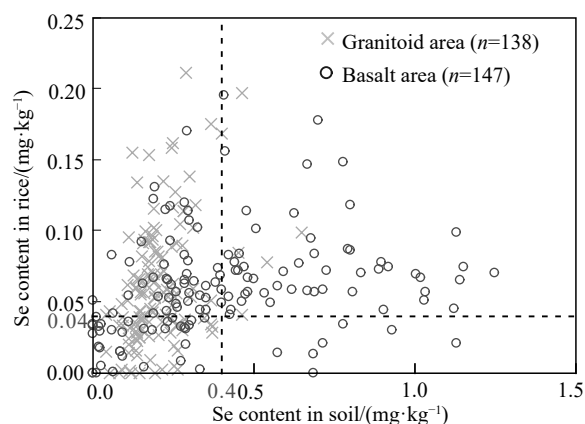
#### 5.1. Effects of Se content in parent rocks

The Se contents of igneous rocks are generally low and tend to decrease from mafic to felsic rocks because of magmatic differentiation (Song Q, 1983; Malisa EP, 2001). Granitoids commonly have the lowest Se contents (Luo SL, 2013). The total average Se contents of granitoids in China and the South China Orogenic Belt are both 0.02 mg/kg (Shi CY et al., 2008). Several studies have reported relatively high Se contents of 0.08–0.33 mg/kg in basalt, mainly tholeiitic and mid-ocean ridge basalt, with much higher Se contents in undegassed basalt (Hertogen J et al., 1980; Yi W et al., 2000; Lissner M et al., 2014; Forrest A et al., 2017; Yierpan A et al., 2019). Therefore, Basalt has much higher Se content than granitoid. Se contents are very low (about 0.08–0.13 mg/kg) in both crust and mantle (McDonough WF and Sun SS, 1995; Lorand JP et al., 2003; König S et al., 2012; Rudnick RL and Gao S, 2014). Selenium likely segregates from silicate melt as Fe-Se complexes similar to Fe-S and so its abundances in melt should be directly related to the FeO content (Yierpan A et al., 2019). Therefore, the higher Se contents in basalt are closely related to higher FeO contents.

Selenium mainly occurs in biotite during the crystallization of granitic melt, for biotite has a much higher ability to adsorb Se than quartz or feldspar (Alonso U et al., 2014; Videnská K et al., 2015; Li XD et al., 2018, and references therein). The Fe-minerals (e.g., Fe-oxides) in basalt exhibit specific sorption capacity for Se (Ticknor KV and McMurry J, 1996; Su C and Suarez DL, 2000; Peak D and Sparks DL, 2002; Duc M et al., 2003, 2006), while Fe-



**Fig. 3.** Tukey boxplots of Se content in soil (a), Se content in rice (b), and BCF of Se (c) in the soil-rice system from the granitoid and basalt areas. The BCF of Se is the ratio of Se in rice to Se in soil. The soil-rice sample numbers in granitoid and basalt areas are 138 and 147, respectively.



**Fig. 4.** Binary correlation diagram displaying characteristics of Se content in soil and rice from granitoid and basalt areas.

**Table 4.** Statistical summary of mobile fractions and bioavailability of Se in rhizosphere soils in granitoid and basalt from Hainan Province, China.

	Parent rocks	Max.	Min.	Median	Mean	SD
Soluble Se/(mg/kg)	Granitoid	0.0114	0.0022	0.0036	0.0049	0.0027
	Basalt	0.0034	0.0009	0.0020	0.0020	0.0011
Ion exchangeable Se/(mg/kg)	Granitoid	0.0051	0.0004	0.0025	0.0026	0.0011
	Basalt	0.0048	0.0004	0.0013	0.0018	0.0018
Carbonate-bound Se/(mg/kg)	Granitoid	0.0038	0.0015	0.0023	0.0025	0.0006
	Basalt	0.0031	0.0002	0.0018	0.0016	0.0013
Mobile fractions/(mg/kg)	Granitoid	0.0170	0.0049	0.0098	0.0100	0.0034
	Basalt	0.0107	0.0016	0.0058	0.0054	0.0039
Bioavailability/%	Granitoid	8.95	2.58	5.16	4.12	1.81
	Basalt	3.90	2.17	3.52	3.23	1.11

minerals (such as biotite) in granitic rocks show much weaker sorption capacity of Se (Tachi Y et al., 1998; Jan YL et al., 2008; Bruggeman C et al., 2012; Videnská K and Havlova V, 2012; Iida Y et al., 2014).

In this study, soils derived from granitoid have lower Se content than those derived from basalt (Fig. 3), which is consistent with the difference of Se content between the granitoid and basalt. Therefore, the Se content in the parent rock strongly influence the Se content in the corresponding soils. The Se content in the soils is also influenced by the sorption capacities of Se-containing minerals in the parent material; in this case, the sorption capacity was higher in the basalt than in the granitoid.

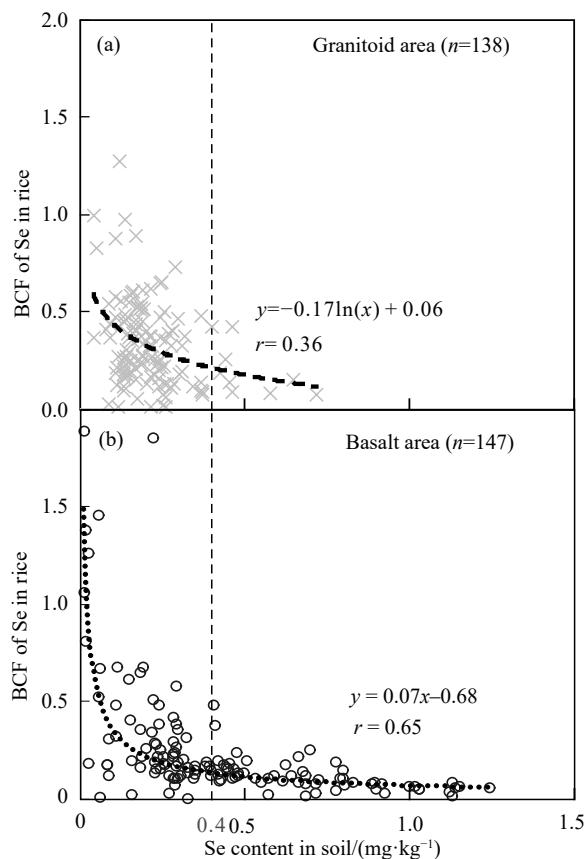
## 5.2. Effects of the mineralogical and chemical composition of parent rocks

The Se contents in soils are negatively correlated with the BCF of Se in both granitoid and basalt areas, with correlation coefficients of 0.36 and 0.65, respectively (Fig. 5). The adsorption and retention capacities of soil (especially organic matter and other soil colloids) on Se control the Se content and bioavailability in soil, and strong sorption on soil

compounds will cause soils enriched in Se, but with low Se bioavailability (Floor GH and Román-Ross G, 2012).

The amount of Se in soils is closely correlated with soil mineralogical composition (Winkel LHE et al., 2012). The components, which exert significant effects on adsorption of Se in soil and were inherited from the parent rock, are amorphous Fe and Al oxides and clay minerals (kaolinite, montmorillonite, and illite) (Missana T et al., 2009; Su C and Suarez DL, 2000; Goldberg S, 2013, 2014). Moreover, soils in wet and tropical environments generally have low pH (acidic) and contain abundant pH-dependent charges, such as Fe oxides (Fontes MPF and Alleoni LRF, 2006; Goh KH and Lim TT, 2004). Both Se (IV) and Se (VI) are prone to adsorb on Fe oxides, hydroxides, and clays in acid conditions, and thus control their solubility, especially in tropical and wet environments (Ziemkiewicz PF et al., 2011).

In the granitoid, quartz is one of the most resistant minerals to chemical and physical weathering. Feldspars are commonly weathered to sericite and clay minerals (kaolinite). Weathering of biotite and amphibole in tropical areas usually produce vermiculite, chlorite, epidote, and Fe-Ti oxides, which are unstable under surface weathering and decompose to clay (especially kaolinite) and Fe-containing compounds (Ma ZP et al., 1996; Ceryan S and Sen C, 1999). Granitoid contains much less biotite and amphibole than quartz and feldspar, so soils from the weathering of granitoid are rich in clay minerals, but are deficient in Fe-containing compounds



**Fig. 5.** Binary correlation diagram displaying the correlation between BCF of Se in the soil-rice system and Se content in soil from granitoid and basalt areas.

(iron oxides or hydroxides).

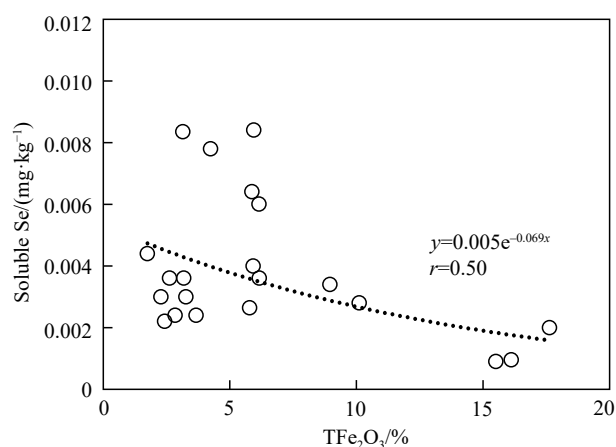
Basalt in the Hainan area is dominated by tholeiite, which contains Fe-rich enstatite, pigeonite, olivine, and calcic plagioclase (Huang CM and Gong ZT, 2001; Mei SW, 2018). These minerals are susceptible to weathering and form Fe-containing minerals (mainly goethite and hematite) and clay minerals, especially in tropical and humid environments (Huang CM and Gong ZT, 2001).

### 5.2.1. Iron oxides: Goethite and hematite

The  $\text{TFe}_2\text{O}_3$  contents in the basalt-derived soils are about 4–5 times higher than those in the granitoid-derived soils (Table 2). Amorphous goethite and hematite are the most common Fe oxide in soils derived from basalt and granitoid in Hainan Province (Yang ZF et al., 2002). It is well known that goethite and hematite play important roles in the adsorption of Se (Duc M et al., 2003, 2006). Therefore, the Fe-rich basalt produces soil with high contents of goethite and hematite and further results in consequent high Se content in the soil.

The experiments show that Se (IV), which has a great affinity for naturally occurring Fe oxides, was adsorbed more strongly than Se (VI) (Balistrieri LS and Chao TT, 1987; Kang Y et al., 2002; Duc M et al., 2003; Jang M et al., 2015). Furthermore, Se (IV) binds strongly to the goethite or hematite surface by forming stronger inner-sphere bidentate surface complexes than Se (VI), thus makes Se (IV) immobilization (Hayes KF et al., 1987; Zhang P and Sparks DL, 1990; Peak D and Sparks DL, 2002; Rovira M et al., 2008; Chan YT et al., 2009). The higher contents of Fe oxides and the resultant dominance of Se (IV) in the basalt-derived soils could be partly responsible for the higher Se content but lower Se bioavailability.

As shown in Fig. 6, the contents of water-soluble Se decrease with increasing Fe content in the soils. Plant JA et al. (2014) attributed it that iron hydroxide and water-soluble Se may interact to form insoluble iron selenite [such as  $\text{Fe}_2(\text{OH})_4\text{SeO}_3$ ]. This is also a reason for Fe-rich soils containing high total Se concentration but low Se bioavailability.



**Fig. 6.** Binary correlation diagram displaying the correlation between soluble Se and  $\text{TFe}_2\text{O}_3$  content in soil from granitoid and basalt areas.

### 5.2.2. Clay minerals: Kaolinite, illite, and chlorite

In the study area, soils in the granitoid area show much lower contents of clay particles and  $\text{Al}_2\text{O}_3$  than soils in the basalt area (Fig. 2), which suggests that lower clay minerals in the former. Furthermore, the XRD analytical result shows that the illite and chlorite contents in the granitoid- and basalt-derived soils were similar, but the kaolinite content was much lower in the former than in the latter (Table 3). Kaolinite has a much higher capacity to absorb selenite than selenate (Wang Y and Wei FS, 1995; Goldberg S, 2013, 2014), which is much more soluble and available to plants than selenite (Ali F et al., 2017, and references therein). Thus, kaolinite could influence the content and bioavailability of Se in the basalt-derived soils.

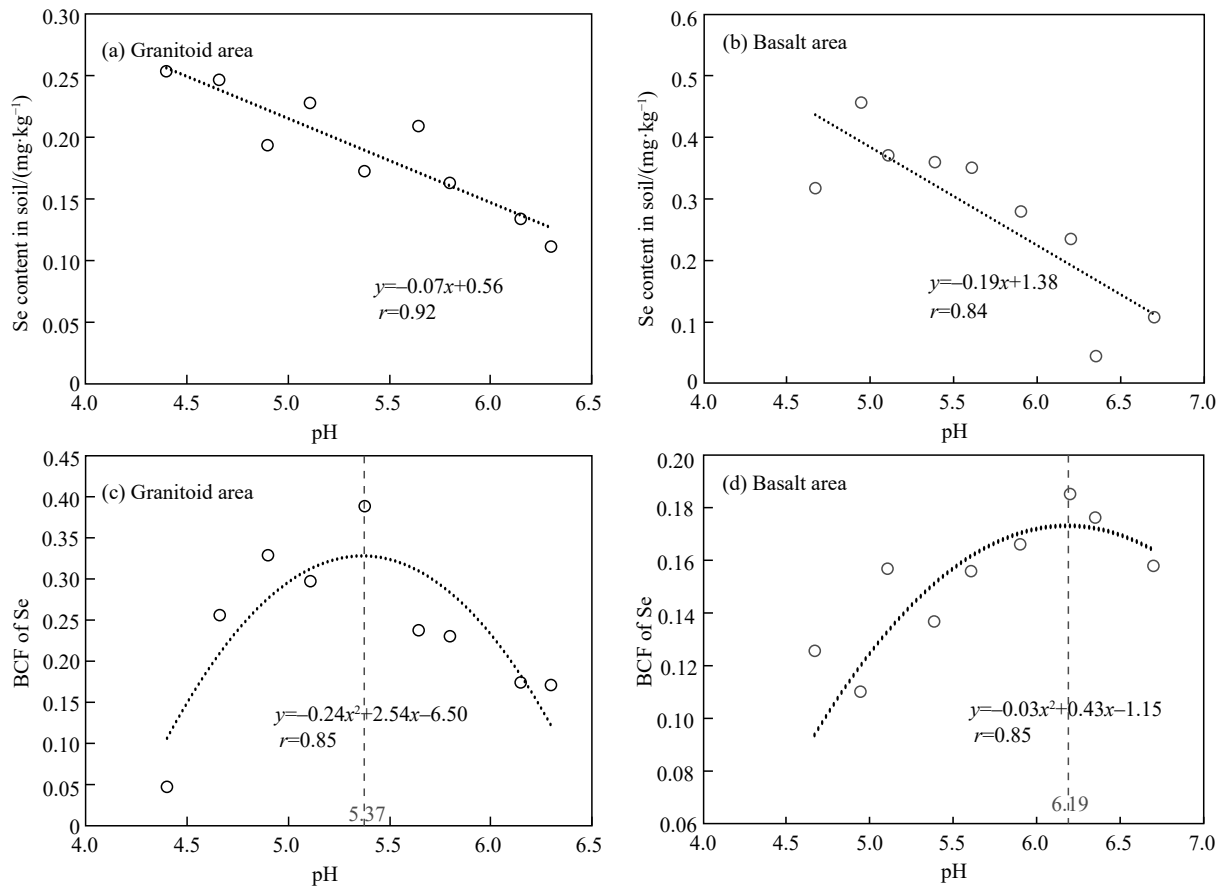
### 5.2.3. Soil CEC

The soil CEC was identified as an important factor in Se sorption, and the increase of CEC commonly results in the increase of Se adsorption capacity of soils, and consequently reduce Se bioavailability (Yang ZF et al., 2012; Gobas MB et al., 2014). In this study, the CEC is higher in the soil derived from basalt than that from granitoid (Fig. 2), which is attributed to the higher content of soil colloids and the finer soil texture in the former. In other words, the parent rocks largely determine the soil CEC content. The higher CEC content may also be partly responsible for the slightly higher Se contents but lower Se bioavailability in the basalt-derived soils than in the granitoid-derived soils.

### 5.3. Effects of pH on Se in rhizosphere soil-rice systems

The pH of soils in Hainan ranges from 4.3 to 6.7 (mainly 4.8–6.2). The climate may be responsible for the relatively acidic soil. In Hainan Province, the annual average temperature (23–26°C) is high and the annual average rainfall (1639 mm) is intense. Under these conditions, base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) are easily leached, thereby enhancing soil acidity (Chen HM, 2010). The pH of the studied granitoid-derived soils was slightly lower than the pH in the basalt-derived soil (Fig. 2), which is attributed to the relatively lower CaO content in the former. Basalt consists of pyroxene and calcic plagioclase, which have higher CaO contents than quartz, sodium plagioclase, and alkali plagioclase in granitoid. Therefore, the CaO content is higher in basalt-derived soils than in granitoid-derived soils under the same geographical conditions.  $\text{Ca}^{2+}$  acts as a buffering agent to retard obvious acidification of natural soils, thus pH will be relatively high in Ca-rich soils (Wang J et al., 2013).

Taking 0.25 pH as the unit, the data were divided into nine segments to calculate the median content and BCF of Se in soils derived from granitoid and basalt, respectively. The total Se concentrations and pH values are negatively correlated, with correlation coefficients of 0.92 and 0.84 (Figs. 7a, b). The correlation between the pH and BCF of Se is non-linear (Figs. 7c, d). Taking  $\text{pH}=5.37$  as the inflection point in soils from the granitoid area, the BCF of Se increases as pH increases when  $\text{pH}<5.37$ , while the BCF of Se decreases as



**Fig. 7.** Binary correlation diagram displaying the correlation between soil pH and Se content and BCF of Se in soil from granitoid and basalt areas, respectively.

pH increases when  $pH > 5.37$ . In the basalt-derived soils, the BCF of Se first increased as the pH increased to an inflection point at 6.19, and subsequently decreased as the pH increased further. This indicates that the pH is an important factor influencing the Se content in the soil, rather than the BCF of Se in the study area.

Adsorption of Se to soil controls the fate and mobility of Se in soils, and the pH affects Se content and availability in soil by influencing the Se adsorption onto oxy-hydroxides, clay minerals, and organic matter (Ticknor KV and McMurry J, 1996; Kuan WH et al., 1997; Xu YF et al., 2018). Adsorption experiments have shown that Se adsorption decreases with increasing pH in tropical soils (Barrow NJ and Whelan BR, 1980; Goh KH and Lim TT, 2004; Lee S et al., 2011; Gabos MB et al., 2014). This behavior was interpreted to be a consequence of the decrease in the number of positive charges on the variable charge on sesquioxides, clay minerals, and organic matter in humid tropical soils (Alleoni LRF et al., 2009; Gabos MB et al., 2014). Moreover, Goh KH and Lim TT (2004) attribute this to an increase in the  $OH^-$ , which could trigger electrostatic repulsion between Se (IV) or Se (VI) oxyanions and hydroxylic functional groups (generated by the accumulation of  $OH^-$ ) on the soil surface.

Commonly, the bioavailability of Se will decrease with increasing pH (Fordyce FM et al., 2000; Wang J et al., 2013). However, no simple linear relationship between the pH and

BCF of Se was observed in the present study (Figs. 7c, d). The mechanism behind this remains unclear, but it may be affected by the complicated process at the soil-root interface.

## 6. Conclusions

This study systematically analyzed the distribution characteristics of Se in soil and rice and explored the effects of parent rocks on Se content and bioavailability in soil-rice systems in granitoid and basalt areas, Hainan Province. The rhizosphere soil samples show relatively low Se contents, but rice samples exhibit high Se contents, which indicates a relatively high Se bioavailability.

(i) Soils derived from basalt show higher Se contents but lower Se mobile fractions than soils derived from granitoid. Soils in granitoid and basalt areas are beneficial to utilize as selenium-rich land to produce Se-rich agricultural products.

(ii) The content and occurrence form of Se in parent rocks play an important role in the Se contents and bioavailability in soils. Basalt has higher Se content than granitoid, and Fe-minerals in basalt have much stronger capacities to adsorb Se than biotite in granitoid.

(iii) The mineralogical and chemical compositions of parent rocks affect the content and bioavailability of Se in soils by controlling soil properties, including iron oxides, clay minerals, CEC, and pH. The basalt-derived soils had a higher capacity to adsorb Se than the granite-derived soils, because



of their higher CEC and higher contents of goethite, hematite, and clay minerals. They also had more selenite than selenate, with the result that the basalt-derived soils had slightly higher Se contents but lower Se bioavailability than the granitoid-derived soils. The higher pH in soils derived from basalt is also a significant factor to explain their higher Se content in soils. However, the mechanism of pH effect on Se BCF still needs further studies.

### CRedit authorship contribution statement

Xiu-jin Liu conceived the presented idea and prepared the manuscript. Ying-han Liu and Fei Liu collected soil and rice samples in the field. Fei Guo, Shi-qi Tang and Li Zhang processed geochemical data and drew all the figures. Hang-xin Cheng and Ke Yang supervised the findings of this work. All authors discussed the results and contributed to the final manuscript.

### Declaration of competing interest

The authors declare no conflict of interest.

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