КРАТКОЕ СООБЩЕНИЕ

SELENIUM FRACTIONS IN TWO FAMOUS HIGH-Se AREAS OF CHINA: ENSHI, HUBEI PROVINCE AND ZIYANG, SHAANXI PROVINCE

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ABSTRACT. Selenium (Se) fractions of 31 rocks/soils (Enshi and Ziyang) were analysed for better understanding Se biogeochemical cycling, assessing geological environment, utilizing Se sources and preventing Se poisoning. The Se content of Enshi rocks/soils is higher than those of Ziyang. Sulfide/selenide and elemental Se, base-soluble organic Se and residual Se are predominated in Ziyang carbonaceous slate, and the bioavailable Se is 5.12±3.60% (*n*=5); base-soluble organic Se, sulfide/selenide and elemental Se, and ligand-exchangeable Se are the main fractions in Enshi carbonaceous shale, and the bioavailable Se is 17.81±6.80% (*n*=8). The soil Se fractions present a high succession of the underlying strata. The soil bioavailable Se of Ziyang (4.17±3.35%, *n*=8) is lower than that of Enshi (14.14±8.43%, *n*=10). Thus, the Se bioavailability in geological samples is largely controlled by its fractions and species.

KEYWORDS: selenium, soil, fractions and species, bioavailability, biogeochemical province.

OBJECTIVE

Selenium (Se) content in soils is most possibly heritaged from the rocks, called parent materials, by weathering and pedogenic processes, and transported to plantation and finally to affect animals and humans by uptake of the products growing in the soil. On the other hand, the effectiveness of the transportation of Se from soil to plantation is not completely controlled by the total concentration of the element, but its chemical species, or fractions, which are mainly controlled by the geological parent materials, organic matter content, pH and redox conditions and a number of bio-physiochemical parameters (Plant et al., 2003; Qin et al., 2012; Wang et al., 2012). Therefore, obtaining the Se fractions in rocks and soils of highly Se-enriched areas is of great significant for better understanding Se biogeochemical cycling, assessing the geological environment, utilizing the Se sources and preventing Se poisoning.

MATERIALS AND METHODS

A total of 31 samples were collected from two famous Se-enriched areas: Enshi (5 rocks and 8 soils), Hubei Province and Ziyang (8 rocks and 10 soils), Shaanxi Province. Se concentrations in bulk sample and extracting solution were determined by hydride generation-atomic fluorescence spectrometry (HG-AFS) with a detection limit of 0.1 μg/L. For bulk Se measurement, the powdered samples were digested with mixed acids (HNO_3, $HClO_4$ and HF). For Se fractions measurement, a modified 5-step sequential extraction method was used (Martens and Suarez, 1997a,1997b; Qu et al., 1997; Zhang et al., 1997; Kulp and Pratt, 2004), including (1) water-soluble (extracted by Milli-Q water, 18.0 MΩ/cm), (2) phosphate exchangeable (extracted by 0.1 mol/L K_2HPO_4-KH_2PO_4 buffer, (3) base-extractable organic matter-bound (by 0.1 mol/L NaOH), (4) sulfide/selenide associated and elemental Se (by 0.5 g $KClO_3$ and 10 ml concentrated HCl) and (5) residual Se (digested by mixed acids). Before HG-AFS determination (only Se(IV) could be detected), the former three extracting solutions should oxidized by 1ml HNO_3 and 0.5 ml H_2O_2, then reduced by 6 mol/L HCl.

RESULTS

The bulk analysis showed, the rock Se concentration ranged from 193 to 1977 mg/kg (590±777 mg/kg) and from 8.88 to 57.0 mg/kg (25.8±17.8 mg/kg) in Enshi City and Ziyang County, respec-

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tively. In addition, the average Se content was 65.0±101 mg/kg（2.46–295 mg/kg） in Enshi soils and 13.2±15.7 mg/kg (0.35–51.8 mg/kg) in Ziyang soils. The Se recovery rate for the sequential extraction was 76.69–120.85% (average 94.85±13.85%) for rocks and 82.32–117.07% (101.76±7.35%) for soils. However, few Se recovery rates were less than 85%. This phenomenon might be related to the insoluble suspended solids in water and phosphate buffer extracts, for their adsorbability for Se compounds and their uneven distribution.

For rock Se fractions, the average percentage of water-soluble and ligand-exchangeable Se were 4.80±5.24% and 4.80±5.24% in carbonaceous shale of Enshi, respectively, which are consistent with those of lower Cambrian black shale (5.04% and 16.47%) in south China (Fan et al., 2011). And the percentage of water-soluble Se (1.30±1.24%) and exchangeable Se (3.81±2.76%) of Ziyang carbonaceous slate are very similar to upper Cretaceous shale of America (Kulp and Pratt, 2004). Generally, water-soluble and exchangeable Se was regarded as bioavailable Se, because they are more easily to be adsorbed by plant (Martens and Suarez, 1997a). Therefore, the bioavailable Se of Enshi carbonaceous shale accounted for 17.81±6.80% of the bulk Se, which is quite high than that of Ziyang carbonaceous slate (5.12±3.60%). The base-soluble organic Se accounted for 47.13±21.66% of the Se budget for Enshi shale, a little higher than that of Ziyang slate (32.82±9.59%). On the contrary, except for sample 15YTB01-4 with an extreme high content of sulfide/selenide and elemental Se (82.54%), all the shales of Enshi contained a low proportion (14.14±2.21%) of this fraction, which is only one third of that of Ziyang slate (42.87±12.84%). Similarly, the proportion of residual Se in Enshi shale (7.23±5.92%) was also lower than Ziyang slate (19.19±5.15%), this fraction are probably contained in silicates or kerogen and quite stable in the environment (Kulp and Pratt, 2004).

As showed in Enshi soil Se fractions, Se extracted by water and phosphate buffer were 1.75±0.95% and 12.39±7.69%, respectively, and the percentage was 44.39±16.70% for base-soluble organic Se, 29.25±30.47% for sulfide/selenide and elemental Se, and 12.23±8.93% for residual Se. Correspondingly, the proportions of five Se fractions in Ziyang soils were 0.84±0.78%, 3.33±3.34%, 15.75±17.49%, 49.30±32.50% and 30.78±19.97%, respectively. It is worth to concern that the proportion of sulfide/selenide and elemental Se reached as high as 65.74% in Naore Village, Ziyang County, where a Se poisoning occurred in animals and local resident, this result was highly related to the outcropped Se-enriched pyritic carbonaceous strata (Kunli et al., 2004). The content of bioavailable Se in Enshi soils was 14.14±8.43%, correspond to the previous data (18.44% and 16.06%) reported by Qin et al. (2012), which is much higher than that of Ziyang soils with a average percentage of 4.17±3.35%. Especially, the bioavailable Se in Naore Village was a small part (2.81±2.14%) of the bulk Se in soil, which is consistent with other researchers' data, for example, < 1% and 2.99% of Se was extracted by water and phosphate buffer from surface soil and upland soil of Naore Village (Wang et al., 2012; Wang et al., 2014). The large variation of bioavailable Se between Enshi and Ziyang soil might be interpreted by 3 reasons: (1) the difference of Se fractions in the underlying strata, (2) the difference of pH and redox conditions, (3) the different concentrations of iron oxide and oxyhydroxide complexes, clay and organic matter.

CONCLUSIONS

In summary, the Se fractions in rock are dependent on its age and lithology. In Ziyang Se-enriched carbonaceous slate, the main Se fractions are sulfide/selenide and elemental Se, base-soluble organic Se and residual Se, and the bioavailable Se is 5.12±3.60%; in Enshi Se-enriched carbonaceous shale, the main Se fractions are base-soluble organic Se, sulfide/selenide and elemental Se, and ligand-exchangeable Se, and the bioavailable Se is as high as 17.81±6.80%. In addition, the characteristics of soil Se fractions present a high succession of the underlying strata. Similar to the rocks, the predominant Se fractions are sulfide/selenide and elemental Se, residual Se and base-soluble organic Se in Ziyang Se-enriched soils, and base-soluble organic Se, sulfide/selenide and elemental Se, and ligand-exchangeable Se in Enshi Se-enriched soils, respectively. Also the bioavailable Se in Ziyang soils (4.17±3.35%) is lower than that of Enshi soils (14.14±8.43%). Therefore, the bioavailability of Se in geological samples is not only controlled by its fractions and species, but also dependent on the physicochemical properties of the matrix and its surrounding environment, such as the pH value, the redox condition, soil texture, mineralogy, the presence of competitive ions and so on.

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СЕЛЕНОВЫЕ ФРАКЦИИ В ДВУХ ОБЛАСТЯХ КИТАЯ, ИЗВЕСТНЫХ ВЫСОКИМ УРОВНЕМ СЕЛЕНА: ЭНЬШИ, ПРОВИНЦИЯ ХУБЭЙ И ЦЗЫЯН, ПРОВИНЦИЯ ШЭНЬСИ

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РЕЗЮМЕ. Были проанализированы селеновые (Se) фракции 31 разновидности горных пород/почв из областей Эньши и Цзыян для лучшего понимания биогеохимического цикла селена, оценки геологической среды, использования источников селена и предотвращения отравления селеном. Содержание Se в породах/почвах Эньши выше, чем в Цзыян. В карбонатных сланцах Цзыян преобладают сульфиды/селениды и элементарный Se, а также щелоче-растворимый органический Se и остаточный Se, при этом биодоступный Se составляет 5,12±3,60% (n = 5); в угленосных сланцах Эньши основными фракциями являются щелоче-растворимый органический Se, сульфиды/селениды и элементарный Se, а также лиганд-обменный Se, при этом биодоступный Se составляет 17,81±6,80% (n = 8). Почвенные фракции Se представляют последовательность подстилающих слоев. Биодоступного почвенного селена Se в Цзыян (4,17±3,35%, n = 8) меньше, чем в Эньши (14,14±8,43%, n = 10). Таким образом, биологическая доступность селена в геологических образцах в значительной степени определяется его фракциями и химическими формами.

КЛЮЧЕВЫЕ СЛОВА: селен, почва, фракции и химические формы, биодоступность, биогеохимическая провинция.