

## Isotopic fractionation of selenium in higher plants

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The extent of isotopic fractionation of selenium in plants is poorly understood, but potentially is important to understand and quantify the fractionation processes involved in Se biogeochemical cycling in surface environments[1]. Here, by <sup>74</sup>Se-<sup>77</sup>Se double spike technique with high precision developed on HG (hydride generator)-MC-ICP-MS[2], we determined Se isotopic composition of different plant components including roots, stems, leaves and seeds of rice (*oryza sativa* L.) and corn (*zea mays* L.), and the Se accumulating herb booor's mustard (*thlaspi arvense* L.). The  $\delta^{82/76}\text{Se}$  values ranged from -1.41‰ to -0.24‰ in rice, from -3.56‰ to -1.80 ‰ in corn, and from -0.62 ‰ to 2.21‰ in mustard herb. The overall range of  $\delta^{82/76}\text{Se}$  was 5.77‰, indicating Se isotopic variation can occur in plants to a small extent.

For all three species, roots are shifted isotopically relative to total Se in the soils they grew in, but not in any systematic way. This probably reflects Se isotopic fractionation among the various Se species in the soils, which is expected to result from redox cycling. Since Se is taken up mainly as selenate, selenite and certain organic compounds, the roots' isotopic composition may differ from the total soil, and is expected to depend on several variables[3].

A slight systematic enrichment in heavy Se isotopes in shoots (above ground) relative to roots occurred in corn and mustard herb with up to 0.22 ‰ in  $\Delta\delta^{82/76}\text{Se}_{\text{shoot-root}}$ , but not in rice. This shows the transport of Se in plants from root to shoot does not induce obvious fractionation. In contrast,  $\Delta\delta^{82/76}\text{Se}_{\text{leave-root}}$  and  $\Delta\delta^{82/76}\text{Se}_{\text{leave-shoot}}$  in all three plants show the obvious heavy isotope enrichment in leaves of at least 0.35‰ (the maximum is 1.85‰), indicating there are at least two different types of mechanism to explain Se isotopic variations. One is transport from rhizome to stems which involves no or smaller fractionation; another is from stem to leaves and/or leaves to atmosphere which cause significant fractionation. In the latter case, we envision Se methylation and loss of this volatile species from leaves during growth could induce heavy Se isotope enrichment in leaves, particular in Se accumulated plants such as *thlaspi arvense* L.

The work was supported by the National Natural Science Foundation of China (41073017, 40973085) and the Knowledge Innovation Program of the Chinese Academy of Sciences (KZCX2-YW-JC101).

[1] Johnson (2004) *Chem Geol* 201-214. [2]Zhu et al. (2008) *Chinese J Anal Chem* 36, 1385-1390. [3] Sors et al. (2005) *Photosynthesis Rev.* 86, 373-389.

## Peraluminous rare metal granites in South China

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There exist many alumina-saturated Sn-W-Ta-Nb bearing granites in South China, including the Yichun Li-Ta-Nb granite in Jiangxi Province, the Limu Ta-Nb-Sn granite in Guangxi Province, the Xianghualing Ta-Nb-W-Sn granite in Hunan Province, etc. They are usually stocks in occurrence, ultra-acidic in chemistry, rich in Al, Na, Li, Rb, Ta, Nb, Sn, W, F etc. elements, mostly P-rich, but in some cases P-barren.

One of the most fundamental features for these granites is well developed vertical zonation. From the upper contact downwards to the deeper levels the following zones are usually successively observed: the pegmatoid stockscheider (pegmatite, aplite and massive quartz assemblage), the greisen zone, the lepidolite-topaz-albite granite zone, the Li-muscovite granite zone, the two-mica granite zone, and the protolithionite granite zone. Along with the direction from protolithionite granite upwards, Li, Rb, F and rare-metal contents gradually increase, but Zr and REE concentrations gradually decrease. Geological, textural, geochemical evidences and coexisting coeval subvolcanic-volcanic rare metal bearing dykes suggest that this kind of vertical zonation and rare metal mineralization were caused by fractional crystallization and magmatic-hydrothermal differentiation of rare metal-rich parental magmas. This evolutionary process led to gradual depletion of Zr and REE, and gradual enrichment of Li, Rb, Ta, Nb, Sn, W etc. rare metals and F etc. volatiles in the apical parts of the stocks.

The original rocks of the peraluminous rare metal granites in South China are considered to be of S-type derived from the crustal materials, especially for the P-rich ones. However, the aluminous A-type granites are also should be considered, especially for the P-barren ones. For example, the protolithionite granite in the deeper part of the Xianghualing granite has high contents of REE, Y, Zr, Nb, Th, U etc. HFSEs, relatively higher zircon  $\epsilon_{\text{Hf}}$  values (from -5.9 to -1.9, averaging -4.2) and relatively lower two stage Hf model ages ( $T_{\text{DM}}$  values from 1.32 Ga to 1.58 Ga, averaging 1.47 Ga), which evidently indicate that this granite belongs to the aluminous A-type and was derived from the crust-mantle mixed sources.