## Investigation of Hg species binding biomolecules in dolphin liver: Use of isotopic tracers for sample treatment optimization

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Despite mercury being well recognised as an important pollutant in marine animals, the metabolic pathways of this element has not been fully elucidated. It has been suggested that Hg can bind thiol containing proteins/biomolecules [1]. The study of mercury containing biomolecules is essential for the assessment of its biotransformation mechanisms and toxicological impact. In general terms, most of the speciation studies have been carried out in fish muscles because of its consumption by humans and were restricted to the discrimination of an inorganic and monomethyl (MeHg) mercury 'pool' in these samples. However, speciation of this heavy metal in vital organs like liver has not been extensively studied. In fact, the main problem is to maintain the original speciation avoiding all possible transformations during the analytical process in order to elucidate the structure of Hg containing biomolecules, which is a great challenge. Multiple isotopic tracers spiking, used in isotopic dilution methodologies, is a powerful tool and its potential to deal with these problematic is investigated.

The main aim of this work is the study of Hg species (i. e. IHg and MeHg) binding biomolecules in the aqueous soluble protein fraction of white-sided dolphin (Lagenorhynchus acutus) liver homogenate (QC04LH4). By using stable enriched isotopic tracers (199IHg and 201MeHg), the rate of species transformation during sample treatment steps, such as lyophylization and protein extraction by ultrasonication, was evaluated. IHg and MeHg distribution into pellets and protein soluble fraction was determined. The analysis of the soluble protein fraction by size exclusion chromatography-ICP-MS reveals the association of Hg with biomolecules in a wide molecular weight range. This was followed by the GC-ICP-MS speciation in order to determine the ratio of IHg and MeHg into the different protein fractions. In this work, isotopically labeled Hg species were also used as tracers to optimize the sample treatment to assess Hg species in protein fractions.

[1] I. Onyido, A.R. Norris, E. Buncel (2004) *Chemical Reviews* **104**, 5911-5929.

## Heterogeneity of the lower continental crust beneath southern Jilin Province, NE China: Evidence from geochemical and Sr–Nd–Pb isotopic compositions of Early Cretaceous granitoids

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The spatial variations of geochemical and Sr-Nd-Pb isotopic compositions of Early Cretaceous granitoids from southern Jilin province, China, provide insight into the nature and its variation of the lower continental crust beneath the northeast segemant of the North China Craton (NCC). Zircon U-Pb dating results show that the granitoids formed in the Early Cretaceous (119-130 Ma). The Early Cretaceous granitoids have SiO<sub>2</sub> = 61.8~76.6%, Mg# =7~55, A/CNK = 0.86~1.12, ( $^{87}\text{Sr}/^{86}\text{Sr})i$  = 0.7054~0.7107,  $\epsilon_{Nd}$  (t) = -1.93  $\sim$ -13.9, and are characterized by enrichment in large ion lithophile elements (LILEs) and light rare earth elements (LREEs), and depletion in high field strongth elements (HSFEs) such as Nb, Ta, and Ti and heavy rare earth elements (HREEs). These geochemical features reveal that they could be derived from partial melting of the lower continental crust. Chemically, the spatial variations of their compositions exist among these coeval granitoids. For example, their initial <sup>87</sup>Sr/<sup>86</sup>Sr ratios increase from 0.7054 to 0.7107 whereas their  $\varepsilon_{\rm Nd}$  (t) values decrease from -2.33 to -13.9 from the northeast to the southwest in southern Jilin province. The abovementioned results indicate that the Early Cretaceous granitoids could be mainly derived from partial melting of ancient lower continental crust in southwestern segment of southern Jilin province, whereas the coeval granitoids could chiefly originate from partal melting of the juvenile lower continental crust besides minor ancient basement in northeastern segment of southern Jilin province, which is also supported by their twostage Nd model ages (TDM2), i. e., the former is 2058 Ma, the latter is 1081Ma. Combined with the coeval mafic-ultramafic intrusive rocks [1], it is suggested that these granitoids formed under an extensional environment in the Early Cretaceous.

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[1] Fei et al. (2006) Sci. in China (D Series) 49, 368-374.