

## Cinnabar exists as non-methylmercury form after exposure to human intestinal bacteria

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### Introduction

Cinnabar (Cin), in the form of mercuric sulfide (HgS), is a mineral widely used in traditional Chinese medicine throughout history. As for the toxicity of cinnabar, it is unclear that whether cinnabar can be transformed into highly toxic methylmercury (MeHg) by gastrointestinal flora.

Therefore, we carried out experiments to uncover the actual chemical states of cinnabar after exposure to human intestinal bacteria, which is crucial to evaluate their possible toxicity and availability in medicine. Here, synchrotron-radiation XANES was employed to study the chemical features of Hg and sulfur in cinnabar exposed to microbe. [1]

### Experiments

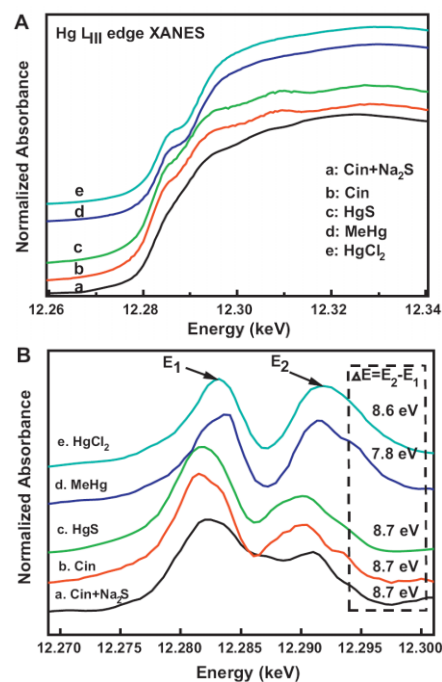
To obtain near-edge absorption structures of sulfur, we used cinnabar, human intestinal bacteria, and bacteria incubated with HgS, cinnabar, HgCl<sub>2</sub>, and reaction extraction from cinnabar and Na<sub>2</sub>S mixture as experimental samples. And element S, HgS, HgCl<sub>2</sub>, Na<sub>2</sub>S, Na<sub>2</sub>S<sub>2</sub>, and Na<sub>2</sub>S<sub>4</sub> were used as reference ones for sulfur. For Hg L<sub>III</sub>-edge XANES, experimental samples included reaction extraction from cinnabar and Na<sub>2</sub>S (to simulate the sulfur form in bacteria) mixture, and cinnabar and reference ones included methylmercury, HgCl<sub>2</sub> and HgS.

All samples were lyophilized, ground, pressed into pellets. Then, sulfur K-edge XANES of samples was carried out at BL-11B at PF, KEK, Tsukuba, Japan. And Hg L<sub>III</sub>-edge XANES of samples were measured at BL-14W1 in Shanghai Synchrotron Radiation Facility (SSRF), China.

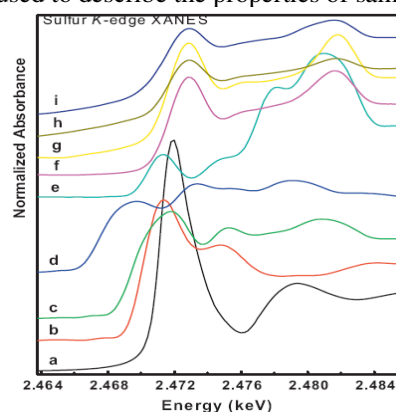
### Results and Discussions

In Fig.1, both the spectra and first derivatives of Hg L<sub>III</sub>-edge XANES showed that chemical forms of cinnabar and HgS are identical and significant differences exist between HgS and other reference compounds such as MeHg and HgCl<sub>2</sub>. Interestingly, the chemical forms of mercury in extracted products of cinnabar and Na<sub>2</sub>S mixture were similar to HgS, while quite different from HgCl<sub>2</sub> and MeHg.

According to Fig.2, sulfur K-edge XAFS suggested that sulfur in intestinal bacteria probably show polysulfide forms like Na<sub>2</sub>S<sub>2</sub> after incubating with HgS and cinnabar.



**Fig.1** Hg L<sub>III</sub>-edge XANES spectra (A) and their first derivatives (B). (a) Reaction extraction from cinnabar and Na<sub>2</sub>S mixture (Cin+Na<sub>2</sub>S) as experimental sample; (b) cinnabar (Cin), (c) HgS, (d) methylmercury (MeHg), and (e) HgCl<sub>2</sub> as standard compounds. The first and second inflections (E1 and E2) and the distance between them ( $\Delta E$ ) are used to describe the properties of samples.



**Fig.2** K-edge absorption spectra for sulfur speciation. The reference compounds are: (a) element S; (b) HgS; (c) Na<sub>2</sub>S<sub>2</sub>; (d) Na<sub>2</sub>S<sub>4</sub>. The experimental samples are: (e) reaction extraction from cinnabar and Na<sub>2</sub>S mixture; (f) bacteria; (g) cinnabar incubated with bacteria; (h) HgS incubated with bacteria; (i) HgCl<sub>2</sub> incubated with bacteria.

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In conclusion, these results suggested that cinnabar will convert into mercuric polysulfides rather than methyl-mercury form after interaction with intestinal bacteria.

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**References**

- [1] X. Zhou, L. Wang, X. Sun, X. Yang, C. Chen, Q. Wang, X. Yang, et al., J. Ethnopharmacol. 135, 110 (2011)  
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