

## Potential utility of Cu isotopes to recognize secondary Cu mineralization and the degree of enrichment

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In this contribution we examined the copper isotope ratio of both Cu-oxides and Cu-sulfides from hypogene and supergene mineralization in porphyry copper deposits (PCD). Copper isotope ratios are reported as  $\delta^{65}\text{Cu}\text{‰} = ((^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}} / (^{65}\text{Cu}/^{63}\text{Cu})_{\text{NIST 976 standard}} - 1) * 10^3$ . Errors for the all analyses are  $\pm 0.14\text{‰}$  (determined by multiple analyses of the samples) and mass bias was corrected through standard-sample-standard bracketing. Primary high temperature chalcocite and bornite (hypogene mineralization) from 15 PCD varied between -0.72 to 0.92‰. In comparison, Cu-oxides and chalcocite from 8 enrichment blankets (supergene mineralization) varied between 0.45 to 5.4‰. Although the collected dataset is relatively small (n=54 total minerals analyzed), a distinct pattern shift to heavier copper in supergene samples exists. The heavier copper isotope signature present in the supergene samples is consistent with experimental batch leach experiments. The causes of fractionation could relate to kinetic, biologic, crystallographic and/or equilibrium isotope effects. Regardless of the cause, the magnitude of isotopic fractionation can be modeled using Rayleigh fractionation trends to indicate the degree of leaching that occurred.

## The diurnal variation of carbon isotopic ratios of carbon dioxide in human breath

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The carbon dioxide of our human breath reflects the digestion and assimilation of our human body and could be a good indicator of our health condition. Dodds (1920) first measured the partial pressure of CO<sub>2</sub> in the breath to examine the digestive function. Nowadays, <sup>13</sup>C- breath tests are widely carried out using <sup>13</sup>C-labelled compounds. Among them, the most famous one is the <sup>13</sup>C-urea breath test (UBT). This test is very sensitive and safe to check *Helicobacter pylori* infection. In these tests, infrared spectroscopy is generally used to measure the carbon isotopic ratios.

It is also known that the carbon isotopic ratios reflect those of the diet in our daily life. For example, the carbon isotopic ratios of the hair correlated with the calculated values of the dietary protein on the country where the individual lives (Nakamura *et al.*, 1982). The changes in the carbon isotopic composition of beard samples were 2-3 per mil when German residents traveled to Japan and United States.

In this study, we have examined the diurnal variation of the concentration and the carbon isotopic ratios of carbon dioxide of the natural human breath using the mass spectrometer ANCA-SL installed in Osaka University. We found that there is about 2.5 per mil variation of carbon isotopic ratios during a day. This variation is rather large, comparing to the beard variation of 2-3 per mil reported by Nakamura *et al.* (1982). We also carried out the measurement of blood pressure, body temperature, and blood sugar level at the same time. There was no correlation between carbon isotopic ratios and these fundamental data values. Thus it was supposed that the variation of carbon isotopic ratios of the human breath depend on the diet itself rather than the digestion and assimilation inside the human body. To confirm this, we carried out the experiment in case that examinee did not take diet. The variation of carbon isotopic ratios of the breath was only 1 per mil in this experiment. Thus we can conclude that the diurnal variation of 2.5 per mil is mainly attributed to the variation of carbon isotopic ratios of the diet that the examinee took in his human bodies.

### References

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