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Daily Circle of Calcium Concentration in Hair Observed by X-ray Fluorescence Analysis

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Iida and Noma realized X-ray fluorescence analysis (XFA) with a high signal-to-noise ratio to analyze a single piece of hair [1]. Akirov et al. observed a correlation between [Ca] and [Br] in hair [2].

Using the focusing system at BL-4A, the vertical beam size is 50μm and corresponds to the hair length grown for 4 hrs. By scanning the beam along a hair shaft, daily circles of hair [Ca] have been observed.

Ca plays as a messenger in the universal cellular signal transduction, and therefore a strict balance is maintained between bone and blood under the homeostatic control employing parathyroid hormone (PTH). Serum $[Ca^{2+}]$ is always constant at ~5mg/dL by a chemical equilibrium with [Ca] on protein molecules in serum, which decrease with lower pH of serum. PTH acts to lower the serum pH (acidosis). When serum $[Ca^{2+}]$ decreases, PTH is more secreted and Ca atoms on the protein move to the liquid. The standard [PTH] for healthy subjects is in a fairly wide range (intact [PTH]=13~53pg/ml). [PTH] varies in a daily circle with the peak at night.

Although hair [Ca] distinctively increases with Ca deficiency, it was found for healthy cases (Ca sufficiency) that [Ca] in hair is equal to that in serum dried after removing Ca^{2+} [3]. (The hair is formed as if the protein and amino-acid in serum moved without water into hair). Therefore, hair must record the daily variations in the protein [Ca] due to the [PTH] variation.

Figure 1(a) shows [Ca], [Fe], [Cu], and [Br] measured with an interval of 50μm along hair shaft from the root end. Since hair grows at a rate of 300 μm/day, dips of hair [Ca] are seen with an interval of 300 μm due to the peak secretion of PTH at night. Figure 1(b) is the result obtained for the tip end in the same way. The dip interval is about 250μm due to age distortion. Since the hair is 13 cm long (growth rate = 1cm/month), there is a lapse of 13 months between Figures 1(a) and (b). This result means that the daily variation of [Ca] is recorded from root to tip over 13 months; hair is excellent memory medium.

The hair [Ca] level in Figure 1(a) is lower with extra-ordinary high [Br] values than that of Figure 1(b) having the normal [Br]=10. Br is a congener of Cl, which is difficult to detect by the XFA, and [Br] and [Cl] in hair are proportional. In acidosis, serum has a high $[H^+]$ and, to compensate the positive ions, $[Cl^-]$ is increased. Therefore the high [Br] values mean the acidosis which results in a very low [Ca] in hair. It was found that the low [Ca] with acidosis was completely recovered by Ca supplementation to suppress PTH secretion.
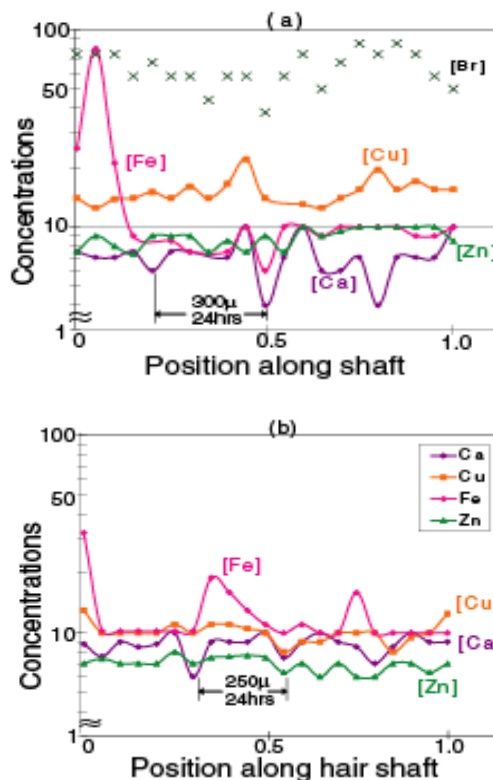

Figure 1. Daily variation of hair [Ca] measured with an interval of 50 μm along a hair shaft by XFA. (a) Root. (b) Tip.

The daily variation is very sensitive to disorder of Ca metabolism and can be used for physical examination. To avoid the error due to variety in hair thickness, XF spectra were recorded in a logarithmic scale, and the concentrations were normalized by plotting M according to the equation,

$$[\log P - \log S]/[\log P - \log S]_{st} = \log M. \qquad (1)$$

where $\log P$ is the spectral peak height, $\log S$ is the background due to X-rays scattered by the sample, and $[\log P - \log S]_{st}$ is for healthy standard.

References
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