

# **Environmental Control of Chemical Composition of the Secondary Hydroxyapatite from Japan**

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## **1. Introduction**

The mineral hydroxyapatite is very common species in secondary phosphates originating from guanos(HILL *et al.*, 1997). Several mineralogical analyses of spelean hydroxyapatite exist(*e.g.*, KASHIMA, 1968, 1979 ; MAKI *et al.*, 1977 ; SUH *et al.*, 1978 ; WANG, 1982 a, b), whereas detailed geochemical composition of secondary hydroxyapatites has not been reported in Japan.

As is well known, hydroxyapatite( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) includes a range of composition with variable OH, F, Cl substitutions. According to McCONNEL(1973), secondary hydroxyapatites tend to show mineral variability. Moreover, some of the complexity present in geochemical analysis of secondary hydroxyapatites is sometimes caused by contamination with detrital materials during deposition

In this paper, we are going to report the result of mineralogical and geochemical studies on two types of secondary hydroxyapatite which

belong to a cave deposit and an insular phosphorite deposit, in Kyushu, Southwest Japan. We have attempted to relate the geochemical composition of secondary hydroxyapatites to their depositional environment.

## 2. Materials and methods

The following two specimens were used in this study :

1) Specimen NK385 is typical of that found in the cave deposit in Hakusangongen-dô Limestone Cave, Ôita Prefecture, northern Kyushu. This specimen occurs as leaf-like flakes forming mounds which are directly precipitated on clastic sediments of the cave floor.

2) Specimen NK474 derived from guano occurs as veins or crusts in the fissures and bedding plains of altered-chert and limestone beds at a former commercial phosphorite mine in Kuta-jima Island is situated in about 10 kilometers northwest of Iriki-hama beach, Kagoshima Prefecture, southwestern Kyushu.

*X-ray powder diffraction analysis(XRD)*. XRD was carried out with RIGAKU instruments under ordinary operating conditions. Bulk powder specimens were mounted on the glass slide.

*X ray fluorescence analysis(XRF)*. Quantitative bulk chemical analysis was performed on a Philip PW 1450 automatic sequential spectrometer. Major elements were determined in fused discus using a heavy absorber. Minor and trace-elements were determined using pressed powder pellets.

*Scanning electron microanalysis(SEM).* SEM was carried out with a ISIDS-130 research instrument equipped with an EXD analyzer. Thin sections were coated with Au for pursuing element map.

*Electron probe microanalysis(EPMA).* Thin sections were analyzed for Ca, P, Ba, Sr, Cl, F and O by JAX-8600 JEOL electron microprobe.

*Secondary ion mass spectrometry(SIMS).* SIMS spectra were obtained using a Cameca IMS-3F secondary mass spectrometer. A mass filtered O<sup>+</sup> primary beam produced the positive secondary ion spectrum, showing the presence of major and trace elements including light elements.

### 3. Results

*X-ray powder diffraction analysis(XRD).* Specimen NK385 was identified mainly as hydroxyapatite and contained small amount of an unidentified 18.8Å mineral, whereas the specimen NK474 is composed of hydroxyapatite and quartz, although, in the specimen NK385, quartz peaks cannot be observed.

*X ray fluorescence analysis(XRF).* Specimen NK474(insular hydroxyapatite) has a relatively high SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> content than NK385(spelean hydroxyapatite). In comparison with their trace elements, the specimen NK474 has higher Sr, Zn and Ni content.

*Scanning electron microanalysis(SEM).* SEM image map of Ca, P and Si in the specimen NK385 and of Ca, P, Si, Fe, K and Al in the specimen NK474, showed the occurrence of silica minerals or clay minerals filling materials within the interspaces of zoning platy hydroxyapatite crystals(NK385) or small pockets in hydroxyapatite matrix and crystals(NIK474). Specimen NK474 contains iron minerals.

*Electron probe microanalysis(EPMA).* The data of selected 39 points from the specimen NK385 were averaged 39.52% CaO, 32.19% P<sub>2</sub>O<sub>5</sub>, 0.02% SrO, 0.05% Cl and 0.42% F. Specimen NK474 composition(13 points) averaged 45.06% CaO, 32.36% P<sub>2</sub>O<sub>5</sub>, 0.09% SrO, 0.69% Cl and 0.72% F.

The CaO/P<sub>2</sub>O<sub>5</sub> ratios in the specimen NK385 vary between 1.07 and

1.34 and averaging 1.20. Specimen NK474 has CaO/P<sub>2</sub>O<sub>5</sub> ratios between 1.33 and 1.52 and averaging 1.40, which are distinctly higher than the specimen NK385 values. The F/P<sub>2</sub>O<sub>5</sub> ratios of analytical points in the specimens NK385 and NK474 average 0.014 and 0.024, respectively.

*Secondary ion mass spectrometry(SIMS).* SIMS bar-graph data revealed 18-19 elements in the secondary hydroxyapatite specimens NK385 and NK474.

In the specimen NK385 was observed mainly two areas, light and dark, which were the only visible difference under SIMS observation. In darker area, N, F, Al, Cl, K and Fe are associated with the elements of the light area except Sr. Although the specimen NK474 contains the same two areas as the specimen NK385, the darker area showed an association of more elements than the light area. such as B, F, K, Ti, Sr, Y and Zr and sometimes lack of Cl. It is problematical to separate light and dark areas of hydroxyapatites because distribution of elements does not appear constant.

#### 4. Concluding Remarks

The present study has shown a simple comparison of secondary hydroxyapatite from two, very different environments. The silica mineral (quartz) and clay mineral occur as infill materials within the interspaces of hydroxyapatite crystals and pockets. This contamination of silica and clay minerals is generally due to the effect of depositional process. Note that there will always be a dust-sediment finder in urine phosphates.

Contents of Si, Al and Fe are readily emplaced and leached post-depositionally in hydroxyapatite from circulating groundwater or weathering processes (TAZAKI *et al.*, 1986). In the two secondary hydroxyapatite, the spelean (urine) phosphate (NK385) and the insular phosphate (NK474), the most interesting result is in the variation of CaO and P<sub>2</sub>O<sub>5</sub> weight percentage, a plot of CaO vs. P<sub>2</sub>O<sub>5</sub> showing a positive linear trend. This result suggests that the insular hydroxyapatite (NK474) acquired highly CaO/P<sub>2</sub>O<sub>5</sub> ratios from the meteoric waters which reflected terrestrial weathering of the limestone bed and the guanos in origin. It is clear that the spelean hydroxyapatite (NK385) shows much clearer freshwater vs. urine effect.

F and/or Cl contents in the apatites are very important indicator for description of their species. As has been pointed out (PALACHE *et al.*, 1951), Cl is either absent or present in only very small amounts in

hydroxyapatite. Of particular interest is that the specimen NK474 shows the higher Cl(0.69%) and F(0.72%) averaging content than the specimen NK385(Cl(0.05%), F(0.42%)), in which they must have been reduced by sea-water washing. Phosphate minerals commonly carry fairly large amount of REE and U, and therefore REE and U contents of hydroxyapatite are of very interesting concern.

The principal analytical problem was the determination of REE and U, because of the very low levels of these elements. Although the background ratios are very large, differences are recognized between the specimen NK385 and the specimen NK474.

These values indicate that the specimen NK474 contains higher REE and U concentrations than the specimen NK385.

Considering the geochemical evidences of the two types of secondary hydroxyapatite, the spelean and the insular phosphates, it seems that they are used for "finger-print" too identify environments, viz. rare metals, CaO/P<sub>2</sub>O<sub>5</sub>, F and Cl contents.