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Mechanism of Na and K Substitutions in Bioapatite Within Salty Area

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Introduction

Na and K are two most important cations in salty water, and also are two typical ions in animals' body fluids. The mineral, bioapatite, is a form of carbonated hydroxylapatite, which makes up over 50 wt.% of bones of animals. The study of Na and K in bone mineral of vertebrate and fish living in salt waters, therefore reveals inner biogeochemistry cycle within salty areas. The whale bone was used to investigate the chemistry of bioapatite as its huge bone size allows precise investigation of the biogeochemistry.

X-ray fluorescence analyses of the whale's bioapatite show an average Ca/P atomic ratio of 1.7, with an average composition of $(\text{Ca}_{8.40}\text{Mg}_{0.20}\text{Na}_{0.54})[(\text{PO}_4)_{4.87}(\text{CO}_3)_{1.13}](\text{OH})_{0.87}$.

Compared to the lamb femur and elk antler, the whale bone has 60 wt% more Na, although both minor elements are even less than one-twentieth of the weight of the major element Ca in all studied samples (see Table 1). Concentrations of Na_2O in the Acros synthetic apatite (0.08 wt%) and in the tooth enamel (0.40 wt%) are lower than in the whale bone.

Na is the third most abundant element (excluding oxygen) in the whale bioapatite, following the major elements Ca and P. The substitution of carbonate for phosphate is known to be coupled with that of Na for Ca in bioapatites, which leads to co-incorporation of carbonate and sodium in bone. This complex substitution mechanism is well illustrated by the whale bone. All bones have a markedly higher Na concentration than does usual synthetic OHAP that is not carbonated (see Table 1). The concentration of Na in the whale bone is also higher than that in typically analyzed human bones and tooth enamel and in the ashed lamb femur and elk antler analyzed here. The hypermineralized areas of the whale bone have higher sodium concentrations than the organic-rich areas, which further supports the notion of the crystallographic incorporation of bone's Na component within the mineral.

Potassium are distributed homogeneously in the typical

areas of the whale, but at an extremely low concentration (~1/1000 of the calcium). The low concentration of K in bioapatite is likewise due to its remarkably larger radius than Ca^{2+} (152 pm vs. 114 pm).

The abundant Na in salty water can elevated the Na concentration via coupled substitutions in bone mineral. However, K ions in bone mineral is limited due to its large sizes.

Table 1 Compositions (wt%) of the ashed whale bone, lamb femur, elk antler, Acros synthetic OHAP, and NIST 1486 bone meal (for calibration) based on XRF analysis.

	K^+	Ca^{2+}	Na^+	P	Atomic Ratio	
					$(\text{Ca}+\text{Mg}+1/2\text{Na})/\text{P}$	Ca/P
Whale	0.01	36.8	1.4	16.5	1.8	1.7
Lamb	0.05	37.8	0.8	18.0	1.7	1.6
Elk	0.02	38.6	0.9	18.1	1.7	1.6
Acros	0.01	39.2	0.1	18.2	1.7	1.7
NIST-1486	0.03	26.8	0.5	12.4	1.8	1.7

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