A comparative study of crystal structure of dinosaur and resent bones

G.Batdemberel[1] ,D. Chultem[2] , Sh.Gerbish[2] , H.Fuess[3] , D.Sangaa[2] , D.M.Toebbens[4]

[1]Mongolian University of Science and Technology
[2]National University of Mongolia
[3]Darmstadt Technological University, Germany
[4]Hahn-Meitner-Institut, Berlin, Germany

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Товч утга: Нейтрон дифракцын аргаар археологийн олдвор-динозаврын ясны болон одоогийн зарим амьтны ясны кристалл бүтцийг харьцуулан судалжээ. Эдгээр дээжүүдэд үндсэн бүрдүүлэгч хэсэг нь $P6_3/m$ огторгуйн групп бүхий гидро-апатит кристалл ($Ca_5(PO_4)_3OH$) байгааг тодорхойлсон ба кристаллын торын параметрүүд дулааны боловсруулалтын процессоос ихээхэн хамаардгийг тогтоожээ. Кальцын ислийн химийн стехиометрийн томъёо нь хонины ясны хувьд CaO, динозаврын яс, тахианы өндөгний хальсны хувьд харгалзан $Ca_{3.2}O_2$; $Ca_{3.09}O_2$ байгаа нь тогтоогджээ.

Introduction

The bone has a complex hierarchical structure, which despite much investigation, is still not well understood [1]. Bone is a composite material of collagen and slightly impure hydroxyapatite. The c-axes of the apatite crystal and the collagen fibres are preferentially oriented [2].
This work is devoted to the comparative studies on crystal structure of fossil and resent bones (dinosaur, sheep and skin of egg). Domestic animals, whose bones were studied, lived throughout Mongolia. But dinosaurs, whose remains

were found in the Gobi desert seemed to present Mongolia. The ages of these bones vary astronomical scales, from 50 to 250 million years. It becomes interesting from the point of natural history and biological evolution, in particular [3,4].

Experiment description

The experiments were done on the new high resolution powder neutron diffractometer (E9) installed at the beam tube T5 of the BER II research reactor of the Hahn-Meitner-Institute in Berlin [5]. It is dedicated to collect high - resolution powder diffractograms suited for profile refinements aimed at crystal structure determination as with cell volumes up to 1000 A^3. A typical collection time for one diffraction pattern is 8 h and the best resolution is close to $\delta d/d = 2x10^{-3}$. The principal instrument layout is shown in figure 1.

Bone samples of dinosaur, sheep and skin of egg were exposed to chemical thermal processing in order to isolate organic components. The Rietveld refinement codes FullProf program are used for structure refinements[6].

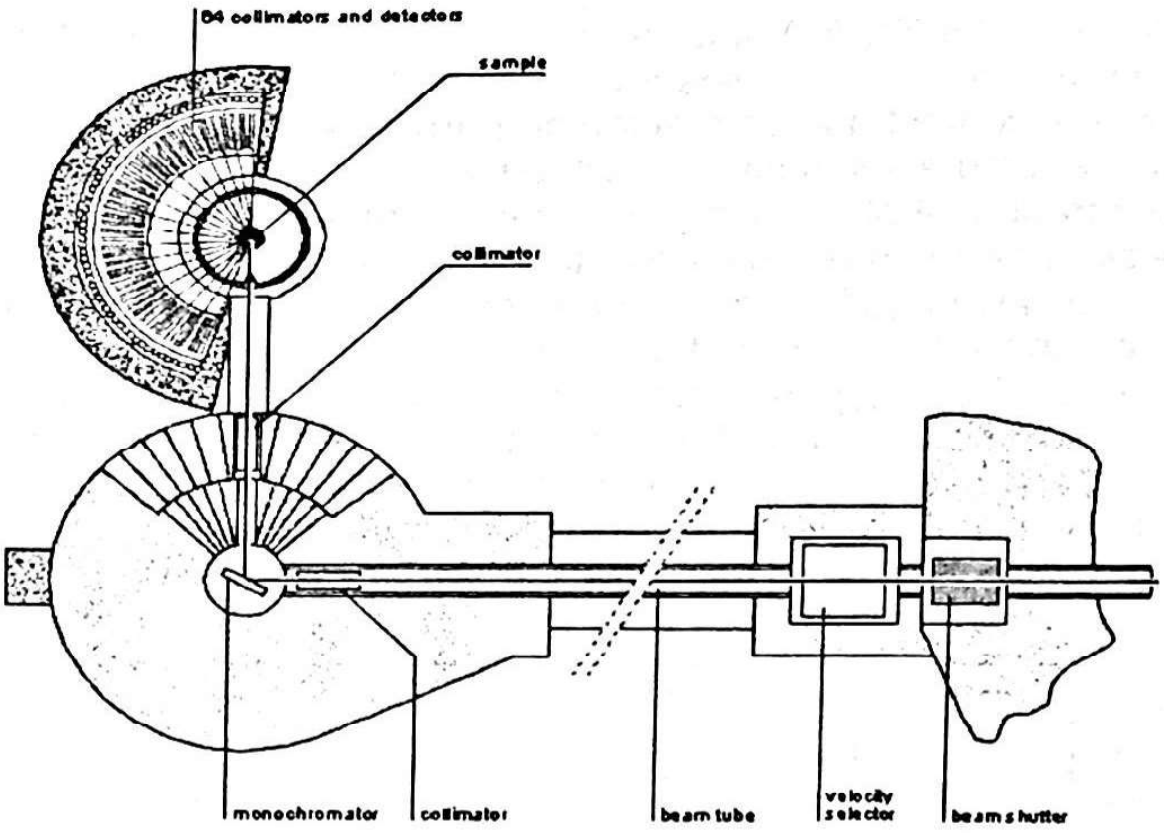


Figure 1: Design of the diffractometer E9

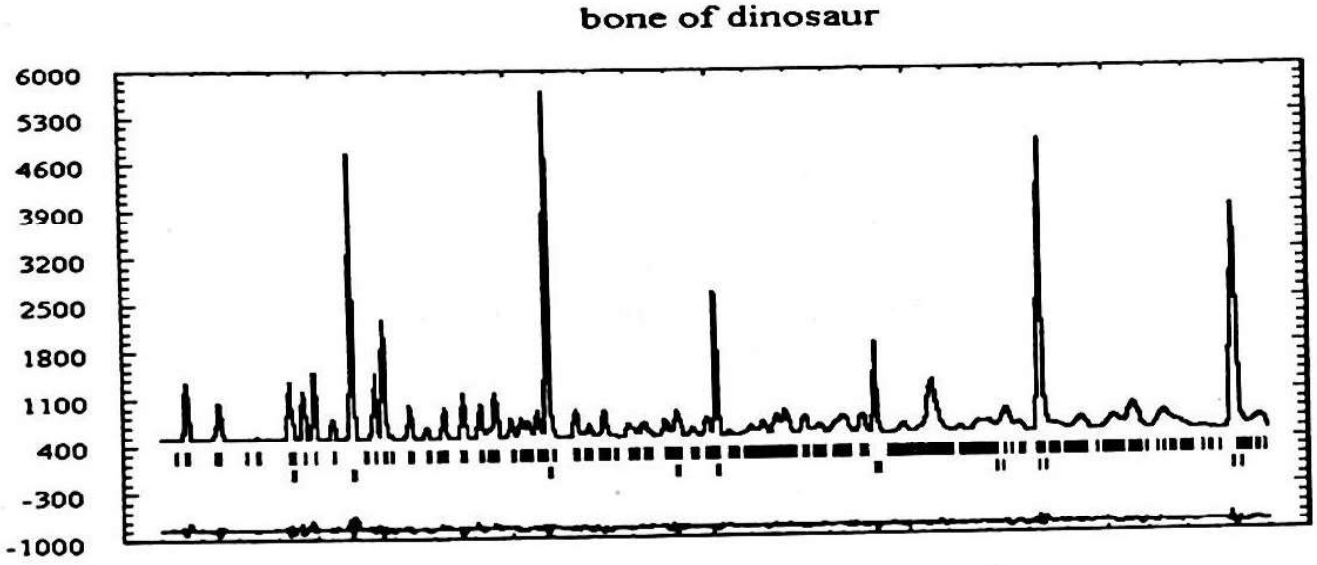
Results

All diffraction peaks in the spectrum were identified within the hexagonal (sp.gr.$P6_3/m$) and cubic(sp.gr.Fd3m) structures. The diffraction spectrums obtained as a results of the refinement is given fig.2. The refined structure data illustrated in table 1, 2, 3.

The basic hydroxyapatite ($Ca_5(PO_4)_3OH$) structure is hexagonal with space group $P6_3/m$, while the values of their structural parameters often depend on the chemical thermal processing.

As a result of the refinement all the three samples consist of two phases. The first main phase is hydroxylapatite

$Ca_5(PO_4)_3OH$ ($P6_3/m$) and the second is calcium oxide CaO ($Fd3m$). For each samples the second phase has different element content and crystal lattice parameters but the same main structural modifications which may be connected with heat treatment of the samples. The chemical formulas of a calcium oxide phase in dinosaurs bones and egg skins are $Ca_{3.2}O_2$ and $Ca_{3.09}O_2$, correspondingly. However, the calcium oxide phase in sheep bones corresponds to the chemical formula: CaO. It shows that in fossil dinosaurs bones and egg skins as a results of heat treatment at 800°C free calcium oxide appears in equal quantities. On the contrary, in egg skins was not observed the hydroxylapatite phase.



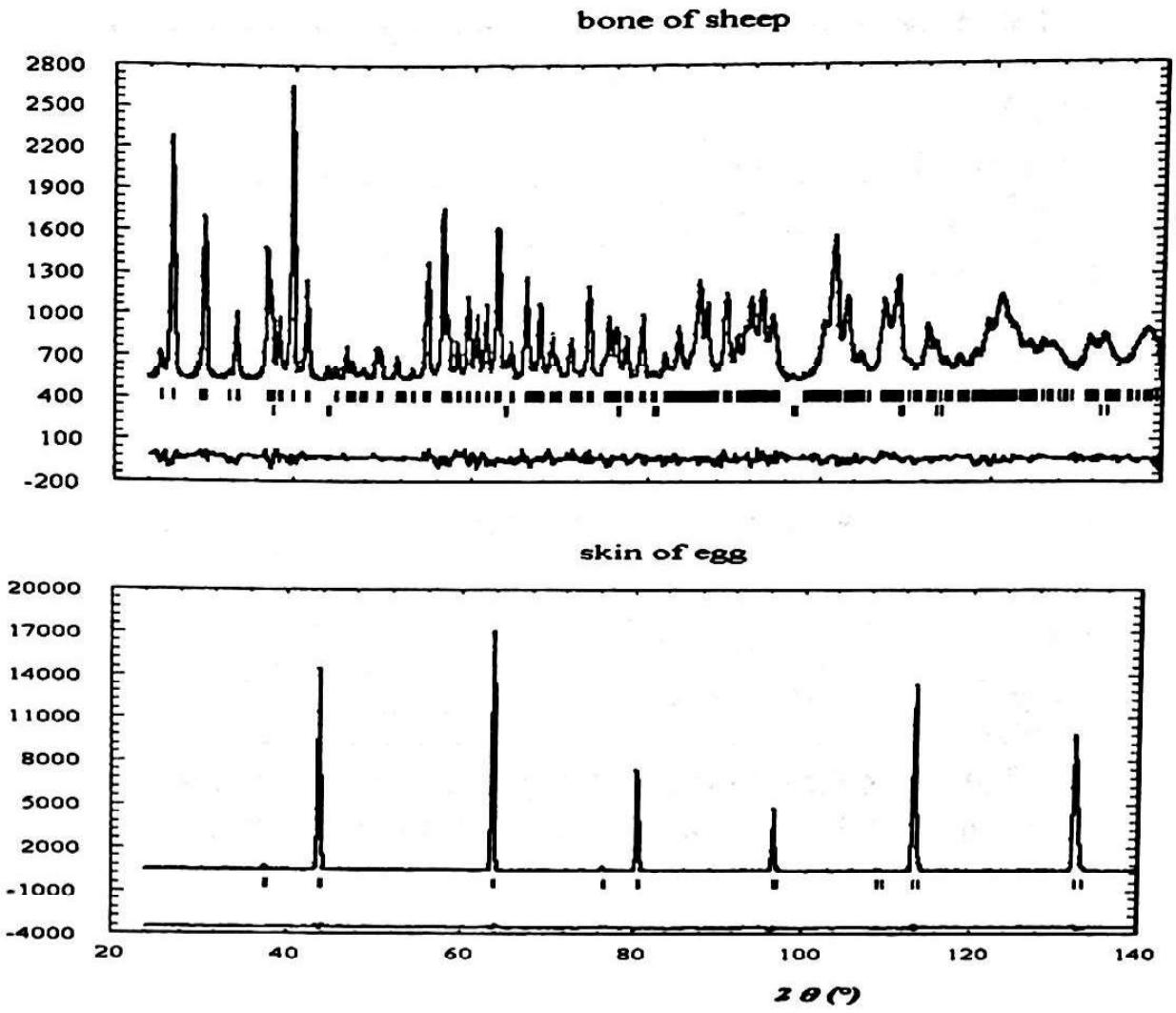


Figure 2: Observed, calculated and difference pattern profile for dinosaur, sheep bones and skin of egg.

Tab.1: Refined crystallographic data for dinosaur bone. (*n-occupation factor, $B_{iso}(10^{-2}$ nm^2) isotropic temperature factor*).

Phase-I $Ca_5(PO_4)_3OH$, sp gr $P6_3/m$ (176)

Atom	site	x/a	y/b	z/c	Biso	n
Ca1	4(f)	0 66667	0 33333	-0 00887(15)	0 41719(07)	0 53270(24)
Ca2	6(h)	0 00640(13)	0 24521(19)	0 25000	0 16275(52)	0 44278(24)
P	6(h)	0 38789(11)	0 36354(99)	0 25000	1 31805(26)	0 47774(85)
O1	6(h)	0 32848(73)	0 48470(82)	0 25000	0 37974(88)	0 51674(93)
O2	6(h)	0 58774(98)	0 46168(03)	0 25000	3 41389(66)	0 61521(36)
O3	12(i)	0 34624(71)	0 25814(69)	0 07366(60)	0 28564(20)	0 94927(20)
O4	2(b)	0 00000	0 00000	0 19790	0 25000	0 50000
H	2(b)	0 00000	0 00000	0 19790	0 25000	0 50000
Lattice parameters a=b=9 356381(57), c=6 907560(28), $\alpha=\beta=90$ 0000, $\gamma=119$ 976624(36)						
R-factors: Rb=5 11%, Rf=3 69%, Re=3 75%, global user-weigthed $\chi^2=0$ 901						

Phase-II: $Ca_3{}_2O_2$, sp gr Fm3m (225)

Atom	site	x/a	y/b	z/c	Biso	n
Ca	4(b)	0 500000	0 500000	0 500000	0 02500	3 20000
O	4(a)	0 000000	0 000000	0 000000	0 02500	2 00000
Lattice parameters a=b=c=4 805664(12), $\alpha=\beta=\gamma=90$ 00000						
R-factors: Rb=2 16%, Rf=1 81%						

Tab.2: Refined crystallographic data for sheep bone. (n-occupation factor, $B_{iso}(10^{-2}$ nm^2) isotropic temperature factor).

Phase-I: $Ca_5(PO_4)_3OH$, sp.gr:$P6_3/m$ (176)

Atom	site	x/a	y/b	z/c	Biso	n
Ca1	4(f)	0.66667	0.33333	-0.00524(56)	0.025000	0.73382(30)
Ca2	6(h)	0.25916(91)	0.28375(02)	0.25000	0.025000	0.48682(11)
P	6(h)	0.41391(40)	0.37054(43)	0.25000	0.025000	0.88257(36)
O1	6(h)	0.32901(56)	0.50679(59)	0.25000	0.025000	0.62536(03)
O2	6(h)	0.58431(31)	0.48332(05)	0.25000	0.025000	0.97988(11)
O3	12(i)	0.23802(77)	0.33428(05)	0.07125(87)	0.025000	0.58055(44)
O4	2(b)	0.00000	0.00000	0.23498	0.025000	0.50391(49)
H	2(b)	0.00000	0.00000	0.23498	0.025000	0.49609(49)
Lattice parameters: a=b=9.416887(28), c=6.887109(33), $\alpha=\beta=90.0000$, $\gamma=119.882767(83)$						
R-factors: Rb=3.12%, Rf=1.88%, Re=3.65%, global user-weigthed $\chi^2=0.646$						

Phase-II: CaO, sp.gr:Fm3m (225)

Atom	site	x/a	y/b	z/c	Biso	n
Ca	4(b)	0.500000	0.500000	0.500000	0.25000	1.00000
O	4(a)	0.000000	0.000000	0.000000	0.25000	1.00000
Lattice parameters: a=b=c=4.809869(15), $\alpha=\beta=\gamma=90.00000$						
R-factors: Rb=5.37%, Rf=2.52%						

Tab.3: Refined crystallographic data for skin of egg. (*n-occupation factor, $B_{iso}(10^{-2}\ nm^2)$ isotropic temperature factor*).

Phase-I: $Ca_{3.09}O_2$, sp.gr:Fm3m (225)

Atom	site	x/a	y/b	z/c	Biso	n
Ca	4(b)	0.500000	0.500000	0.500000	0.69963(05)	3.09612(62)
O	4(a)	0.000000	0.000000	0.000000	0.47176(04)	2.00000(00)
Lattice parameters: a=b=c=4.810580(27), $\alpha=\beta=\gamma=90.00000$						
R-factors: Rb=1.73%, Rf=2.68%, Re=2.71%, global user-weigthed $\chi^2=0.445$						

As a result of neutron diffraction studies we can conclude that the main phase in all the three types of the samples is hydroxylapatite. The method allows to determine exactly hydroxyl anion (OH^-) contents in the phase. This is the advantage of the method. The fact that the chemical

formula of calcium oxide phase, educed in dinosaurs bones and egg skins is $Ca_{3.09}O_2$, does not corresponds to the exact valence balance of calcium and oxygen ions. When the number of calcium ions in the formula is less than three the calculated by theoretical modeling peaks differ having shorter values in comparison with the experimental spectra peaks. But when the number of calcium ion equals to three the coincidence of the theoretical and experimental spectra was good. At this time R-factors for spectra refinement have values less than 5.4%.

Finally, we can conclude that these two kinds of bone samples have hydroxylapatite $Ca_5(PO_4)_3OH$ as the main phase. On the contrary, in egg skins there is not hydroxylapatite phase, the main phase is CaO. But a calcium oxide phase appeared as the second phase in dinosaurs and sheep bones only after heat treatment.

Abstract

This work is devoted to the comparative studies on crystal structure of fossil and recent bones (dinosaur, sheep and skin of egg). The basic hydroxyapatite ($Ca_5(PO_4)_3OH$) structure is hexagonal with space group $P6_3/m$, while the values of their structural parameters often depend on the chemical thermal processing. The chemical formulas of a calcium oxide phase in dinosaurs bones and egg skins are $Ca_{3.2}O_2$ and $Ca_{3.09}O_2$ correspondingly. However, the calcium oxide phase in sheep bones corresponds to the chemical formula: CaO

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