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Fluorapatite diagenetic differences between Cretaceous skeletal fossils of Mongolia and Korea

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A B S T R A C T

The skeletal tissue of modern bones is mostly composed of hydroxyapatite, which contains calcium and phosphate. During diagenesis, calcium, phosphorus and minerals of the hydroxyl group can be exchanged with other elements to form carbonate-fluorapatite. It is well-established that paleoenvironmental evolution and geological events have played a significant role in the compositional changes of fossilized bones. For example, skeletal fossils from the Hasandong Formation (Aptian- early Albian) of the Gyeongsang Basin in Korea are characterized by black and dark colors, whereas dinosaur bones from the Nemegt Formation (early Maastrichtian) of the Nemegt and Altan Uul ranges in Mongolia are light brown and white. This study investigated the mineralogical and geochemical causes for the differences in coloration between these two groups of fossilized bones. Multiple synchrotron-based techniques were utilized, including synchrotron–XRF, –XRD, –X-ray micro-computed tomography (μ-CT), micro-XRF and SEM-EDX data to analyze the elemental composition and mineral phases in dark Korean fossilized bones, which are characterized by the presence of iron, aluminum, magnesium and other trace elements. Chamosite was identified as a secondary mineral at 5% by weight of the total fossil mass, which is primarily composed of carbonate-fluorapatite. However, skeletal fossils from Mongolia are characterized by secondary minerals, such as barite, goethite and calcite, which accumulate in pore spaces. Since different secondary minerals result from different alteration procedures, the presence of chamosite in the Korean fossils suggests alteration by spatial replacement, and the presence of barite in the Mongolian fossils suggests alteration by accumulation. The investigation of these two skeletal groups, analyzed using a suite of synchrotron-based multidisciplinary techniques, revealed contrasting mineralogical and geochemical details and helps to determine the origin of fossil colorization.

1. Introduction

Bones are composed of organic and inorganic constituents of varying amounts. Most of the organic components are removed or replaced during diagenesis, leaving the inorganic components (mostly hydroxylapatite) as fossilized bones. However, fossilized bones across the world have been observed with different textures, colors, and mineralogy due to different diagenetic processes during fossilization. Therefore, diagenesis of fossilized bones helps to elucidate the fossils' geological history (Hedges, 2002). Several techniques (Piga et al., 2011; Keenan et al., 2015) in mineralogical and geochemical analysis have been used to assess the degree of diagenesis (Tuross et al., 1989; Barreto and Albrecht, 1993; Zocco and Schwartz, 1994). Due to the structural and mineralogical diversity in apatite ($Ca_5(PO_4)_3(OH,F,Cl)$), which is the primary component of fossilized bones (McConnell, 1965; Hughes et al., 1989; Wopenka and Pasteris, 2005), previous experimental studies have focused on crystallographic (e.g., Piga et al., 2011; Keenan et al., 2015) and geochemical information from diagenetic apatite (e.g., Nelson et al., 1986; Sillen, 1986; Samoilov and Benjamini, 1996; Park et al., 2001; Trueman et al., 2011). Because bone has high porosity with a large surface area, it is a valuable geochemical indicator in the identification of rare earth elements that have replaced calcium in apatite (Trueman et al., 2011). Similarly, fossilized bones altered via depositional sedimentation have substituent ions that are included in groundwater. As a result, fossilized bones tend to exhibit a range of rare earth elements (Nelson et al., 1986; Sillen, 1986; Samoilov and Benjamini, 1996; Park et al., 2001). In addition to elemental and mineralogical changes in composition, low-grade metamorphism also alters the color of fossilized bones, which can be used to recognize diagenetic history and paleoenvironments (Epstein and Epstein, 1977; Ainsworth et al., 1990; McNeil et al., 1996; Goodhue and Clayton, 2010). Even soft tissue from dinosaur bones have been preserved in

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specific diagenetic environments (Schweitzer et al., 2005, 2007, 2013).

Crystallographic and geochemical information of bones is important in regard to the diagenesis, during which the composition of fossilized bones have changed due to the growth of secondary minerals (Hubert et al., 1996; Ferretti et al., 2012). This composition includes minerals such as calcite and oxide minerals, which can accumulate and/or replace the bone structures. Related geological events supply the constituents of secondary minerals (Pfretzschner, 2001; Zougrou et al., 2014a, 2014b). The identification of secondary minerals is, however, still under-explored in the study of bone diagenesis. This study aimed to identify two representative fossil sites that show contrasting texture and color of fossilized bones and selected Cretaceous skeletal fossils from Mongolia and Korea to characterize the fossil diagenesis. The Mongolian samples consist of bone from two different dinosaur taxa from the Nemegt Formation (early Maastrichtian), southeastern Gobi Desert. The Korean fossils consist of dinosaur and turtle bones from the Hasandong Formation (Aptian- early Albian), southern Korea. A pelecypod shell is also included into the Korean samples to study the differences between vertebrate and invertebrate fossils. To distinguish the different fossilization processes, this study utilizes a combination of multidisciplinary analytical techniques developed in geochemistry and mineralogical studies. All of the specimens were analyzed using various synchrotron radiation and laboratory-based crystallographic and geochemical techniques, such as XRD, XRF, X-ray μ-CT and SEM-EDX. The study's findings suggest that differences in the geochemical evolution of the fossil sites determine secondary mineralization and the characteristic colorization of fossils.

2. Geological setting

The Nemegt Formation (early Maastrichtian) is widely distributed in the southcentral Gobi Desert of Mongolia, including the Nemegt Basin, Altan Uul, Hermiin Tsav, Bügiin Tsav, Guriliin Tsav, and Nogoon Tsav (Fig. 1A) (Jerzykiewicz, 2000). This formation overlies and/or interfingers with the Baruungoyot Formation (Eberth et al., 2009). The Nemegt and Altan Uul ranges were formed by Late Carboniferous collisional deformation and crustal thickening (Cunningham et al., 2009). The Late Jurassic and Early Cretaceous rifting resulted in subsidence and the accumulation of continental sediments. The area is overlain by the extensive and flat lying Upper Cretaceous Baruungoyot and Nemegt formations. Relative stability in the Cenozoic except for transpressional crustal reactivation and uplift of Nemegt-Altan Uul led to the development of extensive pediments. The Nemegt Formation consists primarily of gray and yellow grayish-brown massive sandstones with reworked caliche pebbles and mudstones, which were deposited in the fluvial dominant environment (Jerzykiewicz, 2000). The formation contains a variety of terrestrial vertebrate fossils, especially dinosaurs (Shuvalov, 2000).

During the Cretaceous, the Izanagi Plate subducted under the Asian continent which resulted in continental arc volcanism in the southern part of the Korean Peninsula (Klimetz, 1983). The Gyeongsang Arc System comprises a volcanic arc (Gyeongsang Volcanic Arc) and the adjacent back-arc basin (Gyeongsang Basin) behind the arc, which is the largest Cretaceous sedimentary basin in Korea (Chough and Sohn, 2010). The Gyeongsang Supergroup is divided into the Sindong, Hayang, and Yucheon groups. The Sindong Group comprises the Nakdong, Hasandong, and Jinju formations in ascending order. The Hasandong Formation (Aptian to early Albian) is distributed in the Jinju and Uiseong subbasins. The formation shows alternate depositional conditions distinguished by reddish and gray sandstone, reddish to greenish gray sandy mudstone, and dark gray shale. The overall sedimentary facies are interpreted to be alternating channel and interchannel sediments with occasional floodplain deposits (Choi, 1986). The Hasandong Formation has yielded the most abundant vertebrate body fossils of all formations discussed (Fig. 1B) (Lee et al., 2001). In summary, while the Mongolian Upper Cretaceous basins have been relatively stable to date, the Gyeongsang Basin, which formed in the back-arc region of the eastern margin of the Asian continent, has undergone extrusive volcanism, volcano-tectonic extension, and expansion with accelerated subsidence.

3. Materials and methods

3.1. Fossil samples

The fossil samples from Mongolia consist of ribs from a large *Deinocheirus* (MPC-D 100/127) and a small *Deinocheirus* (MPC-D 100/128) from the Nemegt Formation at Bügiin Tsav and Altan Uul IV, for which femur lengths are 1320 mm and 980 mm, respectively (Lee et al., 2014). Histological studies have not been performed on these specimens. Another Mongolian sample is a tibia of an eight year-old *Tarbosaurus* (MPC-D 107/18) from the Nemegt Formation at Altan Uul III. Korean samples consist of a theropod tooth from the Hasandong Formation on Juji Island, Hadong County (Lee, 2007), as well as a turtle carapace and a pelecypod shell from the Hasandong Formation on Gae Island, Sacheon City. The theropod tooth was collected at a lower level than the other fossils. For the Mongolian fossils, compact bones have an overall bright, ivory color while spongy bones are filled with either brown or dark yellow secondary minerals. However, all of the Korean fossils are characterized by dark gray or black colors, suggesting they have undergone major alteration and diagenesis (Fig. 2, Table 1).

XRF elemental mapping and SEM-EDX were performed using thin sections of all fossil samples. Powdered corundum (Al_2O_3) was used as an abrasive from sizes #600, #1000, #2000 and #3000. Additionally, fossils were cut into small pieces and analyzed using transmission X-ray μ-CT. Small pieces of all samples were ground down in order to identify the mineral phases using XRD measurement.

3.2. Micro-X-ray fluorescence analysis

To perform 2-dimensional elemental mapping, the Synchrotron Rapid Scanning X-Ray Fluorescence (SRS-XRF) method was used on selected thin-sectioned specimens at the BL10-2a beamline at Stanford Synchrotron Radiation Lightsource. The beam energy used was 12.0 keV, the fluorescent photon count measured using Vortex Silicon Drift Detector. A 50- to 75-μm step was used for the *Tarbosaurus* bone and theropod tooth with a count of 25.0 ms.

For thin sections of the fragments of pelecypod, turtle, and the two *Deinocheirus* specimens, laboratory XRF was used to develop 2-dimensional elemental mapping using an M4 Tornado (Bruker Co.). A micro-focused Rh source (50 kV, 600 μA) and a poly-capillary were employed for making a 25-μm step-scan with a 200-ms count in a low-vacuum environment.

3.3. Micro-X-ray diffraction analysis

Small bone pieces of the *Tarbosaurus* specimen, the two *Deinocheirus* specimens, secondary minerals, and the theropod tooth were ground into powder for phase identification using synchrotron X-ray powder diffraction at the 9B and 5A beamlines at the Pohang Accelerator Laboratory (PAL). At the 9B beamline, data were collected using a monochromatic X-ray with 1.5179(1) Å wavelength and a multiple analyzer-scintillator detector setup with a step size of 0.01° and step count of 5 s. At the 5A beamline, the transmission mode was employed using a 0.6925(1) Å X-ray and Mar345 image plate detector. Alternatively, the laboratory μ-XRD was performed using a MicroMax-007HF (Rigaku Co.) diffractometer operating at 1.2 kW and producing Mo-Kα (λ = 0.7107 Å) radiation on the sample via micro-focusing multilayer optics (Seoung et al., 2012). The powdered turtle sample was packed into a 0.2-mm quartz capillary, and the diffracted beam was analyzed using an imaging plate detector. Either Fit2D (Hammersley et al., 1996) or IP analyzer (Seto et al., 2010) was used to convert the