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Mineral microbial structures in a bone of the Late Cretaceous dinosaur *Saurolophus angustirostris* from the Gobi Desert, Mongolia — a Raman spectroscopy study

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ABSTRACT

Bones, while buried, undergo diagenetic transformations, the intensity of which depends on a variety of geochemical factors. Microbial degradation is one of the main processes acting on bones during early diagenesis. We present mineral microspheres formed during bone diagenesis from the inner walls of the left tibia of the Late Cretaceous dinosaur *Saurolophus angustirostris* from the Gobi Desert (Mongolia). The microspheres occur either as individual bodies, from a few micrometers to about 70 μm in diameter, or aggregated in clusters. Micro-Raman analysis shows that the microspheres are composed of various Fe-oxides – mostly hematite and goethite – that form regular reddish-brown rings, with organic matter at their cores. The bone itself is composed, for the most part, of diagenetically transformed carbonate-fluorapatite. Calcite cement was identified around the spheres and at points of contact with bone tissue. Negative Ce anomalies indicative of Ce(IV) in the diagenetic environment indicate oxic burial conditions. All the size distribution of the microspheres, their mode of occurrence, and the presence of organic matter in cores surrounded by concentric Fe-oxide envelopes indicate early diagenetic microbially-mediated mineralization in aerobic conditions. The presence of microspheres and other mineral phases in the studied bone gives evidence of at least two mineralization episodes: (1) Fe-oxide formation during an early diagenetic microbial attack on the bone, and (2) later calcite/barite/gypsum cementation.

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1. Introduction

Biologically-mediated mineralization processes are common in many environments. The chemical and biological conditions under which this mineralization occurs are, however, not fully understood. Iron oxides (often of mixed valence), as well as iron-bearing carbonates, sulfides, and phosphates, are among the most common bacterially-mediated minerals. These include: hematite (Fe_2O_3); ferro-ferric oxyhydroxides ($Fe(OH)_3$ (approx.)); lepidocrocite (γ-FeO(OH)); goethite (α-FeO(OH)); magnetite (Fe_3O_4), siderite ($FeCO_3$), mackinawite (FeS); greigite (Fe_3S_4); pyrite (FeS_2), and vivianite ($Fe_3(PO_4)_2 \cdot 2H_2O$). Iron-reducing bacteria are able to induce the precipitation of many iron-bearing minerals depending on the ambient chemistry of the depositional microenvironment (e.g., Moskowitz et al., 1989; Bazylinski and Frankel, 2000; Konhauser et al., 2011). Mineralization reactions leading to the formation of biogenic iron oxides can be classified as either "active" or "passive." Active mineralization encompasses the microbially-mediated oxidation of iron Fe (II) to Fe (III) under both oxic and anoxic conditions and a pH ranging from acidic (Clarke et al., 1997; Kozubal et al., 2008) to neutral (Hallberg and Ferris, 2004; for review see Konhauser, 1998; Chan et al., 2009). Passive mineralization is the precipitation of minerals occurring on biological surfaces (e.g. bacterial cell walls) as a consequence of the microenvironment created by the cell's own functions. Microbes can alter the pH of the immediate cellular environment, thus enhancing the binding and nucleation of Fe-oxides on the cell surface. Both types of mineralization belong to the general category of biologically-mediated mineralization.

Raman spectroscopy is used to identify the chemical composition and structure of minerals and carbonaceous matter on the microscale. Recently, this technique has been increasingly employed to distinguish iron oxide and hydroxide minerals in geological samples (e.g. Marshall and Marshall, 2011; Marshall et al., 2011). Because these minerals are also a part of the natural compounds used to produce many ancient pigments, the Raman method has been extensively applied in investigations of the archaeological materials (Clark and Curri, 1998; Edwards, 2001; Edwards et al., 2001; Damiani et al., 2003; de Faria and Lopes, 2007). Iron oxides are also products of corrosion (Thibeau et al., 1978; Oh et al., 1998). They occur as components of many meteorites (Edwards et al., 1999; Rull et al., 2004), and are frequently present in paleontological materials (Marshall et al., 2011; Kremer et al., 2012). In the latter category of analysis, Raman spectroscopy is not yet in widespread use and has only recently been directed towards problems in Precambrian petrology and paleontology (e.g. Schopf et al., 2002, 2005; Edwards et al., 2007; Schiffbauer et al., 2007, 2012; Schopf and Kudryatsev, 2009; Marshall et al., 2010; Schopf et al., 2010; Marshall et al., 2011), Paleozoic sedimentology and paleobiology (e.g. Kazmierczak and Kremer, 2009; Kremer et al., 2012; Meyer et al., 2012) and vertebrate paleontology (Thomas et al.,

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2007; Piga et al., 2011) . The power of the Raman technique has contributed to the understanding the morphology, chemical composition and 3D preservation of microfossils at high spatial resolution.

In this study we report on Raman spectroscopic investigations on the Fe-rich microspheres from dinosaur bones with the purpose of clarifying their mineralogical composition and verifying the hypothesis of their microbial origin. Microbial processes are the main biotic factor altering the bones early post-mortem and after burial (Child, 1995; Jans et al., 2004; Peterson et al., 2010; Müller et al., 2011). However, chemical alterations experienced by bones while buried may significantly overprint primary (authigenic) phases. Post-mortem diagenetic changes which encompass both biotic and abiotic degradation mechanisms reflect the local redox conditions and provide a glimpse into the nature of the burial environment (Fernandez-Jalvo, et al., 2002). A number of techniques has been employed to characterize diagenesis of dinosaur bones (e.g. Tütken et al., 2008; Piga et al., 2011; Thomas et al., 2011). Raman spectroscopy has already been shown as a non-destructive, reliable method to identify the mineral and organic composition of bones and products of their diagenesis (Wopenka and Pasteris, 2005; Thomas et al., 2007, 2011).

2. Geological setting

The analyzed specimen was recovered from Tsagan Khushu exposure belonging to the Nemegt Formation. The Nemegt Valley known in local language as “The Valley of Dragons” is one of the most fossiliferous formations in the world, which produced one of most famous dinosaur faunas (Gradziński, 1969; Jerzykiewicz, 1998, 2000; Shuvalov, 2000). The Upper Cretaceous sediments in the Nemegt Basin have been divided into two formations: the Lower and Upper Nemegt Beds (Gradziński et al., 1968; Gradziński, 1969). The Lower Nemegt Beds are unfossiliferous, whereas the Upper Nemegt Beds are fossiliferous, containing numerous dinosaurs. Both, the Lower and Upper Nemegt Beds, are composed exclusively of clastic sediments. The major constituents of the Nemegt Beds are: quartz, feldspars, rock fragments and clay minerals. Admixtures of micas, chamosite, turingite, chlorite, psilomelane, barite, and rare crystals of gypsum have also been found (Gradziński, 1969).

The main Tsagan Khushu exposures (Fig. 1a) are located between 100°21′00″E and 100°23′30″E and 43°27′40″N and 43°29′20″N. Lack of the marine fossils in the central Asian Cretaceous precludes any direct biostratigraphic correlation with the international marine stages of the Cretaceous Period. Ages of the Upper Cretaceous formations of the Gobi Desert are inferred from the evolutionary changes of the contemporary and analogous fauna in the North American non-marine stages (which are constrained both by the ammonite zonation, palynology, and chronostratigraphic methods) (Jerzykiewicz, 1998; Jerzykiewicz, 2000 and reference therein). Therefore, the age of the bone-bearing Upper Nemegt Beds is estimated as Late Campanian to Early Maastrychtian (Gradziński, 1969). Most of the dinosaur remains have been found in the sandy and gravelly sediments.

Dinosaur bones from the Tsagan Khushu locality are hosted in point bar and channel bar sediments.

These are siliciclastic continental sediments of the red-bed type, dominated by arkoses with thin mudstone intercalations (Gradziński et al., 1968). Common sedimentary features of the Nemegt Beds are scoured surfaces and erosional channels filled with conglomerates and siliciclastic sediments with inclined stratification, large-scale cross-stratification, climbing ripples, and fining-upward cycles. These features are indicative of a fluvial depositional environment, in which sediments accumulated in alluvial plains as point bars and channel bars; channel bottom and overbank sediments occur less frequently (Gradziński, 1969; Jerzykiewicz, 1998).

Besides dinosaurs, fragments of dinosaur eggs, tortoises, crocodiles, fishes, pelecypods, phyllopods and ostracods have been found (Gradziński, 1969). Calcified wood and *Charophyta* charophyte oogonia have also been reported from these deposits (Gradziński, 1969).

Gradziński (1969) suggested that the Upper Nemegt Beds were deposited in a warm, humid climate. Lithological variations in the channel sediments indicate changes in channel performance, which is indicative of alternating dry and rainy seasons. Jerzykiewicz (1998) postulated that these bone beds may represent deposits of an inland river delta, like those of the present-day Okavango delta, Botswana. The absence of bone breccias and lack of bone deformations (apart from mechanical breaking and splitting) indicate that the bones were not moved and transported post-mortem over long distances; rather, they were more or less *in situ*. Preservation of articulated bones, often articulated skeletons with skin imprints and casts in surrounding sediment (e.g. Maryanska and Osmólska, 1984) indicates consequently either rapid burial or/and anoxia. Either of these conditions would prevent scavengers and bioturbators from disrupting the skeletons. Hence a rapid burial coupled with a short period of subaerial decomposition seems in this case to be the most likely taphonomic scenario.

3. Material and methods

The studied material was collected during the Polish–Mongolian Palaeontological Expeditions, 1963–1965, in the Late Cretaceous sediments of the Nemegt Basin (Kielan-Jaworowska and Dovchin, 1968/69). Dinosaur skeletons of the Upper Nemegt Beds display a variable state of preservation. Most of them is preserved as a complete skeletal material; single bones and bone fragments are rare (Gradziński, 1969). Skeletons of *Saurolophus angustirostris* have been discovered within a bed of very strongly cemented sandstone. The original structure of the bone is very well preserved. Pawlicki et al. (1966) observed, using an etching and replication technique, osteocytes and vessels from bones of this dinosaur species.

The part of the dinosaur hind limb studied here was found in the Tsagan Khushu area (Fig. 1a). The bone chosen to study represents the most common and the best preserved one among the bones sampled from the area of study. Petrographic transparent sections about 30 μm thick, containing microbial mineralization have been investigated by standard optical methods. Polished slabs were analyzed with a scanning electron microscope (SEM). Thin sections and slabs were made from the left tibia of *Saurolophus angustirostris* (Cat. No. ZPAL MGD-I/167, Institute of Paleobiology, Polish Academy of Sciences, Warsaw) (Fig. 1b, c).

Histological observations were carried out with the optical microscope Nikon Eclipse LV 100 POL, and opaque authigenic minerals were identified with a reflected-light microscope and a Philips XL-20 scanning electron microscope (SEM) equipped with an EDS (energy dispersive X-ray spectroscopy) detector ECON 6, system EDX-DX4i, and a backscattered electrons (BSE) TOPO or COMPO detector (a product of FEI). This instrument was operated at an accelerating voltage of 25 keV, a beam current of 98–103 nA, and a spot diameter of 3.5 μm.

3.1. Raman data collection

Measurements were performed at the Laboratory of Intermolecular Interactions, Faculty of Chemistry, Warsaw University. Raman point mapping was performed with a LabRAM HR800 (Horiba Jobin Yvon) spectrometer, coupled with an Olympus BX61 confocal microscope. The instrument was equipped with a Peltier-cooled CCD detector (1024×256 pixels). The measurements were carried out utilizing a diode-pumped, frequency-doubled Nd:YAG laser (532 nm, Pmax = 100 mW on the head). Spectra were collected in a backscattering configuration, using a $100\times$ magnification Olympus objective. The confocal pinhole size was set to 200 μm and a holographic grating with 600 grooves/mm was used. The calibration of the instrument was performed utilizing a 520 cm^{-1} Raman signal from a silicon wafer. The laser spot size was about 500 nm.

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