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Author: Dawid Surmik, Jerzy Cabała, Katarzyna Balin, Jacek Szade

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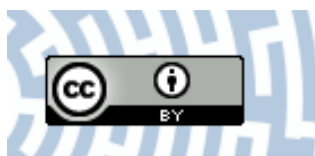
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An awkward contaminant: are mercury concentrations in historically collected fossils a result of storage conditions?

Dawid Surmik[1], Jerzy Cabała[2], Katarzyna Balin[3], Jacek Szade[4]

[1] University of Silesia, Institute of Earth Sciences, Faculty of Natural Sciences, Sosnowiec, Poland,
e-mail: dawid.surmik@us.edu.pl (corresponding author), ORCID ID: 0000-0003-0121-9592
[2] University of Silesia, Institute of Earth Sciences, Faculty of Natural Sciences, Sosnowiec, Poland,
ORCID ID: 0000-0002-2247-4827
[3] University of Silesia, August Chełkowski Institute of Physics, Faculty of Science and Technology, Chorzów, Poland,
ORCID ID: 0000-0002-1811-3033
[4] University of Silesia, August Chełkowski Institute of Physics, Faculty of Science and Technology, Chorzów, Poland,
ORCID ID: 0000-0003-2083-4275

Abstract: High concentrations of mercury (Hg), reaching astonishing values in two cases, have recently been detected in Middle and Late Triassic fossil reptile bones, housed for over 100 years in several Polish museum collections. Since no correlation between either the life modes of these taxa or their burial environment was observed, the studied contaminations seem to be associated with housing conditions. The specimens were kept for an extended amount of time in boxes, in which they were stored soon after finding. A proximity of mercury-containing materials, like mercury fulminate, and unstandardized conditions of storage and conservation of the remains may result in contamination of porous bone with mercury. A detailed knowledge about the housing history of old museum collections has great importance to their prospective studies.

Keywords: mercury, contamination, vertebrates, bones

INTRODUCTION

Due to the intensive development of modern fine-scale techniques, the restudies of historically collected fossils can be a precious source of new, important findings, but they can also lead to pitfalls. Among such problems, particularly prominent are the lack or incomplete documentation and disorder in specimen labelling. Nonetheless, the knowledge about storage history of specimens from the moment of their finding in the field to their "re-discovery" in museum storage is crucial. Even if we assume that the original documentation of the specimens was conducted with great solicitude to the old, European paleontological school of the 19th century, the ways in which the specimens were preserved and stored may exclude their usability in specific analyses. For example, if subfossil vertebrate remains were treated or painted with organic-based compounds, it would be impossible to correctly date them using the radiocarbon method because of the secondary delivery of modern carbon. Similarly, the usage of animal bone-glues, commonly used prior to polymeric-based adhesives, may give a false-positive result of the presence of organic matter in the analysed bone (Lindgren et al. 2011), which limits their usefulness in molecular studies.

The biophilicity of mercury means that the causes of its bioaccumulation in living organisms

are the subject of various biological studies (Sinkus et al. 2017, Leong & Chang 2020, Yao et al. 2020). There is less information on the concentration of Hg in bone material from museum collections or paleontological and archeological fieldwork. Recently, mercury enrichment has become a novel proxy for deciphering large-scale volcanism in the geological past (Sanei et al. 2012, Racki et al. 2018a, Rakociński et al. 2020), especially in relation to global events, and in the context of the toxic poisoning of organisms during mass extinctions (Bond & Grasby 2017, Rakociński et al. 2020).

Mercury is a heavy metal, and its specific characteristics influence its large migration potential in the environment, including rock and biotic systems. It has a strong, toxic impact on living organisms (Rice et al. 2014). On the other hand, mercury or its compounds have been used at various stages of civilizational development, e.g., in medicines, cosmetics, bactericides, and rodenticides. Beginning in the 19th century, mercury fulminate $(C_2N_2O_2Hg)$ was commonly used as an explosive in mining and construction works. The ease with which it amalgamates with gold made it useful in recovering gold from its ores. During the 20th century, it was used in batteries, fluorescent lights, felt production, thermometers, and barometers, etc. Since the 19th century, the global production of mercury grew, and only by the end of the 20th century had restrictions in its mining production and usage been introduced. At the same time, an increase in mercury contamination in the biotic and abiotic environments was observed, related to artisanal and small-scale gold mining, coal combustion, non-ferrous metal and cement production, and chlor-alkali industry. The restrictions of mercury emission gained special importance after the Minamata Convention on Mercury which met in 2013 (Mackey et al. 2014).

Levels of mercury concentration were most frequently studied in aquatic environments, soils, atmosphere, and food (Watras et al. 1998, Ericksen & Gustin 2004). No data exists, however, on a secondary concentration of mercury in museum exhibits, archaeological artefacts, or specimens in palaeontological collections.

In this study, we present unexpectedly high concentrations of mercury in fossil bones housed in the historic collections of several Polish museums. The anomaly concerns both the specimens kept in museum storage and those presented on the museum displays. For comparative purposes, we also present concentrations of mercury in fossil bones, coprolites, teeth, and scales from recently created museum collections or samples gathered directly from field excursions.

GEOLOGICAL AND GEOCHEMICAL BACKGROUND

The fossil bones, teeth, scales, and coprolites which were analysed for mercury content came from the Middle and Upper Triassic sediments (Tab. 1) of the Silesia-Kraków area (southern Poland). The fossils are found in organogenic carbonate rocks, such as limestones, limestone clays (Middle Triassic), or claystone formations (Upper Triassic). The Middle Triassic (Gogolin Formation) sediments had been deposited in a shallow epicontinental marine reservoir. During the Mesozoic (probably in the Cretaceous – cf. Heijlen et al. 2003), these deposits were locally dolomitized by the hydrothermal influence of low-temperature aqueous solutions. These processes are responsible for the creation of the Zn-Pb ore deposits in the Silesia-Kraków region. No mercury concentrations were detected within the Triassic rocks of that region or within the Zn-Pb deposits (Leach et al. 1996). Subsequent, post-Mesozoic platform vulcanism, which is evidenced by basalt occurrences, likewise did not result in mercury alteration. There is a little available data about the mercury concentration in the soil and aquatic environments of Silesia-Kraków region (Pasieczna 2014).

An open-air exploitation of limestones and marls (especially in the Tarnowskie Góry area) facilitated the acquirement of fossils in form of isolated bones or fragmentary skeletons. The oldest private collections of the Triassic vertebrate remains from that area, particularly of marine reptiles (order Sauropterygia), were created in the 19th century by amateur geologists – Baron Carl August Ludwig von Oeyenhausen, Carl Rudolph Mentzel, Eduard Kleemann (Surmik et al. 2016, 2017) and Maximilian Grundey – and successively studied by researchers such as Hermann von Meyer (von Meyer 1847), Anton Schrammen (Schrammen 1899), and (related to the University of Wrocław) Herman Kunisch (Kunisch 1888) and Georg Julius Ernst Gürich (Gürich 1884).

MATERIALS

Institutional abbreviations

The following abbreviations of institution names are used in the article: SUT-MG – Museum of Deposit Geology, Silesian University of Technology (Gliwice, Poland); MG UWr. – Museum of Geology, University of Wrocław (Wrocław, Poland); GIUS – Faculty of Earth Sciences, University of Silesia (Sosnowiec, Poland); ZPAL – Institute of Paleobiology, Polish Academy of Sciences (Warsaw, Poland).

Samples

The samples studied here include historical (gathered before the year 1900) museum collections (eleven specimens), present-day (gathered since the year 1990) museum collections (four specimens), and eleven specimens collected during the fieldwork no longer than five years before study (Tab. 1). Furthermore, among the historical collections' specimens, seven were stored in a warehouse following their collection (Tab. 1, footnote *storage* in brackets), and four are exhibited in a glass cabinet (Tab. 1, footnote *exhibition* in brackets). The exact date of moving these specimens from the warehouse to the exhibition is not known but, according to the collection curators, they were moved around the year 1945 (pers. comm.). The samples were collected in the several localities in the Upper Silesia and western Lesser Poland regions (Fig. 1).
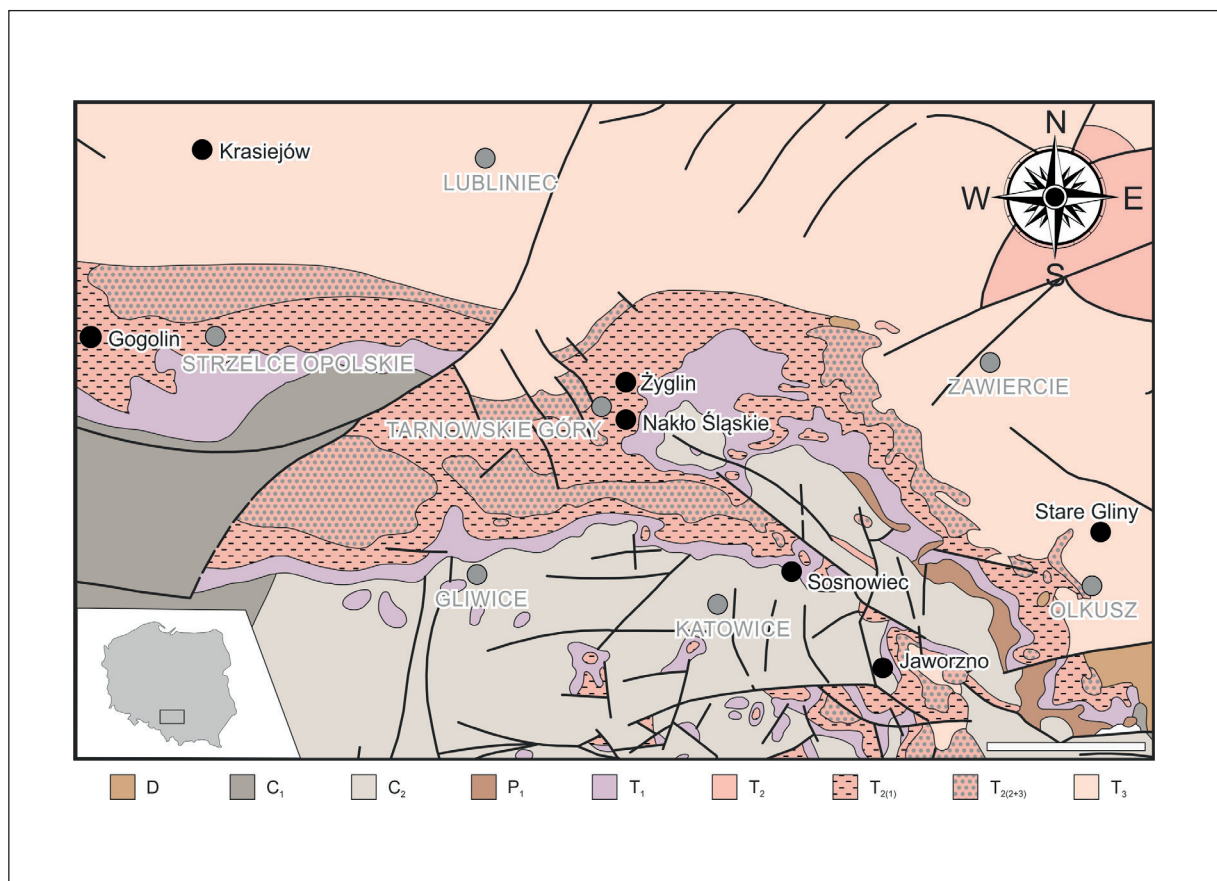

Fig. 1. *Locations from which the collected fossils originate presented on the geological map without Cenozoic, Cretaceous and Jurassic sediments; based on Rühle et al. (1980): D – Devonian, C1 – Mississippian, C2 – Pennsylvanian, P1 – Lower Permian, T1 – Lower Triassic, T2 – Middle Triassic (not separated), T2(1) – Lower Middle Triassic, Gogolin Formation (limestones and epigenetic dolomites), T2(2+3) – Middle and Upper Middle Triassic (Diplopora dolomites, limestones and dolomites), T3 – Upper Triassic. Scalebar equals 50 km*

METHODS

Sampling

All samples were weighed on a RADWAG AS 220/X electronic analytical balance (max. 220 g; min. 10 mg; accuracy 0.1 mg). The fossil bones, fossil tooth, coprolites, and sediment sample were powdered using an agate mortar prior to the analyses of mercury content.

Mercury analysis

The mercury concentration analyses were performed using pyrolyzer-type Milestone Inc. Direct Mercury Analyzer (DMA-80) equipment with a low-pressure mercury lamp, with a wavelength $\lambda = 253.65$ nm, and the atomic absorption spectroscopy (AAS) technique with a detection limit up to 0.005 ng Hg. The mercury concentration [ppb = μg/kg] presented in Table 1 is the arithmetic average of these two measurements.

Based on the AAS method, this measurement system applied in this study is significantly correlated with ICP-MS, an analytical standard usually applied for trace elements including mercury (Racki et al. 2018b). The instrument was calibrated using INCT-OBTL-5, a basma-type tobacco leaves, the Polish standard certified reference material for inorganic analysis, with a mercury content of 20.9 ppb and an accuracy not exceeding 2%.

The powdered sample was weighed on an analytical balance, moved directly to a nickel sample boat (max. 100 mg), and placed in auto-sampler. The sample was dried in a catalyst furnace (in an oxygen stream at 200ºC, 99.995% pure O_2, 4 bar pressure, 200 ml/min flow) and mineralized in a release furnace (650ºC). During the mineralization process, the mercury is released from the sample, and other gaseous by-products (nitrogen oxides, sulphur oxides, and halides) form. The mercury is transported by a carrier gas to the amalgamator and gaseous by-products to the device outlet port. In an amalgamator unit, the Hg-Au amalgam forms (170ºC), and then, at a temperature of 850ºC, the isolated metallic mercury is exhaled and enters the measuring system. In this system, the quantity of mercury is measured using the atomic absorption spectrometry method (AAS). As a result of radiation absorption, the mercury atoms enter an excited state. The

radiation not absorbed by the mercury atoms is passed to the detector, and there the absorbance (ABS), i.e., the common logarithm of the ratio of the radiation entering the measuring cell (I0) to the (non-absorbed) radiation leaving the cell (I), is measured:

$$ABS = \log (I0/I)$$

Finally, from the resulting absorbance DMA software calculates the absolute amount of Hg in the sample, and calculates the concentration presented as ppb.

SEM/EDS technique

Scanning electron microscopy imaging (SEM) was performed and energy-dispersive X-ray spectra (EDS) were collected using the Philips XL30 ESEM/EDAX equipped with an EDAX Sapphire energy-dispersive X-ray spectroscope. The measurements were done using several uncoated bone fragments (low vacuum, accelerated voltage 15 kV). 50 ESEM/BSE images were obtained, and 20 EDS analyses were performed.

XPS technique

X-ray photoelectron spectroscopy (XPS), a surface-sensitive quantitative technique, provides detailed information about the elemental composition and chemical states (bonding environments) of the samples. The electronic structure of the sample was measured using the Physical Electronics 5700 spectrometer with the use of monochromatized AlKα radiation (1486.6 eV) and the chemical composition of the sample surfaces was determined from the XPS spectra with precision of about 0.01 at. %. The samples were cleaned in situ in an ultra-high vacuum by etching with an argon (Ar) ion beam with an energy of 0.2 keV. The region of interest focused on several spots of isolated bone fragment (obtained from UT-MG/F/Tvert/74-1 sample), 1000 μm × 1000 μm in size.

The sample characterized by the highest mercury concentration (SUT-MG/F/Tvert/74-1) was examined using X-ray photoelectron spectroscopy. Several regions of bone were chosen for the analysis.

Resulted images and spectra were processed using CorelDRAW X6 Graphics Suite.

RESULTS

Hg concentration by AAS

The Hg concentration levels measured in the studied specimens are shown in Table 1. The highest mercury contents were found in bones (*Nothosaurus* femur, *Pistosaurus* vertebra). Of these, the bones from historical collections were found to exhibit the highest concentrations. The specimens from collections collected right before the study exhibit at least four times lower Hg concentration levels.

BSE and EDS investigation

In low-vacuum environmental mode of measurement (ESEM, 0.3 Torr) with backscattered electrons (BSE) imaging (Fig. 2A), the possibility of the identification of mercury-containing phases is severely limited. In over a dozen BSE images of bone (SUT-MG/F/Tvert/74-1, *Nothosaurus* femur) in which the highest concentrations of mercury were identified (according to AAS analysis), a weak signal of Hg was only noted in two EDS spectra (Fig. 2B, C). These spectra were obtained from an area of the bone covered during the fossilization process by a thin layer of fine-crystalline iron oxides, which locally form crystals up to 30 μm in size (Fig. 2A). The surface of these oxides is strongly porous, the size of the pores usually does not exceed 1 μm. The oxides, therefore, have a skeletal (sponge-like) structure.

X-ray photoelectron spectroscopy

This surface-sensitive technique was applied to reveal the detailed chemical composition of the sample. By measuring the most prominent photoemission lines from the constituent elements, the information about the chemical state of the elements was obtained.

The sample presents a typical elemental composition of: fossilized bone, consisting mainly of

– calcium (Ca),
– phosphorus (P),
– oxygen (O)
– carbon (C) (Fig. 3, consistent with the EDS results).

The presence of additional elements (F, Fe, Na, Si, S) often accompanying the main components was confirmed. We found no traces of Hg with an accuracy of approximately 0.01 at. %.
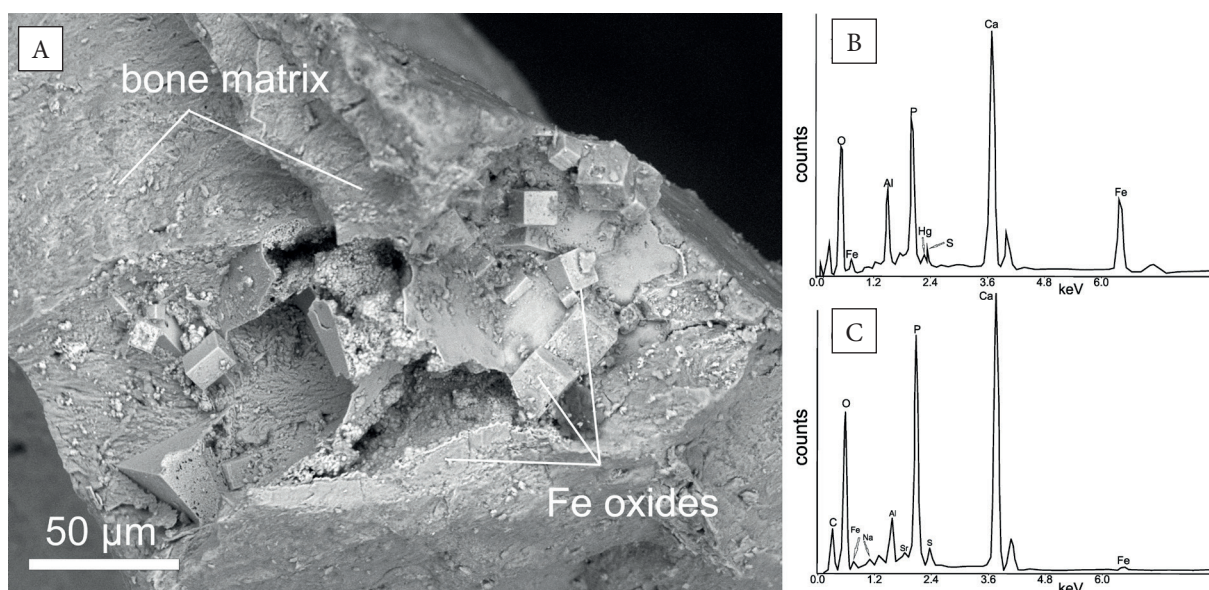

Fig. 2. *ESEM image and EDS spectra obtained from the specimen SUT-MG/F/Tvert/74-1: A) ESEM-BSE image of bone; B) and C) EDS spectra*

Table 1
Mercury concentrations in specimens from historical and current museum collections

| Acronym	Taxon/specimen	Locality	Age	Individual's life environment	Individual's diet	Hg concentration (AAS method) [ppb]
Historical museum collections						
ZPAL/Rep/Nosp/2	Sauropterygia femur (exhibition)	Gogolin	Anisian	near shore/marine	piscivorous	263.8
SUT-MG/F/Tvert/74-1	Nothosaurus femur (storage)	Gogolin	Anisian	near shore/marine	piscivorous	49 926.5
MG UWr. 3889s	Tanystropheus vertebra (storage)	Gogolin	Anisian	semi-aquatic/terrestrial	piscivorous?	1 678.3
SUT-MG/F/Tvert/80-1	archosaur bone (storage)	unknown	Late Triassic	terrestrial	carnivorous	786.4
SUT-MG/F/Tvert/80-2	?therapsid bone (storage)	unknown	Late Triassic	terrestrial	herbivorous?	1 115.4
SUT-MG/F/Tvert/92	Pistosaurus vertebra (storage)	Nakło Śląskie	Anisian?	marine	piscivorous	1 166.0
SUT-MG/F/Tvert/92-1	Pistosaurus vertebra (storage)	Nakło Śląskie	Anisian?	marine	piscivorous	2 022.9
SUT-MG/F/Tvert/92-2	Pistosaurus vertebra (storage)	Nakło Śląskie	Anisian?	marine	piscivorous	1 306.2
SUT-MG/F/Tvert/92-3	Pistosaurus vertebra (storage)	Nakło Śląskie	Anisian?	marine	piscivorous	16 344.5
MG UWr. 3868	Nothosaurus femur (storage)	Gogolin	Anisian	near shore/marine	piscivorous	4 386.5
SUT-MG/F/Tvert/2	Tanystropheus vertebra (exhibition)	Gogolin	Anisian	semi-aquatic/terrestrial	piscivorous?	412.8
Present museum collections						
GIUS uncatalogued	prolacertiform bone	Stare Gliny	Anisian	near shore/terrestrial	carnivorous	174.3
GIUS uncatalogued	prolacertiform bone	Stare Gliny	Anisian	near shore/terrestrial	carnivorous	71.9
GIUS uncatalogued	prolacertiform bone	Stare Gliny	Anisian	near shore/terrestrial	carnivorous	36.6
GIUS uncatalogued	ganoid fish scales (five specimens powdered together in an agate mortar)	Stare Gliny	Anisian	marine	piscivorous	88.2
Fieldwork collections						
GIUS 7-63/24FS	reptile coprolite	Żyglin	Anisian	marine/near shore	N/A	196.6
GIUS 7-63/6M	reptile coprolite	Żyglin	Anisian	marine/near shore	N/A	82.9
GIUS-7-3674	Tanystropheus vertebra	Żyglin	Anisian	semi-aquatic/terrestrial	piscivorous?	102.9
GIUS uncatalogued	archosaur tooth	Żyglin	Anisian	terrestrial	carnivorous	109.1
ZPAL P18	coelacanth dermal bone	Żyglin	Anisian	near shore/marine	piscivorous	171.4
WNoZ/S/7/118	marine reptile (nothosaurid?) bone fragment	Sosnowiec	Anisian	near shore/marine	piscivorous	59.0
OEEG/s-023	Nothosaurus vertebra	Jaworzno	Anisian	near shore/marine	piscivorous	49.4
OEEG/s-021	Nothosaurus rib	Jaworzno	Anisian	near shore/marine	piscivorous	13.5
OEEG/s-063	reptile coprolite	Jaworzno	Anisian	marine/near shore	N/A	17.2
GIUS uncatalogued	Metoposaurus vertebra	Krasiejów	Late Triassic	fresh water	piscivorous	43.0
GIUS uncatalogued	quartz sand (control sample)	sand beach	N/A	near shore	N/A	3.0

N/A – not applicable.
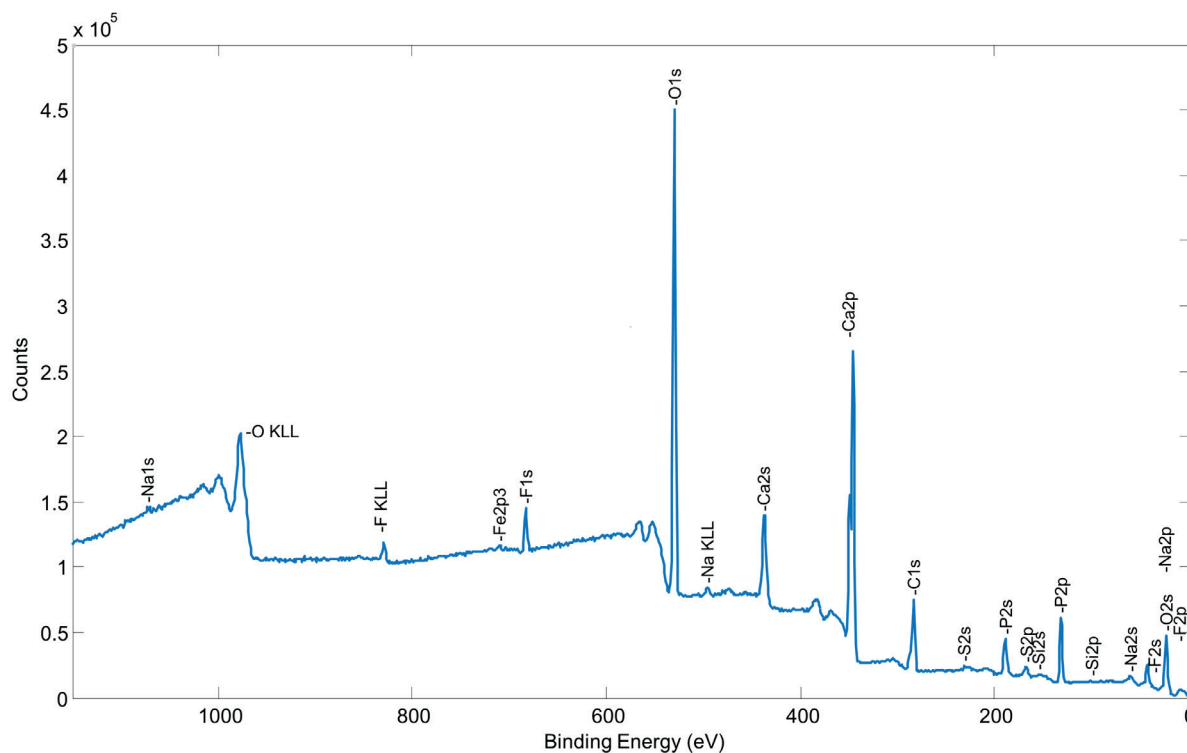
Fig. 3. *The X-ray photoelectron survey spectrum obtained from the specimen SUT-MG/F/Tvert/74-1 (see Fig. 2A) showing main elements (Ca, P, O, C) as well as iron, sodium, fluorine, sulphur, and silicon as accessory elements*

DISCUSSION

The environmental pollution of mercury may have two sources: the primary is natural and the secondary is anthropogenic (Ebinghaus et al. 1999, Pirrone et al. 2010).

The natural sources of mercury include volcanic and submarine hydrothermal processes (Varekamp & Buseck 1981, Pyle & Mather 2003, Higueras et al. 2013, Bergquist 2017) and weathering of mercury-containing mineral deposits (e.g., cinnabar). In the Triassic formations from which the studied specimens were obtained, no increased concentrations of mercury were detected (Leach et al. 1996), therefore the primary (e.g., volcanic) presence of the mercury in the rock matrix must be refuted. Some (especially aquatic) organisms tend to exhibit a large capability for mercury accumulation (Benson et al. 2007, Gworek et al. 2016), even when the water concentrations of Hg are relatively low.

Living organisms absorb mercury from the environment, both from inorganic and organic forms, but methylmercury (CH_3Hg), the product of mercury methylation performed by microorganisms (Cossa et al. 1994), is mostly transferred through food chains. Methylmercury (or MeHg) is characterized by a relatively long biological half-life and especially accumulates in the tissues of organisms living in the aquatic environment (bioaccumulation), with increasing concentrations in each succeeding trophic level (biomagnification) (Schaefer & Morel 2009, Lin et al. 2014, Rakociński et al. 2020). Marine animals, including fishes (Swain & Helwig 1989), are most vulnerable to mercury exposure. In turn, they constitute an essential food source for numerous piscivorous (fish-eating) animals (including humans), which close the trophic chain (Renzoni et al. 1998, Benson et al. 2007). Therefore, environmental pollution by means of mercury may result in human diseases (Harada 1995).

An increased mercury content was described from historic human bone remains (Yamada et al. 1995, Rasmussen et al. 2008, 2013) and in a Pleistocene Pacific cod (Murray et al. 2015), but not in older fossils. Therefore, the bioaccumulation and biomagnification processes may potentially be considered as a possible origin of such a significant amount of mercury in the examined fossil material. However, the results of our studies do not show a clear trend between the high concentration of mercury in fossil bones and the piscivorous diet of animal. For example, bone fragments of piscivorous marine reptiles (*Nothosaurus* spp.) which came directly from the fieldwork show incredibly low concentrations of mercury, in contrast to the specimens from the same locality which originated from historic collections. Following this line of thought, we observe a clear association between high concentration of mercury in historic findings, whilst mercury concentration in the specimens collected during fieldwork is negligible. Moreover, mercury and its compounds are not particularly stable over longer (older than Hercynian and Alpine) geological time-spans (Rytuba 2003, Hazen et al. 2012). Stable mercury minerals most often represent mineralization less than 500 million years (Hazen et al. 2012). The accumulations of mercury created before the Alpine orogeny have since then been geochemically dispersed (Thibodeau et al. 2016, Percival et al. 2017). It seems unlikely that methylmercury accumulations would have survived in Middle-Late Triassic (247–220 Ma) bones deposited in shallow-marine and semi-aquatic environments. However, a recent study (Rakociński et al. 2020) indicates the preservation of MeHg of deep-water, pelagic sedimentary rocks dated back to 360 Ma. Furthermore, we have observed no correlation between the diet, environment, and sample age with the mercury content (see Tab. 1).

Having excluded any natural source of mercury in the investigated fossil material (absorption with food intake or due to paleo-environmental pollution), we consider a secondary source of contamination.

Anthropogenic sources of mercury are to be found in the products and waste of many industrial processes (Driscoll et al. 2013). The following scenarios for the contamination of the studied samples seem most probable:

1) Caused by mercury-based explosives (e.g., mercury fulminate) used during fossil-yielding rock fragmentation or at the moment of packaging fossils into boxes, in which they might have had contact with the explosives. It can be assumed that fossilized bones – occasionally found in mining plants during their routine operation – were kept in local warehouses or powder storages, situated in proximity to a quarry. The specimens were most likely kept in boxes in which mercury-based explosive materials were previously stored. Mercury fulminate, $Hg(OCN)_2$, used as primary explosive, was invented at the beginning of the nineteenth century (Howard 1800), but its molecular structure was finally determined over 200 years later (Beck et al. 2007). Mercury fulminate was widely used as an initially explosive in the nineteenth and early twentieth century (Garner & Hailes 1933). Such a widespread use might have resulted in local environmental pollution, for example the soils and vegetation in the area of a former Hg-fulminate production plant near Oviedo (Spain) are contaminated with mercury (Arbestain et al. 2009). Furthermore, repeated use of dynamite with fulminate caps might have also led to mercury pollution of the area, as documented in the case of shooting ranges where fulminate is used as primary explosives in ammunition (Gębka et al. 2016).

2) During the exposition in museums, where mercury minerals might have been kept. Unstable mercury minerals such as native mercury, calomel, or coccinite, which frequently were included in the collections of natural history museums, might have been the cause of contamination of nearby fossils. Stable mercury sulphates such as cinnabar, metacinnabar, and livingstonite have a much lower capability for mercury transfer, but may also be a potential source of mercury contamination. Even though the storage history of the palaeontological specimens is unknown, it should be noted that at the moment of their loaning they did not neighbour mineralogical collections.

3) During the exposition in museums or storage in archives, where mercury-based rodenticides, fungicides, or insecticides were used. Calomel (mercury (I) chloride, Hg_2Cl_2), known for over 100 years, was used as a herbicide and a fungicidal agent (Thakore 2005), so its use for conservation purposes at the beginning of the 20th century cannot be excluded. Mercuric chloride (corrosive sublimate, $HgCl_2$) was used as an insecticide, in rat poisons, and as a disinfectant. In all of the mentioned above compounds, mercury is volatile, and could easily vaporize into porous trabecular or even cracked dense cortical bone.

Taking the above into account, we have no doubt that high mercury concentration levels are associated with the method of protection or storing of the specimens. Therefore, the highest concentrations of mercury were recognized in the specimens kept in boxes in museum stores. The specimens from museum exhibitions were also characterized by high concentrations of mercury, but these concentrations were significantly (even up to ten times) lower, because a substantial amount of mercury vaporized in contact with atmospheric air. The presence of mercury in the dataset obtained from the X-ray photoelectron survey was not unequivocal due to the poor signal quality. Therefore, the contamination may only be reliably detected with mercury-sensitive atomic absorption spectroscopic-based techniques. In this case, the thermal decomposition of samples releases mercury, which was not possible in a vacuum-pressure environment, either in XPS or EDS measurements.

CONCLUSIONS

The comparison of mercury content in the specimens from museum collections and those recently gathered in the field suggests that the contamination occurred during specimen storage, which often spanned a period of more than a hundred years. Embracing the seemingly plausible hypothesis about the secondary transfer of mercury to fossil specimens which are part of museum collections indicates that the time of their exposition to mercury emission may be a very important factor. The sorption of mercury might have

been facilitated by: (a) the porous structure of fossil specimens, (b) the geometry, size and type of the pores (open vs. closed), and (c) the presence of iron oxides, which exhibit large sorption potential (Tiffreau et al. 1995). The identification of mercury present in unstable mineral phases is possible with the employment of dedicated chemical procedures. Standard EDS analyses performed in high- or low-vacuum mode and X-ray photoelectron spectroscopy are not suitable for the detection of mercury and its compounds. The results of our studies demonstrate that targeted examination of historical specimens without detailed knowledge on their storage conditions can be very risky.

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