Heavy-metal-induced malformations in the Late Devonian brachiopods from western Junggar, NW China

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Abstract

Although malformations are found in both extant organisms and the fossil record, they are more rare in the fossil record than in living organisms, and the environmental factors causing the malformations are much more difficult to ~~determine~~ identify for the fossil record~~s~~. ~~Athyrid~~ Two athyrid brachiopod~~s~~ taxa ~~were collected~~ from the Upper Devonian Hongguleleng Formation in western Junggar~~, –~~ (Xinjiang, NW China) show distinctive shell malformation. Of 198 *Cleiothyridina* and 405 *Crinisarina* specimens, 18 and 39 individuals were deformed, respectively~~, –~~; a deformity rate of nearly 10%. Considering the preservation status and buried environment of the deformed specimens, combined with such a high probability of deformity, we conclude that the appearance of deformed athyrids may have been related to their ~~abnormal~~ specific habitat. Analysis of trace elements and rare earth elements ~~in sediments~~from bulk rock ~~suggested~~ suggests that ~~the~~ shell-malformation~~s~~ may have been caused by a high content of heavy metal, especially lead, in the sea. The increased heavy ~~metals~~ metal content observed in the Hongguleleng Formation ~~are~~ seems to relate~~d~~ to the Late Devonian volcanic activity in western Junggar and is interpreted here as harmful limiting factor for some athyrid taxa. ~~At that time, increased volcanic activity led to higher levels of heavy metals in the sea, which created a survival crisis for athyrids.~~

Introduction

Deformities are common in living organisms; the term usually refers to abnormalities of individuals that occur during ontogeny. ~~Malformations~~ However,

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"…uncommon habitat"

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Besides that, I would also suggest to substitute the term <normal> and <abnormal> in relation to species/specimens – how can we say a specimen is abnormal? – concerning the fossil record of the shell material that we find (not even having preserved any soft tissue), the terms <deformed> or <malformed> would much better fit.

Kommentiert [TS2]: Please be careful: both genera did not extinct during or in the direct aftermaths of the crisis. – That there is no fossil record of these taxa in the Hongguleleng can be related to migration of next generation larvae in order to escape regional polluted environments and rebound directly thereafter.

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malformations are known from the fossil record too, and have been reported ~~in~~ from individuals of ~~many~~ different fossil groups, including foraminifera (*Ballent & Carignano, 2008*), trilobites (*Owen, 1985; Babcock, 1993*), brachiopods (*Copper, 1967; He et al., 2017*), bivalves (*Savazzi, 1995*), gastropods (*Lindström & Peel, 2010*~~),~~), cephalopods (*Mironenko, 2016*), echinoderms (*Thomka, Malgieri & Brett, 2014*), graptolites (*Han & Chen, 1994*), insects (*Vršanský, Liang & Ren, 2012*), conodonts (Weddige, 1990), shark teeth (*Itano, 2013*), amphibians (*Witzmann et al., 2013*), reptiles (*Buffetaut et al., 2007*), primate teeth (*Tougard & Ducrocq, 1999*), and plankton (*Vandenbroucke et al., 2015; Bralower & Self-Trail, 2016*). In addition to gene mutations or embryonic developmental disorders, deformed fossils may also have resulted from healed injuries and pathology (*Owen, 1985; Babcock, 1993; Kelley Kowalewski & Hansen, 2003*). Malformed fossils provide ~~an~~ important evidence of both organisms-organisms and organisms-environment relationships during geological history. For example, malformed specimens caused by predatory attacks can reflect the food chain at that time or the position of prey in the ecological chain (*Kelley Kowalewski & Hansen, 2003*). Moreover, some malformations ~~caused~~ resulting from ~~by~~ pathological causes or developmental disorders are likely to be related to the habitat of the organism, such as changes in environmental factors, and parasite, viral or bacterial infection.

Although many malformed fossils have been described, deformed fossils (especially macrofossils) are generally rare, with sometimes only one or two specimens known. Therefore, previous studies have generally been limited to description of deformed specimens and simple classification of the cause(s) of malformation, only ~~a~~ in a few cases ~~for~~ the relationship between deformed specimens and their ~~living environment~~ habitat has been discussed (*Copper, 1967; Vandenbroucke et al., 2015; Bralower & Self-Trail, 2016; He et al., 2017*). Although many deformed fossils are believed to have ~~been caused by~~resulted from developmental disorders or pathological causes, the environmental factor responsible for the developmental disorders or diseases is generally ~~not~~ unknown. The low number of malformed specimens available often limits further study.

The Upper Devonian succession in western Junggar, Xinjiang, NW China, contains abundant, well-preserved brachiopods. We collected more than 600 athyrid (*Cleiothyridina* and *Crinisarina*) specimens from the Upper Devonian Hongguleleng Formation in the Buninuer section, of which nearly ten percent of individuals were deformed. ~~From~~ The detailed ~~studying~~ study of ~~the~~ deformed specimens and geochemical analysis of the whole rock~~, we conclude that the~~supports the hypothesis that the increased number ~~existence~~ of deformed athyrid specimens may ~~be related~~ causally be linked to volcanically derived ~~excessive~~ heavy-metal enrichment of local marine deposits ~~of the sea~~ at that time.

Materials and methods

The material studied in this paper was collected from the Upper Devonian Hongguleleng Formation in western Junggar, Xinjiang. The Hongguleleng Formation is a widely distributed marine unit near the Devonian–Carboniferous boundary in western Junggar. The formation is divided into three members: the Lower Member is composed of thin bioclastic limestones, muddy limestones and shales; the Middle Member is mainly made up of fine pyroclastic rocks with a few sandy and muddy limestones; and the Upper Member consists of calcareous clastic rocks with a small amount of bioclastic limestones (*Hou et al., 1993*). The formation is mostly ~~the~~ Famennian in age (*Ma et al., 2017*). In contrast to the general scarcity of fossils after the Frasnian–Famennian (Late Devonian) transitional extinction event in other parts of the world, the Hongguleleng Formation is very rich in many types of the early Famennian fossils, such as brachiopods, corals, echinoderms, trilobites, bivalves, gastropods, ostracods, conodonts, chondrichthyans, bryozoans, cephalopods, conulariids, radiolarians, plants, acritarches, spores and trace fossils. Therefore, western Junggar is considered to have been a refugium during the Frasnian–Famennian extinction event (*Liao, 2002*).

Brachiopods occur in all three members of the Hongguleleng Formation. Brachiopod abundance and diversity ~~are~~ is ~~the~~ highest in the Lower Member, with the groups present including Productida, Orthida, Rhynchonellida, Athyridida and Spiriferida (*Zong et al., 2016; Zong & Ma, 2018*). Athyrids are most abundant in the Lower Member, with only a few athyrid specimen recovered from the base of the Middle Member and the limestone interlayer of the Upper Member (*Zong et al., 2016*). All the athyrids studied in this paper were extracted from the bioclastic limestone in the upper part of the Lower Member of the Hongguleleng Formation in the Buninuer section, 15 km north of Hoxtolgay town (compare Fig. 4: horizon of malformed Athyridae). This section is located about 14 km southwest of the Bulongguoer section,

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which is the type section of the Hongguleleng Formation (*Hou et al., 1993*). The lithology and fossil assemblages of the Buninuer section are the same as those of the stratotype section. A total of 603 athyrids in two genera (*Crinisarina* and *Cleiothyridina*) are non-flattened specimens with well-preserved dorsal and ventral valves. Although athyrids occur in other beds of the Hongguleleng Formation, no abnormal specimens were found in those levels.

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Probably you could use <morphologically deformed> or <malformed specimens> - or <malformed athyrid brachiopod shells>

The 603 specimens include a wide range of size and may include individuals representing different growth stages (Supplemental file 1). We divided the shell height (H) into six size classes: 5 mm≤ H< 10 mm; 10 mm≤ H< 15 mm; 15 mm≤ H< 20 mm; 20 mm≤ H< 25 mm; 25 mm≤ H< 30 mm and 30 mm≤ H< 35 mm, and counted the number of malformed specimens in each class. The height of all athyrids were measured by a ~~vernier~~ vernier caliper. The fossils in Fig. 1 and 3 were whitened with magnesium oxide powder, and all photographs were taken using a Nikon D5100 camera with a Micro-Nikkor 55 mm f3.5 lens.

To explore whether ~~some environmental factors may have caused the~~ athyrid deformities were caused by environmental factors, ~~the whole-rock levels of~~ trace ~~elements~~ and rare earth elements of bulk-rock samples from specific levels within the Hongguleleng Formation were measured. Samples BL–1 and BL–2 were obtained from the lower part of the Lower Member of the Hongguleleng Formation, which yielded abundant normal athyrids. Samples BL–3 and BL–4 came from the upper part of the Lower Member, form where the deformed fossils described in this paper were obtained. Samples BL–5, BL–6 and BL–7 were collected from the Middle Member of

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the Hongguleleng Formation; only a few athyrids occurred at the bottom of this member, and the group almost disappeared above that level. Sample B9b–1 was from the Upper Member, which yielded a small number of athyrids. All samples were ground into powder and analyzed in the ALS Minerals/ALS Chemex (Guangzhou) Co. Ltd. Rare earth and trace elements were fused with lithium borate, and quantitatively analyzed by ICP-MS with Elan 9000 Perkin Elmer that was made in America. The Ce_{anom} is equal to $\lg[3Ce_n/(2La_n+Nd_n)]$, and Ce_n, La_n and Nd_n were NASC-normalized of Ce, La and Nd, respectively.

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Results

Of the 603 athyrid fossils, macroscopic deformities were detected in 57 specimens. The most common teratomorphy is obvious asymmetry on the left and right sides of the shells (Fig. 1B–E, G–J), significantly different from ~~the normal~~common, undeformed specimens (Fig. 1A, F). Malformation is more obvious on the dorsal valves, and is mainly visible as significantly widening or narrowing on one side of the shell (Fig. 1D1, G1, H1, J1). Near the anterior border of the dorsal valves, the grooves on both sides of the fold are significantly different from those of normal specimens, with some grooves being wider (Fig. 1B1, C1, E1, I1), others being narrower, and some almost disappearing (Fig. 1D1, G1). On the ventral valves, in addition to the unequal size on either side of the shell, the sulcus is slightly curved in some malformed specimens (Fig. 1B2, E2, I2). In frontal view, the asymmetry is more obvious, and is mainly manifested as different depths and widths of the grooves on both sides of the fold (Fig. 1B3–E3, G3–J3); for example, the grooves on one side of some specimens become deeper and wider, up to twice as much as those on the non-deformed side (Fig. 1B3). In addition, the grooves of some specimens become shallower and narrower (Fig. 1H3), even almost disappearing on one side of a few specimens (Fig. 1D3, G3). In the abnormal specimens, the commissure on the front of the dorsal and ventral valves forms irregular wavy lines, markedly different from the regular wavy lines in normal specimens (Fig. 1A3, F3).

Of the 198 specimens of *Cleiothyridina* and 405 of *Crinisarina*, 18 (9.1%) *Cleiothyridina* and 39 (9.63%) *Crinisarina* were malformed. The overall malformation rate was 9.45%, nearly one-tenth of all specimens (Fig. 2A). In all malformed specimens, the distribution of malformation is asymmetric on the shells in dorsal view, malformation occur in right side of 25 shells of *Crinisarina*, but there are only in left side of 14 shells. For the *Cleiothyridina*, malformation occur in right side of 14 shells, while in left side of 3 shells, and in both sides of one shell (Supplemental file 1). Moreover, abnormal individuals occur in almost all size classes (Fig. 2B, C). The malformation percentages of *Crinisarina* are 5.56% ($10\text{ mm} \leq H < 15\text{ mm}$), 8.5% ($15\text{ mm} \leq H < 20\text{ mm}$), 13.7% ($20\text{ mm} \leq H < 25\text{ mm}$) and 11.1% ($25\text{ mm} \leq H < 30\text{ mm}$); those of *Cleiothyridina* are 9.68% ($10\text{ mm} \leq H < 15\text{ mm}$), 9.3% ($20\text{ mm} \leq H < 25\text{ mm}$) and 14.8% ($25\text{ mm} \leq H < 30\text{ mm}$). Thus, ~~abnormalities~~ shell-malformation occurs at different athyrid growth stages, and the probability of deformity is higher in larger specimens. Th~~e findings~~ at indicates ~~that the~~a higher probability of deformity ~~increased as~~during advanced ontogenetic stages of the studied brachiopod~~s~~ taxa~~grew~~.

Discussion

Possible cause of malformations

Western Junggar is part of the Central Asian Orogenic Belt. This region experienced strong tectonic activity during the Paleozoic, resulting in different degrees of metamorphism or deformation of the Paleozoic strata in the study area (*Gong & Zong, 2015*). Athyrids exhibiting left-right asymmetry might have resulted from tectonic deformation; however, there is no obvious stratal deformation in the Hongguleleng Formation in the Buninuer section. This section has yielded fossils (~~e.g.~~e.g., trilobites, crinoids and corals) that are well-preserved in three dimensions (Fig. 3A), ~~and~~ which obviously ~~different~~ differs from specimens obtained from distorted strata affected by tectonic deformation (Fig. 3B). Moreover, asymmetry was not detected in other brachiopods from the same layer, so the deformed specimens were not affected by the tectonic activity. A very small number of athyrid specimens damaged by stratal pressure are also significantly different from these asymmetric specimens, and they can be easily distinguished (Fig. 3D). Parasitic organisms can cause malformation of their hosts; such phenomena have also been reported for shelly fossils (*Savazzi, 1995; Zatoń & Borszcz, 2013; Mironenko, 2016*). Some athyrids from the Upper Devonian of western Junggar bear parasitic organisms, such as trumpet corals and bryozoans. However, parasitic organisms are not found on any abnormal specimens; on the contrary, specimens bearing parasitic organisms are all normal shells (Fig. 3C). Therefore, it is unlikely that these athyrid teratomorphies were caused by parasitic organisms.

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Malformations of organisms may be related to their living environment. Changes in certain environmental factors, such as oxygen deficiency or excessive organic matter, heavy metals and toxic elements, often lead to the malformation or even death of organisms. The high number of malformed athyrids from the Upper Devonian strata might be related to the marine environment in western Junggar at that time. Excessive organic matter is a common ~~abnormal~~ factor, and eutrophication has been identified in the Late Devonian sea (*Murphy, Sageman & Hollander, 2000*). *Suttner et al. (2014)* found that there were no obvious changes in the total organic carbon (TOC) content through the Lower Member of the Hongguleleng Formation at its type locality, i.e., the TOC content of the beds with deformed specimens was basically the same as that of sediments with only ~~normal~~ undeformed specimens. *Copper (1967)* studied deformities of the Devonian brachiopod *Kerpina* in the Eifel region, Germany, and concluded that ~~the abnormalities~~ variations in the shell-morphology resulted from the influence of bottom currents on the immobile *Kerpina*, which had a thick, short pedicle. However, this mechanism cannot be used to explain the deformity of these athyrids in western Junggar, because large numbers of other benthic organisms such as brachiopods, corals, bryozoans and stromatoporoids coexisted with them. In addition, the fossils preserved in the upper part of the Lower Member of the Hongguleleng Formation are relatively complete, and there is no evidence of strong bottom currents, so the influence of bottom currents can be excluded as a teratogenic factor. *Hoel (2011)* found the shells of brachiopod *Pentlandina loveni*, from the Sliurian Högklint Formation in Gotland (Sweden), are commonly markedly

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- second: please check the occurrence of stromatoporoids – I do not remember having seen any at the type section. – In case you found some at the Buninuer section, please publish them!!

asymmetric, and some groups of shells occur in tight clusters, each apparently attached to other shells of the same species. He interpreted these asymmetrical shells resulted from the limited space for growth, ~~i.e.~~i.e., overcrowded conditions. However, all specimens from western Junggar are isolated, instead of tight clusters or attached to other shells. Furthermore, if they are living in overcrowded space, the distribution of malformation should be random or almost uniform on both sides of the shells, but the malformations ~~are mostly~~ commonly occur on the right side of athyrids shells (dorsal view) from western Junggar (Supplemental file 1), so the overcrowded conditions also can be excluded.

Marine hypoxia ~~will~~ could lead to brachiopod deformities~~,~~. ~~for example,~~ *He et al. (2017)* for example, proposed that hypoxia was a major factor in the miniaturization of brachiopods during the end-Permian in southern China. V/Cr and Ni/Co ratios as well as Ce_{anom} are often used as indicators of marine hypoxia (*Elderfield & Greaves, 1982; Jones & Manning, 1994; Carmichael et al., 2014, 2016*). For the sediments of the Hongguleleng Formation at the Buninuer section, the V/Cr ratio of sample BL–3 fell into the oxic range, whereas that of sample BL–4 fell into the dysoxic range; both Ni/Co ratios fell into the oxic range; and both Ce_{anom} values were near the oxic-anoxic boundary (Fig. 4, Supplemental file 2). In addition, shallow-marine benthic fossils, such as corals, trilobites, brachiopods and echinoderms, occur in abundance in the same horizon ~~as the abnormal~~ together with malformed athyrids, and the beds lack sedimentary indicators of anoxia (such as black shale), so hypoxia may not have occurred during deposition of the upper part of the Lower Member of the

Kommentiert [TS16]: Carmichael et al should be added here as both papers deal with the question related to hypoxia at the Hongguleleng type section.

– What the authors did not mention is the microframboid method for tracing hypoxic conditions (see Carmichael et al., 2014). – That could become a task for future studies at the Buninuer section.

Hongguleleng Formation.

High levels of heavy metals or toxic elements can also lead to ~~abnormalities~~ malformation of organisms soft and hard tissue, as has been proven for a large number of living organisms (*Wang, Yang & Wang, 2009; Ma et al., 2011; Zhao et al., 2017*). Sediments have been demonstrated to be an important source of heavy metals for benthic animals (*Wang, Stupakoff & Fisher, 1999*). The levels of heavy metals and toxic elements through the Hongguleleng Formation are presented in Fig. 4 and Supplemental file 2. The levels of some heavy metals (e.g., cadmium, lead, barium, and zinc) in the layer with the ~~abnormal~~ malformed athyrid shells are relatively high compared to the levels in the lower part of the Lower Member, particularly cadmium ~~lead~~ and lead ~~cadmium~~. The levels of cadmium are 0.02 and 0.03 ppm in the lower part of the Lower Member, ~~but are~~and 0.03 and 0.04 ppm in the horizon that yielded the deformed fossils. The lead contents are 1.3 and 2.2 ppm in the lower part, but 5.1 and 5.2 ppm in the upper part. In the Middle Member of the Hongguleleng Formation, where athyrids almost disappeared, the heavy metal levels are even higher. In the Upper Member, where athyrids reappear, the heavy-metal content decreases again (Fig. 4). Thus, the abundance of athyrids is negatively correlated with the levels of heavy metals, but the number of ~~abnormalities~~ malformed specimens is positively correlated with that, especially that of lead (Fig. 4). On the basis of the above analysis, we hypothesize that athyrid deformation may be associated with the excessive heavy-metal in the sea. On the basis that the lead content in sediments is positively correlated with the athyrid ~~abnormality~~shell deformation, but negatively correlated

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e.g., Riani et al., 2018
https://doi.org/10.1016/j.marpolbul.2018.06.029

and/or, Lasota et al., 2018
https://doi.org/10.1016/j.marpolbul.2017.11.015

with the abundance, indicating that lead was probably the main teratogenic element.

Effects of excessive heavy-metal on marine organisms

Malformation is also occasionally observed in shelly organisms in modern oceans, such as bivalves, foraminifera and sea urchins (*Dafni, 1980; Sharifi, Croudace & Austin, 1991; Sokołowski et al., 2008; Lü et al., 2017*); these malformations are generally believed to be closely related to ~~the abnormal habitat~~specific environmental conditions. Excessive heavy-metal is an important teratogenic factor, as has been confirmed experimentally; for example, when Cu and Zn were added to the water for feeding the foraminiferan *Ammonia beccarii*, the organisms developed deformities (*Sharifi, Croudace & Austin, 1991*), and when scallops were placed in wastewater from a gold mine with concentrations of 14% and 50% for 6 h, the deformity rate increased by 6% and 21%, respectively (*Ma et al., 2011*). Lead is a common type of marine heavy-metal, and excessive lead content in the sea often leads to ~~abnormalities~~ malformation or even death of shellfish, or at least affects their growth (*Li, Sun & Li, 2011*).

In Upper Devonian strata of western Junggar, the deformity rate of athyrids is nearly one in ten. In addition, the heavy metal (especially lead) content in sediments is significantly higher than that of sediments containing only ~~normal~~ undeformed shells; thus, the deformities are likely to have been associated with Late Devonian marine excessive heavy-metal in the study area. Excess levels of heavy metals (represented by lead) caused the athyrids to develop deformities. Lead is a cumulative poison (*Li, Sun & Li, 2011; Chen et al., 2011*), which may also be an important reason for the gradual increase in the probability of deformity with growth of an individual. Further ~~rises~~ increase in the heavy-metal content in the Middle Member of the Hongguleleng Formation may have led to the disappearance of athyrids. ~~Abnormalities~~ Although shell malformations were observed in two athyrid genera, ~~but~~ such were ~~were not~~ neither detected in other ~~brachiopods~~ brachiopod taxa ~~and other~~nor in other fossils groups from the same beds. This may have been related to the differing sensitivities of different organisms to changing environmental ~~factors~~conditions. In modern organisms, acute toxicity tests have demonstrated different tolerance levels of lead ions in different animals (e.g., *Li, Sun & Li, 2011*).

Western Junggar was located in a volcanic island-arc setting in the Late Devonian (e.g., *Xiao et al., 2008*), meaning that strata formed during this time interval generally contain pyroclastic material (*Gong & Zong, 2015*). From the base of the Hongguleleng Formation upward, there is a gradual increase and then decrease in the amount of volcanic material. Small amounts of pyroclastic materials (e.g., debris and dust) are present in the limestones of the upper part of the Lower Member. In the Middle Member, the content of volcanic material is high, with the strata being almost entirely composed of tuffites. The amount of volcanic material is lower again in the Upper Member. The heavy-metal content (represented by lead) in the Hongguleleng Formation is positively correlated with the amount of volcanic material in the rock. Therefore, we hypothesize that the source of heavy metals was probably from the Late Devonian volcanic activity in western Junggar, i.e., increased volcanic activity resulted in higher levels of heavy metals in the Late Devonian sea, which caused the athyrids to develop deformities.

The discovery of ~~abnormal~~ deformed athyrid shells in the Hongguleleng Formation reveals a relationship between the excessive heavy-metal and malformation, demonstrating that excessive heavy-metal affected ~~in the~~ Late Devonian ~~sea in~~marine environments of western Junggar after the Frasnian–Famennian mass extinction. Thus, the hypothesized refugium (*Liao, 2002*) may not have been as safe and comfortable as previously thought, but also experienced an environmental crisis. Excessive Heavy-metal resulting from volcanic or hydrothermal activity caused massive harm to marine organisms in geological history, and may have led to deformity or death of organisms. This may have been a kill mechanism for extinction events in the past.

Conclusions

Some ~~athyrid~~ specimens of two athyrid genera, *Cleiothyridina* and *Crinisarina*, from the Upper Devonian Hongguleleng Formation in western Junggar are obviously deformed, mainly in the form of asymmetry of the left and right sides of the shells. The deformity rate is nearly 10% of specimens. Malformation is apparent in individuals of different sizes, with larger individuals being more likely to exhibit malformation. ~~Study~~ The study of the burial state and preserved environment of the fossils led to the conclusion that environmental factors caused the deformities. From geochemical analysis of the sediments and comparison with rock material from ~~the~~ horizons that did not contain teratomorphic specimens, we hypothesize that the deformities were caused by excessive heavy-metal (specifically lead) in the sea, rather

Kommentiert [TS18]: nobody said it was "save" – much more these animals survived the UKW Event because they already were used to persistently changing environmental conditions and pollution of their habitat, and thus could probably better deal with the F/F or Hangenberg or any other Famennian crisis, compared to organisms that lived in nice calm tropical settings where never anything had happened.

Kommentiert [TS19]: I would delete that part of the manuscript, because it is a much to general assumption based on the study of only one section. Having a look at the papers of Racki and others, much more intense study was undertaken to come to a similar conclusion for Hg as main responsible for pollution of marine environments related to volcanic activity (compare Racki et al., 2018: DOI: http://dx.doi.org/10.7306/gq.1419; Racki, 2020: https://doi.org/10.1016/j.gloplacha.2020.103174; Rakociński et al, 2021: https://doi.org/10.1038/s41598-021-85043-6).

than parasitism, eutrophication, bottom current activity, overcrowded conditions, hypoxia or other factors. Excessive lead was related to volcanic activity in western Junggar during the Late Devonian; increased volcanic activities led to a rise in the marine lead levels, which in turn resulted in increased deformities and finally the disappearance of the athyrids.

Acknowledgements

We would like to thank Zhen Shen, Chao Guo and Junyan Dong, all from China University of Geosciences (Wuhan) for their help in the field work.

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