

Full Length Research Paper

Crystal phases of calcium carbonate within otoliths of *Cyprinus carpio*. L. from Miyun Reservoir and Baiyangdian Lake, China

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Asteriscus (lagenar otolith) of *Cyprinus Carpio*. L. (Cyprinida, common carp) from the serious intermittent polluted Baiyangdian Lake and the little polluted Miyun Reservoir, all located in northern China, were chemically and mineralogically analyzed. All the analyzed fish showed that the composition of asterisci is dominated by calcium carbonate, with the minor elements As, Ba, Sr, and Zn; and the polymorph of CaCO₃ in the asterisci is vaterite. Three different vaterite X-ray diffraction (XRD) patterns were found in the analyzed samples. For the 60% fish from both localities, two different vaterite XRD patterns coexist in the core area and the edge area in same asteriscus sample. Significant differences of the dimensions of crystalline cells of vaterites exist between these two localities, which reveals that crystal structure of vaterite polymorphs seem sensitive to water quality and water environment, its crystalline cell dimensions might be a potential proxy for monitoring the change of water quality.

Key words: Vaterite, biocrystallization, otoliths, microchemistry, proxy, *Cyprinus Carpio*. L.

INTRODUCTION

Three type paired otoliths respectively exist in the sacculus, utriculus, and lagena of fish, each having an irregular unsymmetrical shape, used for balance and/or hearing (Carlström., 1963). Otoliths are metabolically inert concentric layer structure deposits, formed by alternating layers of protein and calcium carbonate grown around a nucleus (Campana and Neilson., 1985). Plenty of information recorded in otoliths have been studied to resolve fish ecological questions such as fish age, feeding and growth history, recruitment and migration, mortality and stock structure, and so forth (Campana and Neilson., 1985; Jenkins., 1987; Maillet and Checkley., 1991; Noichi et al., 1994; Bailey et al., 1995; Meekan and Fortier., 1996; Song et al., 2006); while microchemistry of otoliths may reflect elemental composition of ambient environments (Campana, 1999) and may also be

controlled by temperature and salinity (Thorrold et al., 1997; Elsdon and Bronwyn., 2002; Zacherl and Georges., 2003; Martin and Thorrold., 2004). Recently, some authors have tried to demonstrate that otolith of common carp may be a potential proxy for monitoring changes in water quality (Yang et al., 2006, 2008; Li et al., 2007b, 2011). Many achievements have also been made with regard to the crystal phase of CaCO₃ in the otoliths of fish, especially sea fish, in the past fifty years. Polymorphs of CaCO₃ in otoliths may be related to the type of otoliths. X-Ray diffraction has confirmed that sagittae and lapilli are usually composed of polycrystalline aragonite, and most asterisci are composed of vaterite (Carlström., 1963; Lowenstam and Weiner., 1989; Oliveira et al., 1996; Irie, 1955; Degens et al., 1969; Mann et al., 1983; Morales, 1986; Maisey., 1987; Lecomte, 1992; Shichiri, 1986). Lenaz et al. (2006) reported that the different calcium carbonate polymorph for otoliths is strictly correlated with some microelements concentrations.

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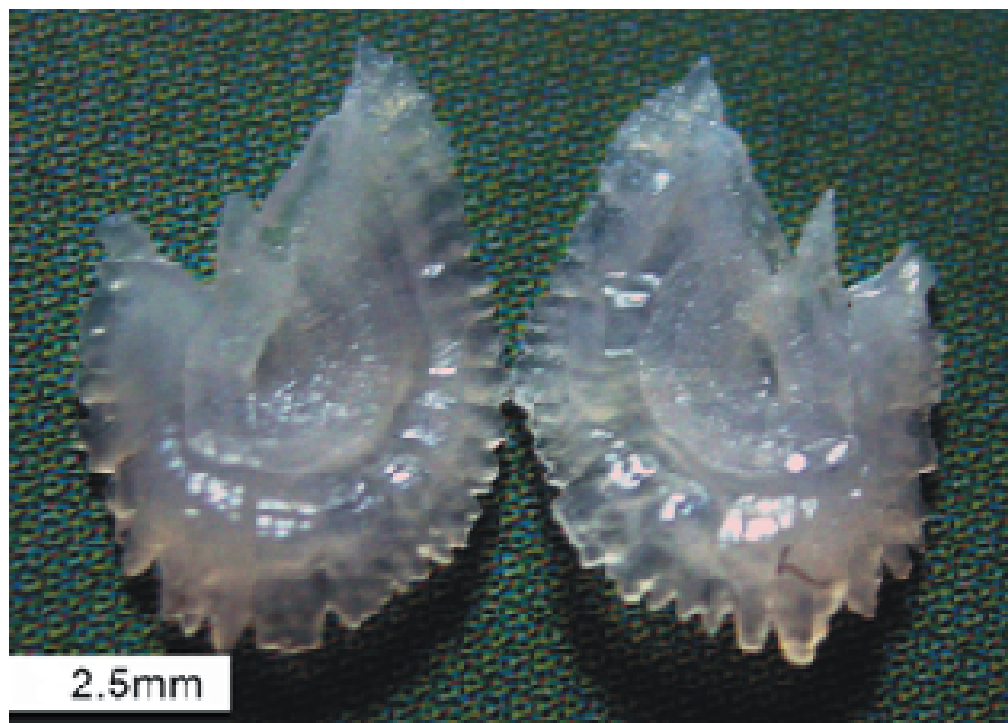


Figure 1. Macroscopical appearance of common carp asterisci. Asteriscii of the carp from Miyun Reservoir; weight = 148 g; length = 4.00 mm; width = 2.44 mm and height = 2.20 mm.

Nevertheless, few studies have examined the CaCO_3 crystal phases in the otoliths of common carp, and there is no report about different XRD-type peak patterns of vaterites within same otolith.

This study preliminarily focuses on the CaCO_3 crystal phases in the asteriscus of common carp. The crystal phase and dimensions of crystalline cells of CaCO_3 and trace elements within asterisci in wild common carp otoliths are reported in detail. Investigating the crystal phase of CaCO_3 plays a key role in the study of the otoliths hierarchical structure, hydro-environmental chemistry and calcium carbonate biomineralization theory. Further studies on the relationship between the CaCO_3 crystalline cell dimensions and the microchemistry concentration in the fish aquatic environment will be summarized in our next study.

MATERIALS AND METHODS

Collection of samples

The adult wild freshwater common carps used in this study were collected from Baiyangdian Lake (N38.43°, E115.38°) and Miyun Reservoir (N40.23°, E116.50°). Baiyangdian Lake suffers from serious intermittent industrial waste. The main contamination are chemical oxygen demand (COD), total protein (TP), total nitrogen (TN), Zn, Pb, Hg, Ge, Cr, As and cyanide (Li, 2006). Miyun Reservoir supplies drinking water for Beijing and is less polluted. Both of these bodies of water are located in northern China. Concentrations of Sr, K, Na, Mn, Mg, Ni, Cu, Ba, Zn, Pb, Cr, Fe, As,

Au and Co in the water of Baiyangdian Lake are all higher than those in the water of Miyun Reservoir, but for Cd (Yang, 2007).

In total, 18 common carp were collected from Baiyangdian Lake and 24 from Miyun Reservoir. We measured the length and weight of the common carp. The asterisci were removed from each common carp with tweezers (Figure 1), cleaned by ultrasound, kept in 75% ethanol for 24 h and then dried in air for use. The fish ages were determined by scale and otoliths; all fish were between 2 and 5 years old. In order to get the minerals separately from the areas near both the core and the edge in the same asterisci of each common carps. One of paired asterisci was cut perpendicular to the sulcus and through its nucleus. A half of it was put on a piece of glass, then clamped by tweezers, and its' outer layer were scraped by bistoury. Collected dropped materials are the minerals near the edge of the asteriscus. While the middle area of section of one half of asteriscus was pierced by the sharp end of bistoury, collected dropped materials are the minerals near the core of the asteriscus.

These two kinds of sample minerals were tested by XRD. Another one of paired astriscii was tested by nucleic acid amplification (NAA).

NAA analysis

The NAA analysis was carried out at the Chinese Academy of Atomic Energy. The samples were powdered using agate pestle and mortar. The sample masses used were in the range of 13-20 mg. The samples were packed in high-purity aluminum foil and irradiated along with standard chemicals and standard reference material in a heavy water reactor, at a neutron flux of 4.83×10^{13} n/cm²·s. The samples were irradiated for 8 h. Following irradiation, the aluminum foils were removed from the samples, and an Ortec high-purity Germanium (HPGe) detector was used to test the γ energy spectrum. The resolving power of the HPGe detector is 1.80

keV, and the testing time was 2 h for each sample. The amount of each element was calculated using the standard reference material as control.

XRD analysis

XRD analysis was carried out in the X-Ray Laboratory of China University of Geosciences. A new method for powder-like diffractograms of small single crystals developed by Li et al. (2005) was used in this study. According to this new method, an SMART APEX-CCD detector X-ray diffractometer was used with a special rotation method and a supporting software program. Using this method, many powder diffraction data of native Si-Fe alloy minerals from podiform chromites of the Luobusha ophiolite in Tibet have been obtained by Li et al. (2007a).

The samples are irregular grains between 0.1-0.3 mm in diameter and white in color. For every sample, only one grain was selected in random to be test. The powder X-ray diffraction was performed on an SMART APEX-CCD area-detector diffractometer using MoK α_1 radiation, 45 kV, 35 mA, rotation with $\Delta\omega = 10^\circ - 20^\circ$. The exposure time was 60 – 120 s. Li's new method (2005) was used by taking powder diffraction Debye image with a small crystal grain, and very clear Debye ring images were obtained (Figure 2). The powder diffraction pattern and diffraction data were obtained using Gadds software. All crystal parameters were calculated based on the Checkcell software (Laugier and Bochu., 2005).

RESULTS AND DISCUSSION

Biological characteristics of common carps

A well-established relationship exists between the length and weight of the common carp from Miyun Reservoir and Baiyangdian Lake. The relationship is $1g(\text{weight}) = 2.8893 \lg(\text{length}) - 4.5355$; R is 0.9336 and b is 2.8893 (Figure 3).

Normal fish usually displays a strong relationship: $\lg y = a + b \lg x$, and b usually varies from 2.5 to 4.0; while the growth rate of length, the growth rate of width and the growth rate of height are the same, the value of b is approximately 3 (Brown, 1957). Furthermore, Yin (1995) confirmed that this relationship actually exist in many various normal fishes of the family Cyprinidae.

In this work, b is 2.8893, near to 3. This can be demonstrated that the relationship of the weight and the length of all common carps from both localities is consistent with that of normal fish. The result can be further demonstrated that all common carp are normal.

Composition of asterisci

The results of NAA demonstrated that composition of asterisci from Miyun Reservoir and Baiyangdian Lake were absolutely dominated by calcium carbonate. The main element Ca and the minor elements As, Ba, Sr, and Zn were detected; values of these elements concentrations were all higher than the detection limits. Concentrations of these elements within asterisci from

Baiyangdian Lake were nearly all higher than those from Miyun Reservoir (Figure 4), being consistent with that concentrations of these elements in the water of Baiyangdian Lake are all higher than those in the water of Miyun Reservoir.

Crystallographic aspects

XRD peak patterns of calcium carbonate in asterisci

The results of current research demonstrate that three types of peak patterns of CaCO $_3$ were found in the asterisci of fishes from both localities, separately represented by sample M19wai, M19nei and BYD06nei. Based on Search-Match result, in each of these three peak patterns, nearly all peaks were matched very well with one of these three corresponding standards in the PDF2 database which are synthetic vaterite with Pbnm space group (ICDD 74-1867), synthetic vaterite with P6 $_3$ /mmc space group (ICDD 74-1867) and vaterite with P6 $_3$ /mmc space group (ICDD 33-268).

XRD peak patterns of these three standards have very similar peak position and shapes of the major reflections with 2θ among $9-25^\circ$, the remaining differences are weak reflections with 2θ around $26-37^\circ$ and $42-45^\circ$. Weak reflections with 2θ among $26-37^\circ$ exist both in the synthetic vaterite with P6 $_3$ /mmc space group (ICDD 74-1867) and in vaterite with P6 $_3$ /mmc space group (ICDD 33-268), weak reflections with 2θ among $42-45^\circ$ only exist in vaterite with P6 $_3$ /mmc space group (ICDD 33-268). The major reflections with 2θ among $9-25^\circ$ were detected in M19wai, M19nei and BYD06nei. Four weak peaks with 2θ around 26, 27, 30 and 37° were detected both in the sample M19wai and in the sample M19nei, while three weak peaks with 2θ around 42, 43 and 44° were detected only in the sample M19wai (Figure 5).

Each mineral species only has one crystal phase. Due to the controversial structure of vaterite, there are several spaces groups proposed for the crystal phase of vaterite based on the research of natural vaterite or synthesized vaterite, with different characteristic XRD peak patterns accordingly (Meyer, 1960, 1969; Kamhi, 1963; Medeiros et al., 2007; Tang et al., 2009) (Table 1). Based on first-principles calculations and molecular-dynamics simulations, Wang and Becker, (2009) considered that the vaterite structure is P6 $_5$ 22 (no. 179) with disordered CO $_3$ ions, which can be ordered in the a and b directions, resulting in two unique CO $_3$ ions; and thus different degree of ordered CO $_3$ ions caused different XRD patterns. Again from first-principles calculations, Demichelis et al. (2011) re-examined all of the possible ordered structures of vaterite, and located five stable structures, with the lowest energy one of P3221 symmetry.

The XRD results of all samples demonstrated that one or more of these three peak patterns was found

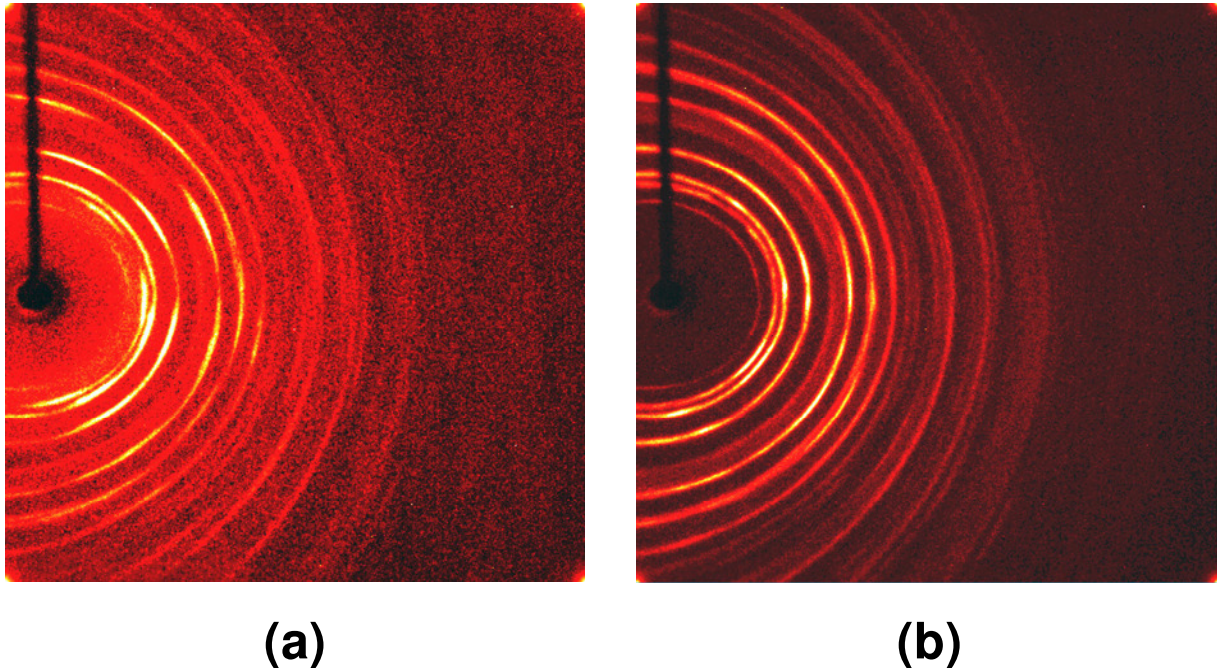


Figure 2. Debye ring of CaCO_3 in the asterici of common carp from Miyun Reservoir and Baiyangdian Lake (a) M19 nei; (b) M19 wai.

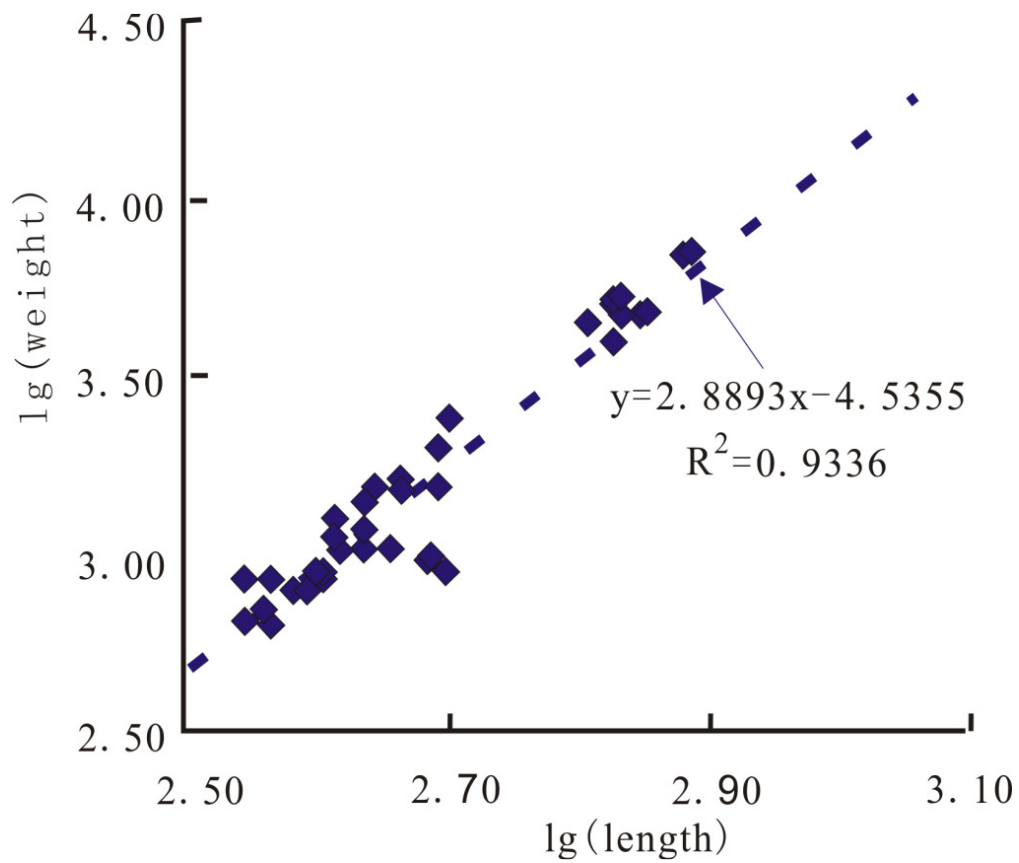


Figure 3. A well-established relationship exists between the length and weight of the common carp from both sites; b is 2.8893, near to 3, being consistent with that of normal fish. The result can be further demonstrated that all common carp samples are normal.

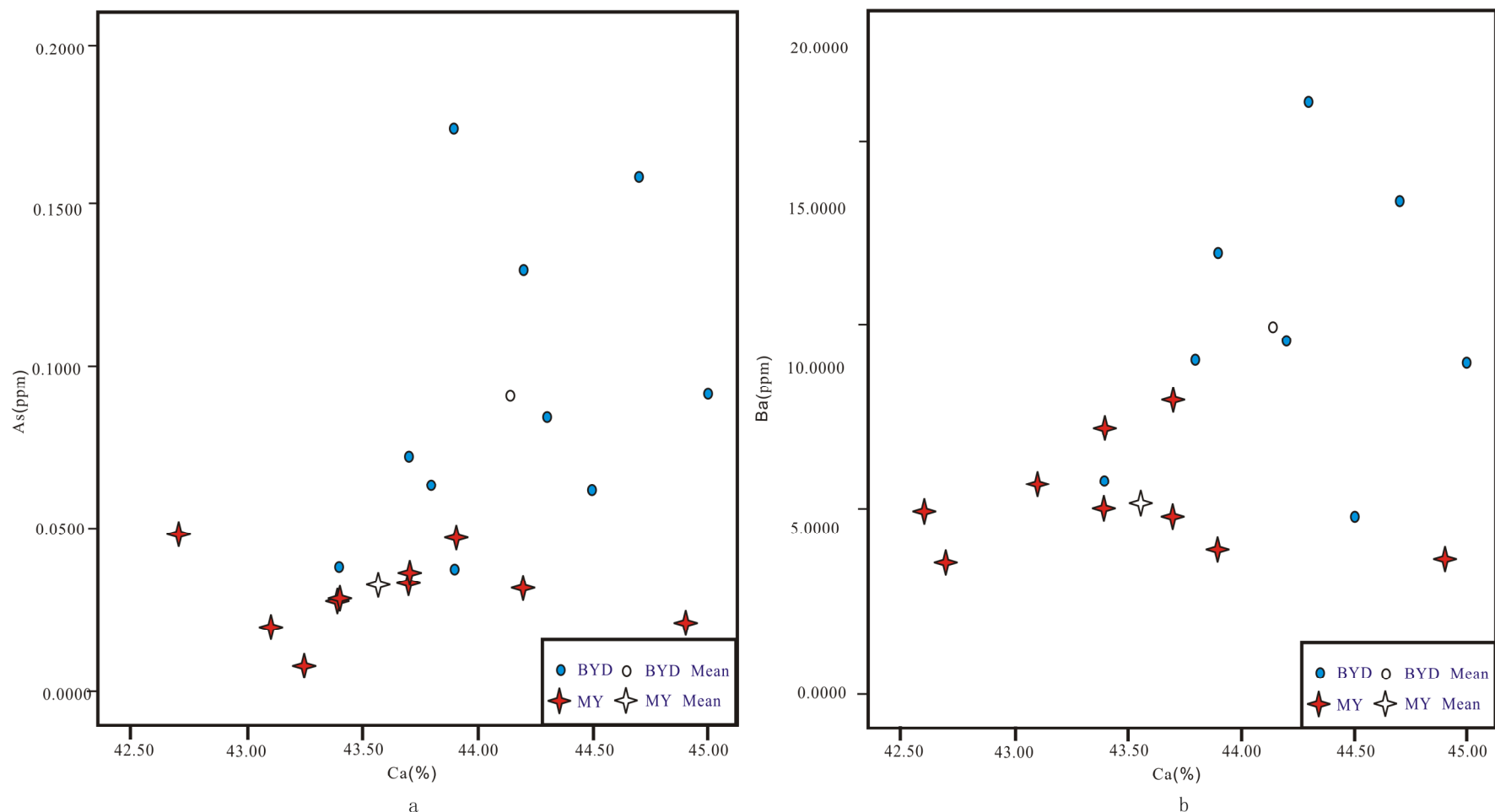


Figure 4. Scatterplot of elemental concentrations within otoliths collected from two localities in 2004. Concentrations of Ca, As, Ba, Sr, and Zn within asterisci from Baiyangdian Lake were nearly all higher than those from Miyun Reservoir.

randomly near the core or near the edge of asterisci from both localities. Based on statistics, two different situations were found. Firstly, the only one peak pattern, vaterite with $P6_3/mmc$ space group (ICDD 33-268), was found in 4 out of

10 fish, numbered M09, M24, BYD16 and BYD17. Secondly, two different peak patterns were respectively found near the core area and near the edge area in one asteriscus of 6 out of 10 fish. The fish samples numbered BYD07, BYD10, M19,

M21 and M22 have the same two peak patterns, synthetic vaterite with $P6_3/mmc$ space group (ICDD 74-1867) and vaterite with $P6_3/mmc$ space group (ICDD 33-268); while fish sample BYD06 shows another two peak patterns, synthetic vaterite

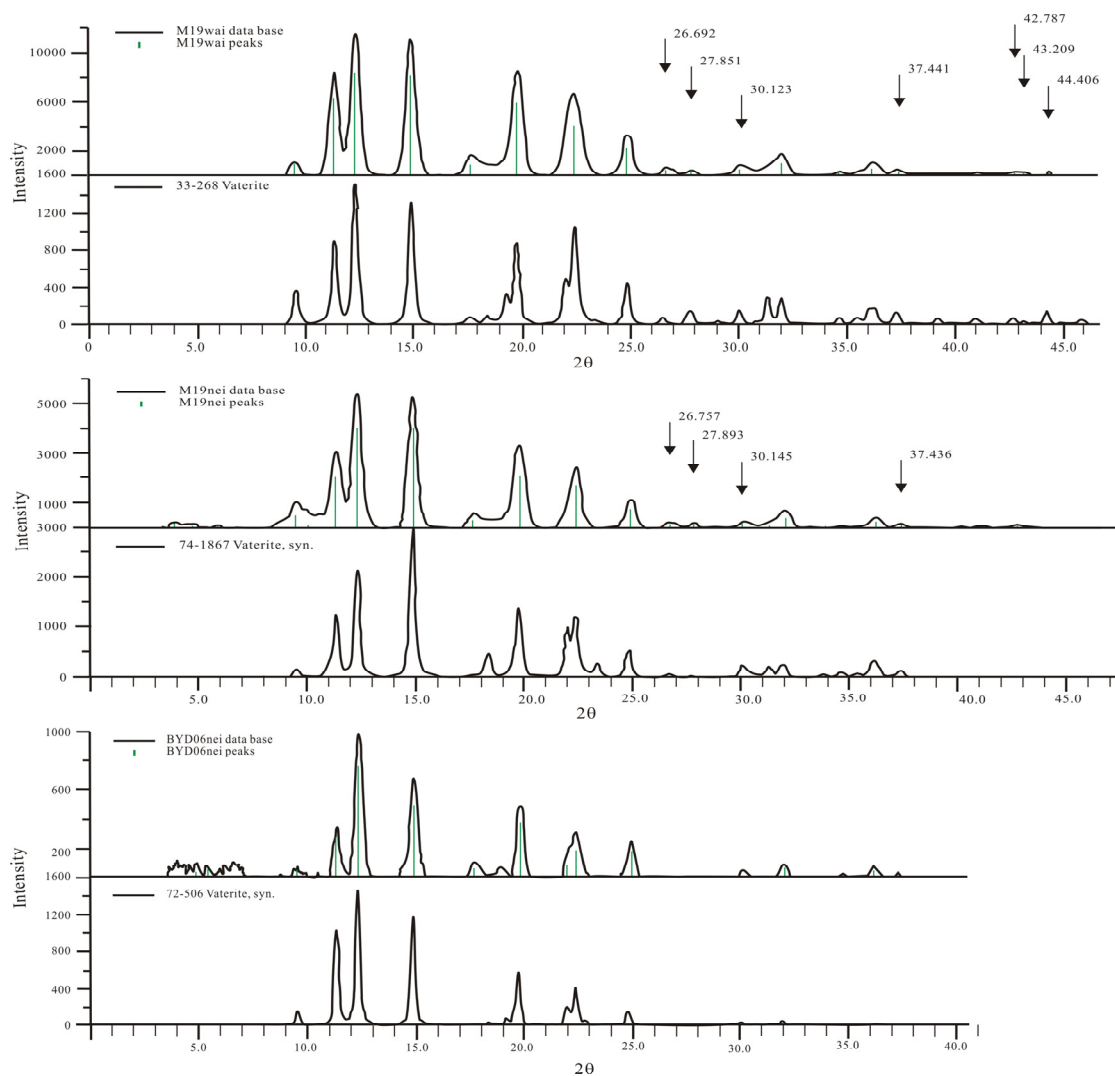


Figure 5. XRD results of CaCO_3 in the asterisci of common carp from Miyun Reservoir and Baiyangdian Lake. These three standards have very similar peak position and shapes of the major reflections with 2θ among $9\text{--}25^\circ$, except that weak reflections with 2θ among $26\text{--}37^\circ$ exist both in 74-1867 and in 33-268, and weak reflections with 2θ among $42\text{--}45^\circ$ only exist in 33-268. Four weak peaks with 2θ around $26, 27, 30$ and 37° were detected both in M19wai and in M19nei; while three weak peaks with 2θ around $42, 43$ and 44° were detected only in M19wai.

Table 1. Crystallographic data for vaterite from the literature.

Space group	Unit-cell parameters (\AA)		Z	Reference	ICDD Number	Nature/Synthesized
$P6_3/mmc$	$a = 7.169$	$c = 16.98$	6	Dupont et al. (1997)	-	-
	$a = 7.135$	$c = 8.524$		McConnell (1960)	-	-
$P6_322$	$a = 7.15$	$c = 8.47$		Bradley et al. (1966)	-	-
$P6_3/mmc$	$a = 7.151$	$c = 16.94$	12	Meyer (1969)	330268	Vaterite
$P6_3/mmc$	$a = 7.16$	$c = 16.98$	12	Kamhi (1963)		
$P6_3/mmc$	$a = 4.13$	$c = 8.49$ (pseudo-cell)	2	Kamhi (1963)	720506	Vaterite, syn
$P6_3/mmc$	$a = 4.13$	$c = 7.15$ $c = 8.48$	4	Meyer (1960)	741867	Vaterite, syn

Table 2. X-Ray diffraction results for asterisci of common carp from the Miyun Reservoir and Baiyangdian Lake.

Sample number	Results of JCPD matching				Refined results via Chekcell							
	ICDD Card number	Mineral species	Space Group	Syngony	a0(Å)	b0(Å)	c0(Å)	Vol. 0	a(Å)	b(Å)	c(Å)	Vol. (Å)
M09wai*	33-268	Vaterite	P6 ₃ /mmc(no.194)	hexagonal	7.1473	7.1473	16.917	748.407	7.1471	7.1471	16.9051	747.835
M09nei*	33-268	Vaterite	P6 ₃ /mmc(no.194)	hexagonal	7.1473	7.1473	16.917	748.407	7.1456	7.1456	16.9172	748.058
M19wai	33-268	Vaterite	P6 ₃ /mmc(no.194)	hexagonal	7.1473	7.1473	16.917	748.407	7.1491	7.1491	16.9216	748.991
M19nei	74-1867	Vaterite (S*)	Pbnm (Pnma no.62)	orthorhombic	4.13	7.15	8.48	250.410	4.1281	7.1341	8.4830	249.825
M21wai	74-1867	Vaterite (S)	Pbnm (Pnma no.62)	orthorhombic	4.13	7.15	8.48	250.410	4.1357	7.1497	8.4790	250.715
M21nei	33-268	Vaterite	P6 ₃ /mmc(no.194)	hexagonal	7.1473	7.1473	16.917	748.407	7.1471	7.1471	16.9185	748.422
M22wai	74-1867	Vaterite (S)	Pbnm (Pnma no.62)	orthorhombic	4.13	7.15	8.48	250.410	4.1238	7.1417	8.4892	250.013
M22nei	33-268	Vaterite	P6 ₃ /mmc(no.194)	hexagonal	7.1473	7.1473	16.917	748.407	7.1473	7.1473	16.9227	748.660
M24wai	33-268	Vaterite	P6 ₃ /mmc(no.194)	hexagonal	7.1473	7.1473	16.917	748.407	7.1465	7.1465	16.9106	747.946
M24nei	33-268	Vaterite	P6 ₃ /mmc(no.194)	hexagonal	7.1473	7.1473	16.917	748.407	7.1526	7.1526	16.8968	748.617
BYD06wai	33-268	Vaterite	P6 ₃ /mmc(no.194)	hexagonal	7.1473	7.1473	16.917	748.407	7.1402	7.1402	16.9305	747.512
BYD06nei	72-506	Vaterite (S)	P6 ₃ /mmc(no.194)	hexagonal	4.13	4.13	8.49	125.41	4.1220	4.1220	8.5026	125.11
BYD07wai	74-1867	Vaterite (S)	Pbnm (Pnma no.62)	orthorhombic	4.13	7.15	8.48	250.410	4.1235	7.1343	8.4793	249.446
BYD07nei	33-268	Vaterite	P6 ₃ /mmc(no.194)	hexagonal	7.1473	7.1473	16.917	748.407	7.1489	7.1489	16.9178	748.768
BYD10wai	33-268	Vaterite	P6 ₃ /mmc(no.194)	hexagonal	7.1473	7.1473	16.917	748.407	7.1438	7.1438	16.9415	748.760
BYD10nei	74-1867	Vaterite (S)	Pbnm (Pnma no.62)	orthorhombic	4.13	7.15	8.48	250.410	4.1310	7.1384	8.4819	250.123
BYD16wai	33-268	Vaterite	P6 ₃ /mmc(no.194)	hexagonal	7.1473	7.1473	16.917	748.407	7.1505	7.1505	16.8860	747.701
BYD16nei	33-268	Vaterite	P6 ₃ /mmc(no.194)	hexagonal	7.1473	7.1473	16.917	748.407	7.139	7.1395	16.9258	747.166
BYD17wai	33-268	Vaterite	P6 ₃ /mmc(no.194)	hexagonal	7.1473	7.1473	16.917	748.407	7.1425	7.1425	16.9203	747.548
BYD17nei	33-268	Vaterite	P6 ₃ /mmc(no.194)	hexagonal	7.1473	7.1473	16.917	748.407	7.1410	7.1410	16.9156	747.035

*-wai means sampling on the exterior of the asteriscus, nei means sampling near the inner core. *S = synthesized.

with P6₃/mmc space group (ICDD 72-506) and vaterite with P6₃/mmc space group (ICDD 33-268).

In this study, it is interesting that two of three different XRD patterns of vaterites, coexist in the same asteriscus samples (Table 2). These phenomena exist in 60% asteriscus samples from both localities with different water quality: less polluted water and serious intermittent water. This suggests that the crystal phase of vaterite formed *in vivo* may be controlled by the organic matrix and may also be affected by water microchemistry which will influence on the concentrations of microelements in the otolith. The relationship

between the microchemistry and the crystal phase of vaterite is worthy of further research. Moreover, that different crystal phase of CaCO₃ decided different morphologies and hierarchical structure of the otoliths is important for functional materials study; hence further study on the crystal phase of CaCO₃ formed in otolith is necessary.

The crystal parameters with morphological features

In order to eliminate the system error caused by

XRD analysis and caused by calculation based on Checkcell software, relative deviation of the crystal parameters of vaterites are defined by the authors as follow:

$$\delta a = \frac{a_{sample} - a_0}{a_0} \times 100 \% ;$$

$$\delta b = \frac{b_{sample} - b_0}{b_0} \times 100 \% ;$$

$$\delta c = \frac{c_{sample} - c_0}{c_0} \times 100 \% ;$$

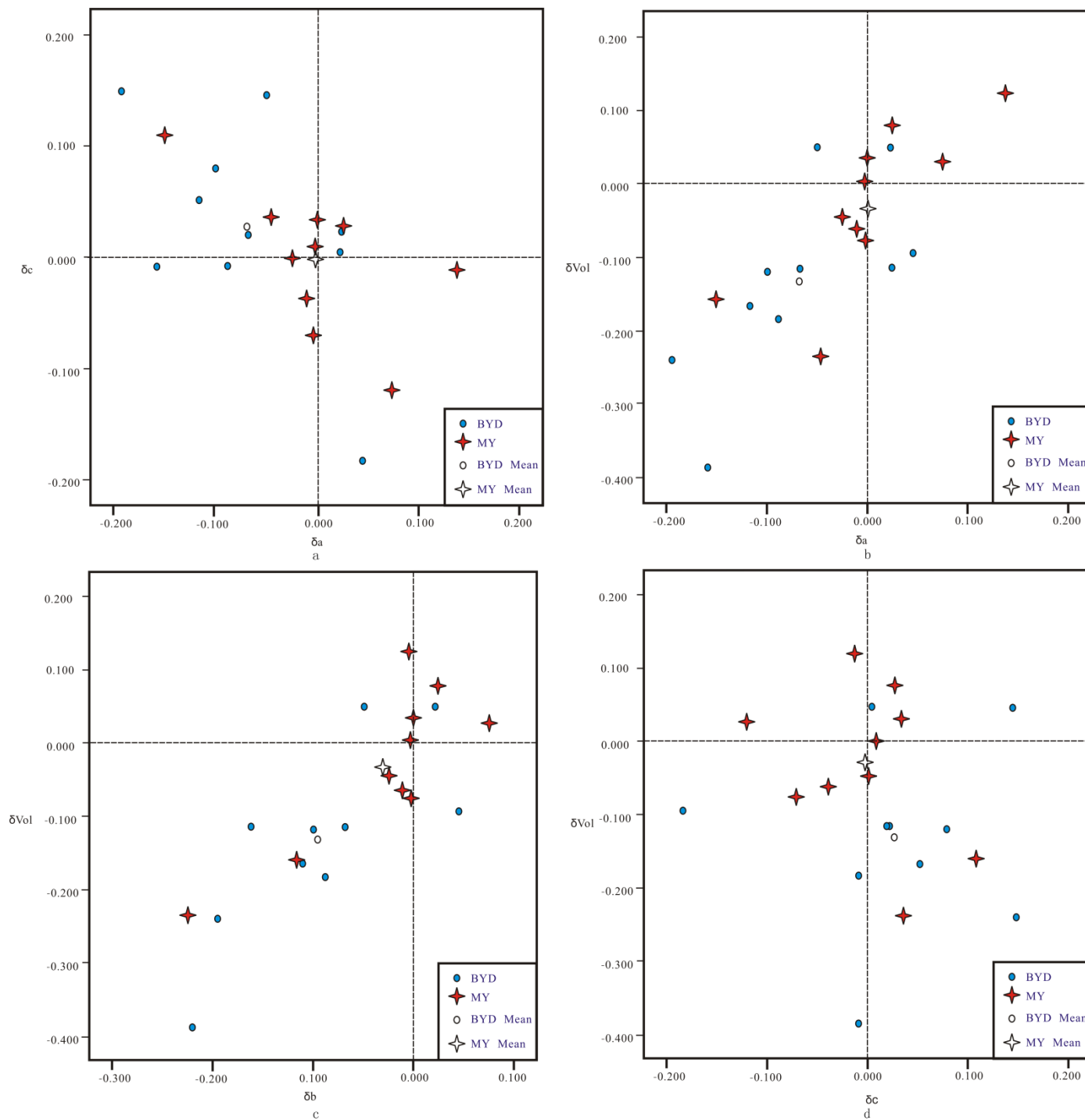


Figure 6. Scatterplots show that significant differences of the dimensions of crystalline cells of vaterites exist between these two localities. The average dimensions of crystalline cells of vaterites in the otoliths from the Miyun Reservoir are much nearer to the standards than those from the Baiyangdian Lake, δa and δVol of the former is relatively bigger than the latter, but things are opposite for δc .

$$\delta Vol = \frac{Vol_{sample} - Vol_0}{Vol_0} \times 100\%$$

δa , δb , δc and δVol are relative deviations; a_{sample} , b_{sample} ,

c_{sample} and Vol_{sample} are crystal parameters of samples calculated based on the checkcell software; a_0 , b_0 , c_0 and Vol_0 are the crystal parameters of the corresponding standards in the PDF2 database.

Scatterplots of δa and δc , δVol and δa , δVol and δb

show that significant differences of the dimensions of crystalline cells of vaterites exist between these two localities. The average dimensions of crystalline cells of vaterites in the otoliths from the Miyun Reservoir are much nearer to the standards than those from the Baiyangdian Lake, and δa of the former is relatively bigger than the latter, but things are opposite for δc . Moreover, the δVol of vaterite from the Miyun Reservoir is bigger than that from the Baiyangdian Lake, and the former is nearer to zero than the latter (Figure 6). This result may be explained by concentrations of these elements As, Ba, Sr, and Zn, which is easily entered into crystal structure, within asterisci from Baiyangdian Lake, is nearly higher than that from Miyun Reservoir. As mentioned above, concentrations of these elements in the water of Baiyangdian Lake are also all higher than those in the water of Miyun Reservoir. The results demonstrate that the dimensions of vaterite polymorphs crystalline cell might be a potential proxy for monitoring the change of water quality.

Feasibility of otoliths as a proxy for changes of the water quality and its potential usage

Why need otoliths as a proxy for changes of the water quality? This can be done directly by measuring certain water parameters providing direct information about the chemical composition of a water body. Why is such a proxy necessary?

Nowadays, there are many achievements made in the monitoring the water quality change. But the limitation for current methods of water quality monitor is obvious: a) large amount of monitor points must be distributed; b) limitation by manpower, material resources, weather, and hydrological conditions; c) continuous and fast monitor is difficult; d) historical changes of water quality may not be obtained. These all cause high expense and difficult work. Especially, the monitor points would be out of work when disaster or big accident occurs. Therefore, we want to find a new method to monitor the water quality changes.

Is there an approach to solve the problem? We think if find a material recorded the information of the water change history; there is a hope to deal with the problem. As we know, otoliths are paired concentric deposit that protein layer and calcium carbonate layer alternatively grow surrounding a nucleus. The chemistry of fish otolith is derived directly from their living environment, and once deposited the elements will be fixed forever.

Therefore, the otolith records the environmental information; analyzing the mineral information of otoliths is useful in chemical evaluation of waters where the fish lived.

Being a common economic fish species in the fresh water, carp can be killed and easy to catch them from different fresh water area.

Carp otolith might be a potential material for monitor

ambient water quality changes. Once such theory is established, otolith in fossil fish might also be used as the proxy for the paleoenvironment.

Conclusion

The polymorph of CaCO_3 in the asterisci of fish from Miyun Reservoir and Baiyangdian Lake is vaterite. Different XRD patterns of vaterites coexist in the same asteriscus samples from both localities. It suggests that the crystal phase of vaterite formed *in vivo* may be controlled by the body and may also be affected by water microchemistry. Findings give important information for morphologies and hierarchical structure study, and also might help us to understand the different XRD patterns of vaterite. Significant differences of the dimensions of crystalline cells of vaterites exist between these two localities. The dimensions of crystalline cells of vaterites from the Miyun Reservoir are much nearer to the standards than those from the Baiyangdian Lake. Significant differences also exist in concentrations of As, Ba, Sr, and Zn within asterisci. These elements concentrations from Baiyangdian Lake were nearly all higher than that from Miyun Reservoir. Crystal structure of vaterite polymorphs seem sensitive to water quality and water environment, would be a potential proxy for monitoring the change of water quality.

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