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Full Length Research Paper

Thermoluminescence (TL) analysis for otoliths of the wild carps (*cyprinoid*) from Baiyangdian Lake and Miyun Reservoir: Some implications for monitoring water environment

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Otolith is a typical biomineral carrier growing on insides of fish skull with prominent zoning structure formed by alternating layers of protein and calcium carbonate growing around the nucleus. Even though thermoluminescence (TL) analysis on biomineral has been widely used to measure the radiation exposure in the recent twenty years, the TL characteristics of the fish otolith have not yet been reported in literature. TL characteristics of otoliths from the wild carps (*cyprinoid*) living in the Baiyangdian Lake, Hebei Province and Miyun Reservoir, Beijing City was first studied, and the differences of energy gap (E) between the fish otoliths in the two waters have also been discussed in this paper. The experimental results indicated that TL curve parameters: peak temperature (Tp), luminous intensity (I), integrated intensity (S) and middle width (Wm) for the glow curves of the *cyprinoid* otoliths from Baiyangdian Lake are greater than those from Miyun reservoir, and the stability of the formers' TL curve parameters value and energy gap (E) was weaker than the latter. In comparison to the Miyun Reservoir, the analysis manifested that the electrons and vacancies trapped in the otoliths from Baiyangdian Lake are more likely to escape. According to the investigation, the contaminative degree and eutrophication in the water of Baiyangdian Lake was heavier than that of Miyun Reservoir. Therefore, the characteristics of TL growth curves of the *cyprinoid* otoliths is quite sensitive to heavier contaminated and less contaminated water, and this could be regarded as an important typomorphic biomineral for monitoring the contaminative degree and environment change of the water.

Key words: *Cyprinoid* otoliths, thermoluminescence, water environment, typomorphic mineral.

INTRODUCTION

Carbonate calcium is among the brightest of thermoluminescent minerals and consequently it was the focus for many of the earliest attempts to record the emission spectra (Calderon et al., 1996). Thermoluminescence (TL) is the emission of visible luminous stimulated by heating the samples (Chen and McKeever, 1997). TL results from a thermal activation of electrons trapped by the lattice defects of a crystal. Therefore, TL requires chemical or physical defects in mineral and the trapping of electrons by these defects. The number and the features of electron traps or the glow curve shapes are chiefly dependent on crystallization or

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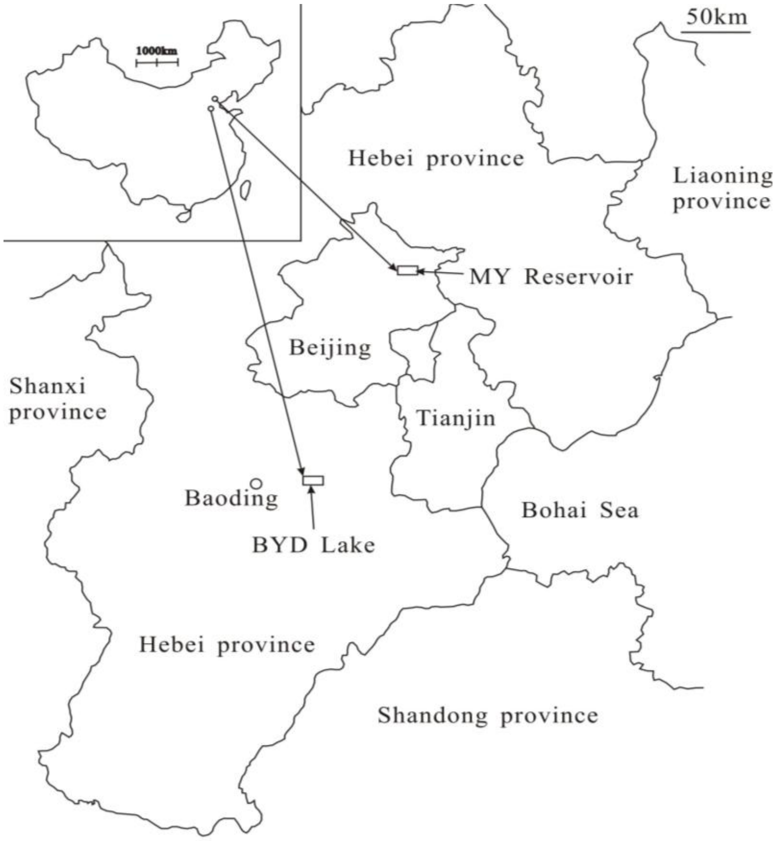

Figure 1. Skeleton map of study area and location of BYD Lake in Hebei province and MY Reservoir in Beijing city.

re-crystallization conditions. Radiation or thermal effects caused by high temperature events can also lead to a displacement process of atoms (Chen, 1984).

Otoliths of *cyprinoid* are paired metabolically inert concentric deposits in which alternating layers of protein and carbonate calcium grow around a nucleus, formed by daily growth increments of calcium carbonate, and are used for balance and/or hearing in all teleost fishes (Pannella, 1971). All teleost fishes have three pairs of otoliths namely, sagittae, asteriscae and lappillae (Lenaz et al., 2006), which can incorporate many trace elements from ambient water environment. As typical biomineral carriers and with typical microstructure, fish otoliths have many common properties with those abiological minerals. Studying otoliths by employing mineralogical methodology is possible and advantageous, especially for the study of genetic and environmental mineralogy of fish otoliths (Li et al., 2008). Like minerals formed by geological processes, calcium carbonate in fish otoliths contain abundant genetic and environmental information (Halden et al., 2000; Travis and Bronwyn, 2004), and study of its TL characteristics is important to biological, mineralogical, environmental research, and especially the inspection and protection of human environment.

Even though TL analysis on biomineral has been widely used to measure the radiation exposure in recent twenty years (Anderle et al., 1998; Christiane and Henry, 2002) and some authors also have tried to demonstrate that otoliths are a potential proxy for monitoring changes in water quality (Yang et al., 2008, 2009; Li et al., 2008, 2011), however, there has been no attempt to use TL as a low-cost and effective tool in constructing mineral typomorphism of fish otoliths for monitoring water environment changes. Glow curves of TL are often complicated and this makes it a good way to discriminate between various growing environments (e.g. contaminated and non-contaminated water). The objectives of this study are to determine peak temperature, luminous intensity, integrated intensity and middle width for TL glow curve of *cyprinoid* otoliths from different waters, and then provide useful information for water quality improvement and drinking water sources management in the two studied areas.

Description of the study area

Baiyangdian Lake (38°43'N to 39°02'N, 115°45'E to 116°07'E) (Figure 1) is the largest natural freshwater inland lake in Northern China, which plays important roles

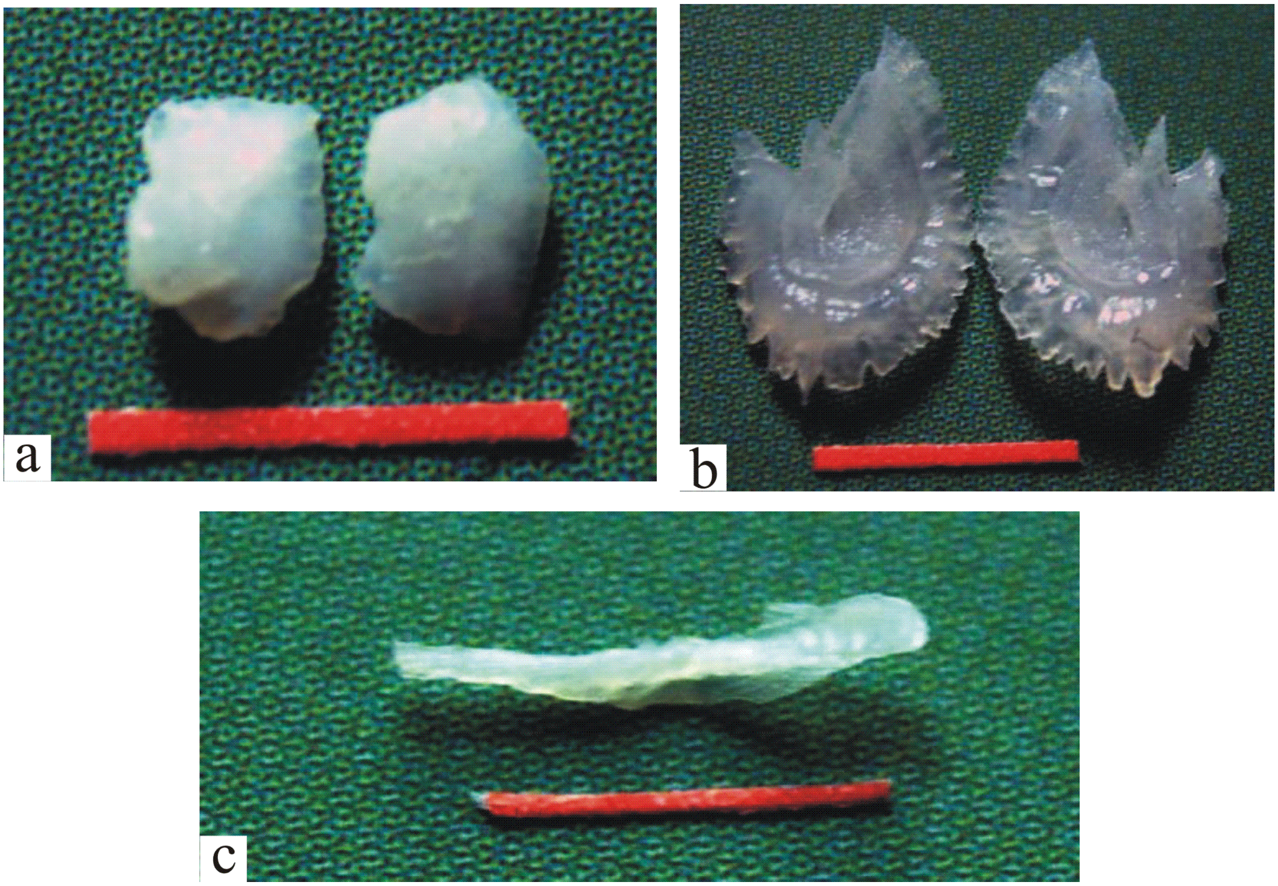

Figure 2. The morphological photos of otoliths from wild Carps (*cyprinoid*). (a) Lapillus; (b) asteriscus; (c) sagittae. The red scale bar represents 5 mm.

in the region's drinking water supply, sustaining agriculture, climate regulation, and flood control (Guo et al., 2011). The lake consists of more than 100 small and shallow lakes that are linked together by thousands of ditches, covering a total area of 366 km^2 within a catchment of 31,200 km^2. Most parts of the lake are not more than 2 m in depth. The catchment has a total population of approximately 2.04 million. As a famous tourist resort in China, Baiyangdian Lake receives more than 850,000 tourists every year. In recent years, the Baiyangdian (BYD) Lake has endured serious pollution, resulting in the deterioration of its water quality due to anthropogenic activities (Cui, 1999). The persistent water withdrawals for irrigation and periods of severe drought have resulted in a major decline in water quantity as well as fish kills associated with anoxic events, thus posing a direct threat to the region's ecological health and drinking water safety.

As the main source of drinking water for Beijing, the Miyun (MY) reservoir watershed is located in the northern area of Beijing, between 40°19'N to 41°38'N, 115°25'E to 117°35'E with an area of about 15,788 km^2 (Figure 1). The northwest part of the MY reservoir is gently mountainous, while the southeast part is mainly hilly and partially plain. The altitude varies between 150 and 1,800 m above sea-level. It has a total storage capacity of 43.75 × 10^8 m^3 and greatest depth at 43.5 m. Annual average temperatures in upper and lower watershed are 9 and 25°C, respectively (Ge et al., 2003). Construction on the reservoir began in September, 1958 and ended in September, 1960, and has since been an integrative water conservancy terminus used primarily for municipal water supply, flood control and irrigation of agricultural land. Owing to scarce water resources in 1980s, the function of the reservoir changed to protect its wildlife and wetland systems, flood control, and ability to supply drinking water for Beijing (Du et al., 1999). In order to ensure a continuous and high-quality water supply, the Beijing city government set up the MY reservoir management department, which is responsible for routine monitoring and management of reservoir water quality.

MATERIALS AND MEDTHODS

Freshwater teleosts *cyprinoid* with different sizes and ages were collected from BYD Lake (n = 10) and MY Reservoir (n = 10). Total length in millimeters was measured for each fish. The three otolith types, sagittae, lapillus and asteriscae (Figure 2), were extracted

Table 1. The thermoluminescence data of the wild carp (*cyprinoid*) otoliths in the Baiyangdian Lake and Miyun reservoir.

Sample no.	Tp/°C	I/mR	S/R	Wm/°C	Sample no.	Tp/°C	I/mR	S/R	Wm/°C
BYD-01	336.00	4000.58	400064.00	90.00	M-01	327.00	3180.87	247405.00	70.00
BYD -02	320.00	3850.12	290903.00	68.00	M-02	335.00	2736.91	221997.00	73.00
BYD -03	334.00	2333.71	210037.00	81.00	M-03	340.00	2350.62	227230.00	87.00
BYD -04	335.00	2020.59	179610.00	80.00	M-04	330.00	2850.39	247038.00	78.00
BYD -05	353.00	4605.29	460539.00	90.00	M-05	332.00	3560.77	324430.00	82.00
BYD -06	325.00	4052.05	369193.00	82.00	M-06	338.00	2520.34	210031.00	75.00
BYD -07	335.00	3550.57	343227.00	87.00	M-07	335.00	2650.49	235603.00	80.00
BYD -08	333.00	3730.59	364774.00	88.00	M-08	340.00	2563.12	227836.00	80.00
BYD -09	345.00	2163.32	197106.00	82.00	M-09	325.00	2652.06	209221.00	71.00
BYD -10	340.00	2431.00	216092.00	80.00	M-10	330.00	3512.69	304437.00	78.00
Average	335.60	3273.78	303154.50	82.80	Average	332.20	2857.83	245522.80	77.40

Tp = Peak temperature; I = the luminous intensity; S = the integrated intensity of TL; Wm = the middle width of TL glow curves.

manually from the fish with non-metallic and acid-washed tools for minimizing contamination. The otoliths were rinsed in water (three times), and then rinsed for 5 min with hydrogen peroxide (36%) to remove organic materials. They were again rinsed (three times) with water, sonicated for 5 min in water, rinsed (three times) with water, and dried under a laminar flow hood at 70°C for 48 h, then individually weighted and stored in polyethylene vials.

Compare to geological carbonate calcium, TL intensity of biological aragonite is often relatively low (Coy et al., 1988), so it is necessary to use an apparatus with a detection system sensitive to low luminous. Therefore, we used a very new model FJ-427A1 TL apparatus developed by Beijing Nuclear Instrument Factory. All experiments were conducted in the Laboratory of Genetic Mineralogy, China University of Geosciences, Beijing. Initially, the samples were crushed to a grain size of approximately 200 to 300 μM using a carefully pre-cleaned agate mortar and pestle. About 100 mg of pure otolith grains was collected and heated in the TL apparatus 470s at a linear heating rate of 1°C/s.

RESULTS AND DISCUSSION

The TL results are summarized in Table 1. All the samples were single-peak curves, no glow curves with more than single-peak peaks were observed.

A plot of luminous emission versus temperature is the glow curve which only shows unique glow peaks. The main TL properties were obtained from the glow curves by plotting the peak temperature against the luminous intensity (Figure 3a), the integrated intensity (Figure 3c), and the middle width (Figure 3e) of glow curves, as well as the integrated intensity vs. the middle width (Figure 3f), the luminous intensity vs. the integrated intensity (Figure 3d) and the middle width (Figure 2b). Table 1 shows the Tp, I, S, and Wm from the BYD otoliths scattered from 320 to 353°C, 2021 to 4605, 1.8 to 4.6 × 10^5 and 68 to 90, respectively, with the average value of 335.6°C, 3274, 3.0 × 10^5 and 82.8, respectively. However, those value from the MY otoliths relatively focused on 325 to 340°C, 2351 to 3561, 2.1 to 3.2 × 10^5 and 70 to 87, respectively, with the average value of 332.2°C, 2868, 2.45 ×10^5 and 77.4, respectively, thus indicating that the former TL values were greater than the latter. Hence, the otoliths with different origin can be distinguished using the peak temperatures (Tp), the luminous intensity (I), the integrated intensity (S) and the middle width (Wm) of the glow curves. The glow peaks may be characterized by a statistical study of the distribution of the luminous emissions temperatures and after that, by a calculation of the mean value, the statistical dispersion and the frequency of the appearance of the glow peaks defined in this way. For the otoliths from Baiyangdian Lake and Miyun Reservoir, two different types of TL characteristics have been classified at least (Figures 3a-f).

Charlet and Quinif (1995) suggested the number of electrons trapped, (which gives the TL intensity) is dependent on the following three factors: (1) TL sensitivity in relation to crystallization or re-crystallization conditions; (2) radioactivity: this increases the number of electrons trapped but with a saturation level related to the nature of the mineral and its radioactive and thermal history; (3) thermal or photodesexcitation effects which decrease the number of trapped electrons. Thus, geothermal effects, luminous and paleoclimatological conditions can modify the filling rate of the traps. So these electron and hole centers in the otoliths for TL are essentially the crystal lattice defects (traps), which are produced by the incorporated impurities into otoliths from the waters that *cyprinoid* grew in (David and Simon, 2001). In the slow heating process, the electron and hole traps captured in otolith could escape into a higher energy level, and then those traps are in a metastable state. The visible luminous light would be emitted from otolith when the traps return to the ground state.

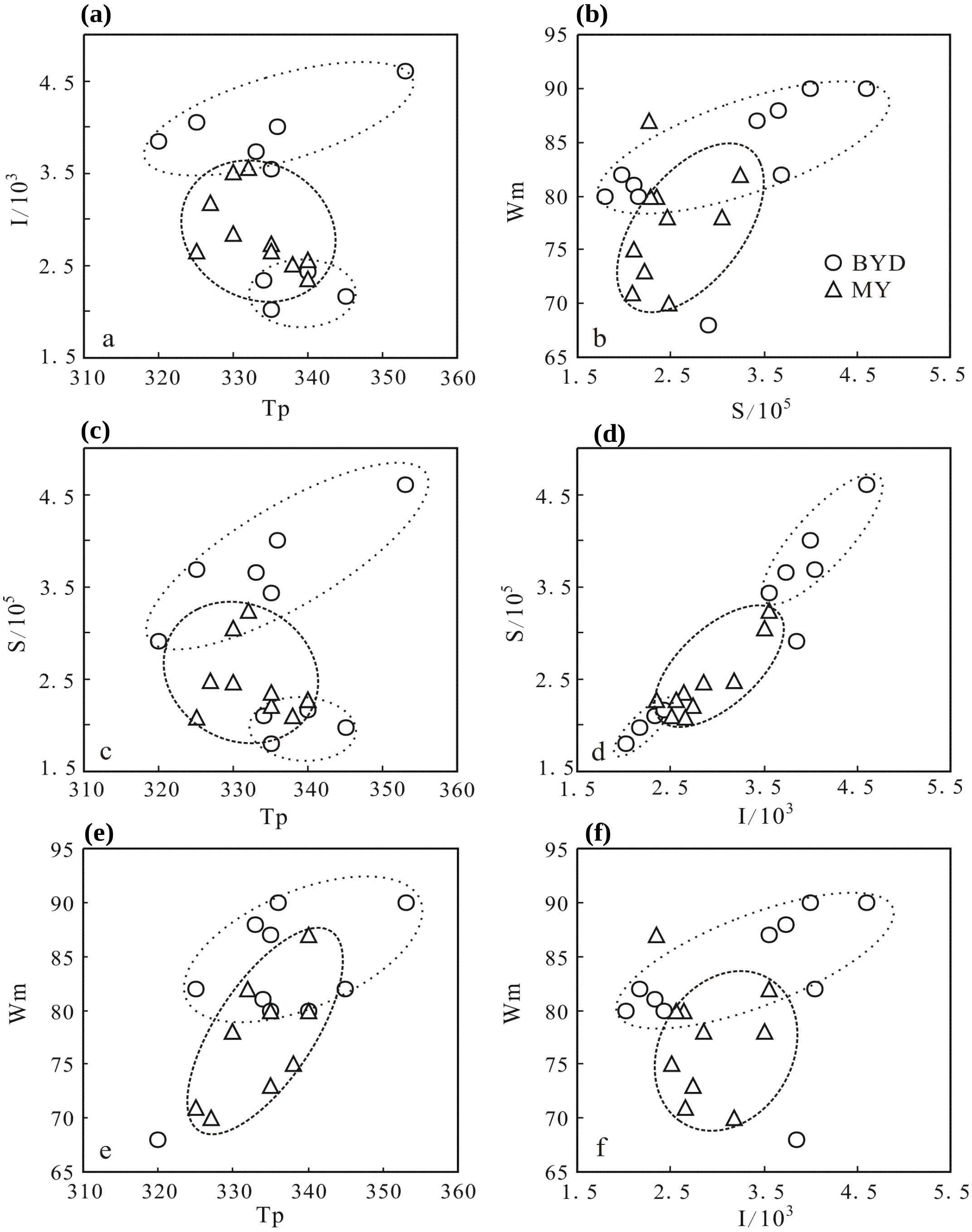

Figure 3. Plot of TL glow curves parameters of otoliths from Baiyangdian Lake (BYD) and Miyun Reservoir (MY). (a) Plot of the peak temperatures (Tp) vs. the luminous intensity (I); (b) plot of the integrated intensity (S) vs. the middle with (Wm); (c) plot of the peak temperatures (Tp) vs. the integrated intensity (S); (d) plot of the luminous intensity (I) vs. the integrated intensity (S); (e) plot of the peak temperatures (Tp) vs. the middle with (Wm); (f) the luminous intensity (I) vs. the middle with (Wm).

In addition, the escape probability (α) of electron and hole traps inside the otoliths can be calculated by the equation of (Chen R,1984): $\alpha = \alpha_0 \bullet \exp(-E/\kappa T)$ (Equation 1), where α_0 is frequency coefficient, E is energy gap or trap depth, which is thermal ionization energy of electronic centers determined by the distance between location of electronic centers in energy levels of forbidden band and conduction band (Basun et al., 2003), κ is Boltzmann constant (8.62×10^{-5}eV/K), T is absolute temperature. The trap depth (E) is usually estimated using the equation: $E = 1.5\kappa T^2/W$ (Equation 2), and the frequency coefficient (α_0) is calculated by $\alpha_0 = (\beta/W) \bullet \exp(T_m/W)$ (Equation 3),

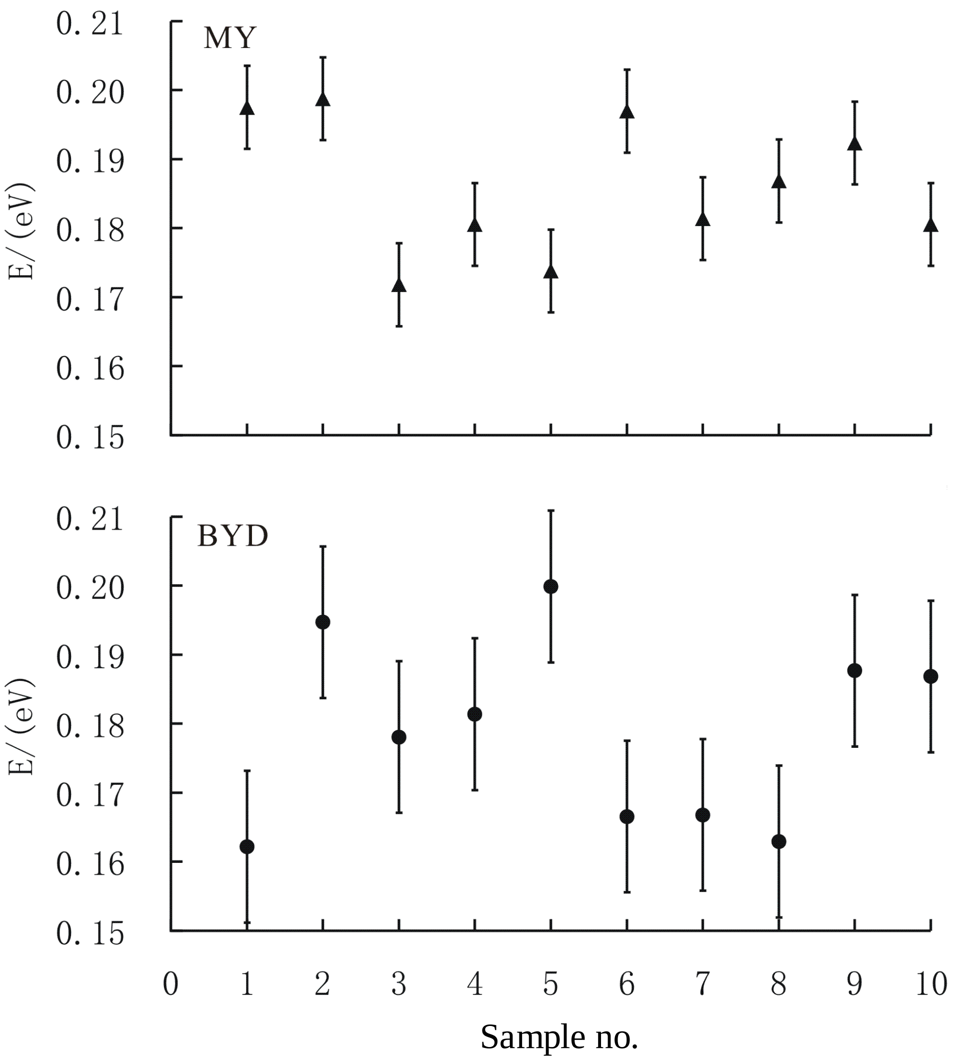

Figure 4. Stability of the energy gap (E) of the wild carp (cyprinoid) otoliths from the Baiyangdian Lake and Miyun reservoir. The length of solid line represents the standard deviation (SEB).

where, β is heating rate = 1°C/s, so α_0 of the otoliths from BYD and MY is 0.890. The final formula is the equation: $\alpha = \alpha_0 \cdot \exp(-1.5T/W)$ (Equation 4), which is simplified by substituting Equation 2 into Equation 1. Therefore, the escape probabilities of these traps (α_B) in the BYD otoliths was 0.145 at 100°C, 0.0242 at 200°C and 0.00410 at 300°C, respectively. However, the MY otoliths (α_M) was 0.128 at 100°C, 0.0187 at 200°C, 0.00278 at 300°C, respectively. This indicated that the escape probabilities (α) of BYD otoliths are always greater than those of MY otolith at the same temperature. At their peak temperature (Tp), the average trap depth (E) of BYD otoliths was 0.177 eV, which was greater than that of MY otoliths of 0.179 eV. Moreover, the standard deviation (SEB) for Tp and E of BYD otoliths was 0.011, and the SEB for MY otoliths was 0.009. This also indicated that the E stability of trapped electrons and vacancies in BYD otoliths were less than MY otoliths (Figure 4).

Altogether, the gradual increase in the luminous intensities coincides with increasing the integrated intensities ($R^2 = 0.92$) (Figure 3d), suggesting a negative correlation between the number of trapped electrons and their depth of trapped energy levels. In general, otolith crystals constantly received and accumulated the dose of external radiation (Sako et al., 2005). Electrons trapped in deep energy traps require high temperatures demanding excitation sufficient to escape from the traps (Rasheedy et al., 2005), whereas, electrons in shallow traps can escape even at lower temperatures. Because these parameters of TL glow curves affected the numbers and types of structure impurities in bicarbonate (Anderle et al., 1998), the otoliths from heavier contaminated waters (BYD) showed relatively high-temperature glow peaks and stronger luminous intensities, while other otoliths from less contaminated waters (MY) showed enhanced low-temperature peaks and weaker intensities. TL characteristics show conspicuous regional differences in their Tp, I, S and Wm throughout the two studied areas. Glow curves characteristics can provide some genetic environment information in judging the properties of otoliths. Thus, lower values of Tp, I, S, Wm, α and SEB, as well as higher E value of fish otoliths are the favorable sign of less contaminated waters.

Conclusion

Otolith TL analysis is an easy and low-cost method applied to assess the monitoring of water environment change and contaminated degree. Promising and original results have been obtained for *cyprinoid* otoliths from Baiyangdian Lake and Miyun Reservoir. Through the comparison of peak temperature (Tp), luminous intensity (I), integrated intensity (S) and middle width (Wm), as well as escape probability (α) and trap depth (E), it was shown that the otoliths from less contaminated and weaker changed waters correlated with lower values of Tp, I, S, Wm, α, SEB and higher E value. This inferred that TL for fish otoliths is a feasible method to be applied for monitoring water environment change. Recognition of TL characteristics of otolith related to the contamination degree of water can provide a rapid and cost-effective way to monitor water quality and environment change by more detailed sampling.

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