Carpathian Journal of Earth and Environmental Sciences, August 2012, Vol. 7, No. 3, p. 199 - 204

THERMOLUMINESCENCE (TL) ANALYSIS FOR OTOLITHS OF THE WILD CARPS (*CYPRINOID*) FROM BAIYANGDIAN LAKE AND MIYUN RESERVIOR: SOME IMPLICATIONS FOR MONITORING WATER ENVIRONMENT

Ye CAO[1], Shengrong LI[1], Meijuan YAO[1], Huapeng NIU[2], Junyan LUO[1], Fengqin DU[1], Yonghua GAO[3], Liangfeng YANG[4] & Jinggui TONG[5]

[1]*State Key Laboratory of geological processes and mineral resources, China University of Geosciences, Beijing 100083, China; corresponding author: cykaiyang@yahoo.com.cn*
[2]*China University of Petroleum, Beijing 102249, China*
[3]*Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China.*
[4]*The Geological Museum of China, Beijing 100034, China.*
[5]*Shenzhen College of Polytechnic, Shenzhen 518055, China.*

Abstract: 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 recent twenty years, the TL characteristics of the fish otolith have not yet been reported in the literature. TL characteristics of otoliths from the wild carps (*cyprinoid*) living in the Baiyangdian Lake, Hebei Province and Miyun Reservoir, Beijing City was firstly studied, as well as the differences of energy gap (E) between the fish otoliths in the two waters have also been discussed in this paper. The experimental results indicate 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) is weaker than the latters'. In comparison to the Miyun Reservoir, the analysis manifest that the electrons and vacancies that 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 is heavier than that of Miyun Reservoir. So the characteristics of TL growth curves of the *cyprinoid* otoliths is quite sensitive to heavier contaminated and less contaminated water, and it could be regarded as an important typomorphic biomineral for monitoring the contaminative degree and environment change of the water.

Keywords: *cyprinoid* otoliths, thermoluminescence, water environment, typomorphic mineral

1. 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 & 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 recrystallization 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 and are formed by daily growth increments of calcium carbonate, 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 incorporated 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 & Bronwyn, 2004; Fekete, 2006), 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 & 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 an 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 the present 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 these two areas.

2. DESCRIPTION OF THE STUDY AREA

Baiyangdian Lake (38º43'N to 39º02'N, 115º45'E to 116º07'E) (Fig. 1) is the largest natural freshwater inland lake in northern China where it plays important roles in the region's drinking water supply, in sustaining agriculture, in climate regulation, and in 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 two meters in depth. The catchment has a total population of approximately 2.04 million. As a famous tourist resort in China, Baiyangdian Lake received more than 850,000 tourists every year. In recent years, the BYD Lake has endured serious pollution, and its water quality has deteriorated greatly due to anthropogenic activities, and its water quality has deteriorated greatly 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. It is a direct threat to the region's ecological health and drinking water safety.

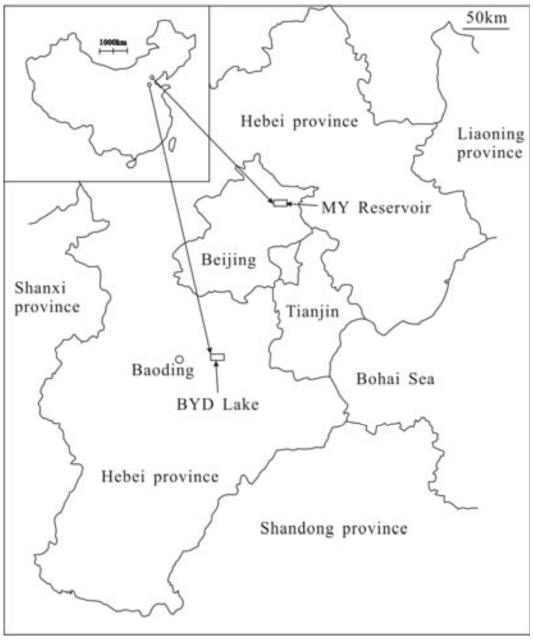

Figure 1. Skeleton map of study area and location of BYD Lake in Hebei province and MY Reservoir in Beijing city

As the main source of drinking water for Beijing, the Miyun reservoir watershed is located in the northern area of Beijing, between 40º19'N to 41º38'N, 115º25'E to 117º35'E with an area of about 15,788 km^2 (Fig. 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 1,800m above sea-level. It has a total storage capacity of 43.75×10^{8}m^3 and greatest depth at 43.5m. Annual average temperatures in upper and lower watershed are 9 and 25ºC, respectively (Ge et al., 2003). Construction on the reservoir began in September 1958 and finished 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.

3. EXPERIMENT MEDTHODS

Freshwater teleosts *cyprinoid* with different sizes and ages were collected from BYD Lake (n=10) and MY Reservoir (n=10). Total length in millimetres was measured for each fish. The three otolith types, sagitta, lapillus and asteriscus, were extracted manually from the fish with non-metallic and acid-washed tools for minimizing contamination. The otoliths were rinsed in water (three times), then rinsed for 5 min with hydrogen peroxide (36%) to remove organic materials, rinsed (three times) again 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 300μm using a carefully pre-cleaned agate mortar and pestle. About 100mg of pure otolith grains was collected, heated in the TL apparatus 470s at a linear heating rate of 1ºC/s.

4. RESULTS AND DISCUSSION

The TL results can be summarized in the following table 1. All the samples are 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 just shows unique glow peaks. The main TL properties are obtained from the glow curves by plotting the peak temperature against the luminous intensity (Fig. 2a), the integrated intensity (Fig. 2c), and the middle width (Fig. 2e) of glow curves, as well as the integrated intensity vs. the middle width (Fig. 2f), the luminous intensity vs. the integrated intensity (Fig. 2d) and the middle width (Fig. 2b). Table 1 shows the Tp, I, S, and Wm from the BYD otoliths scattered from 320-353ºC, 2021-4605, $1.8\text{-}4.6\times10^5$ and 68-90, respectively, with the average value of 335.6ºC, 3274, 3.0×10^5 and 82.8, respectively; however, those value from the MY otoliths relatively focused on 325-340ºC, 2351-3561, $2.1\text{-}3.2\times10^5$ and 70-87, respectively, with the average value of 332.2ºC, 2868, 2.45×10^5 and 77.4, respectively. It indicates the formers' TL values were greater than the latters'. So the otoliths with different origin can be distinguished using the peak temperatures (Tp), the luminous intensity (I), the integrated intensity (S) and the middle with (Wm) of the glow curves.

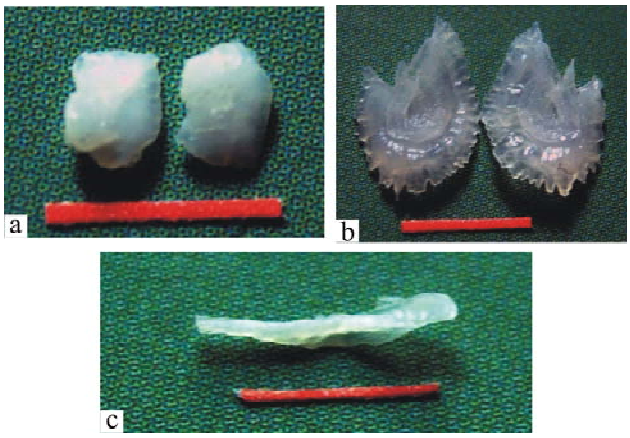

Figure 2. The morphilogical photos of otoliths from wild Carps (*cyprinoid*) a. lapillus; b. asteriscus; c. sagittae. The red scale bar represents five millimeters

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.

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

Sample No.	***Tp/ºC***	***I/mR***	***S/R***	***Wm/ºC***	***Sample No.***	***Tp/ºC***	***I/mR***	***S/R***	***Wm/ºC***
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

Note: Tp = the peak temperature; I = the luminous intensity; S = the integrated intensity of TL, Wm = the middle width of TL glow curves

For the otoliths from Baiyangdian Lake and Miyun Reservoir, two different types of TL characteristics have been classified at least (Fig. 2a-f).

Charlet (1990) 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 recrystallization 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, sunluminous 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 produced by the incorporated impurities into otoliths from the waters that *cyprinoid* grew in (David & 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.

Escape probability (α) of electron and hole traps inside the otoliths can be calculated by the equation of (Chen, 1984): $\alpha=\alpha_0 \bullet \exp(-E/\kappa T)$ □, 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: $E=1.5\kappa T^2/W$ □, and the frequency coefficient (α_0) is calculated by $\alpha_0=(\beta/W) \bullet \exp(T_m/W)$ □, where β is heating rate = 1ºC/s, so α_0 of the otoliths from BYD and MY is 0.890. The final formulae is the equation: $\alpha=\alpha_0 \bullet \exp(-1.5T/W)$ □, which is simplified by was substituting equation □ into equation □. Therefore, the escape probabilities of these traps (α_B) in the BYD otoliths are 0.145 at 100ºC, 0.0242 at 200ºC, 0.00410 at 300ºC, respectively; however, the MY otoliths (α_M) are 0.128 at 100ºC, 0.0187 at 200ºC, 0.00278 at 300ºC, respectively. It indicates 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 is 0.177eV, which is greater than that of MY otoliths of 0.179eV. Moreover, the standard deviation (SEB) for Tp and E of BYD otoliths is 0.011, and the SEB for MY otoliths is 0.009. It indicates the E stability of trapped electrons and vacancies in BYD otoliths less than MY otoliths (Fig. 4).

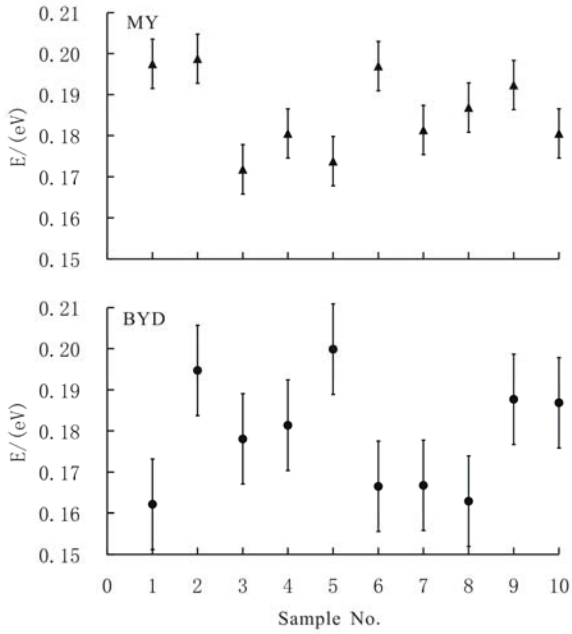

Figure 4. Stability of the energy gap (E) of the wild carp (cyprinoid) otoliths from the Baiyangdian Lake and Miyun reservoir. The length of solid line represents the standard deviation (SEB).

Seen together, the gradual increase in the luminous intensities coincides with increasing the integrated intensities (R^2=0.92) (Fig. 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 are affected the numbers and types of structure impurities in biocarbonate (Anderle et al., 1998), the otoliths from heavier contaminated waters (BYD) show relatively high-temperature glow peaks and stronger luminous intensities, while other otoliths from less contaminated waters (MY) shows 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.

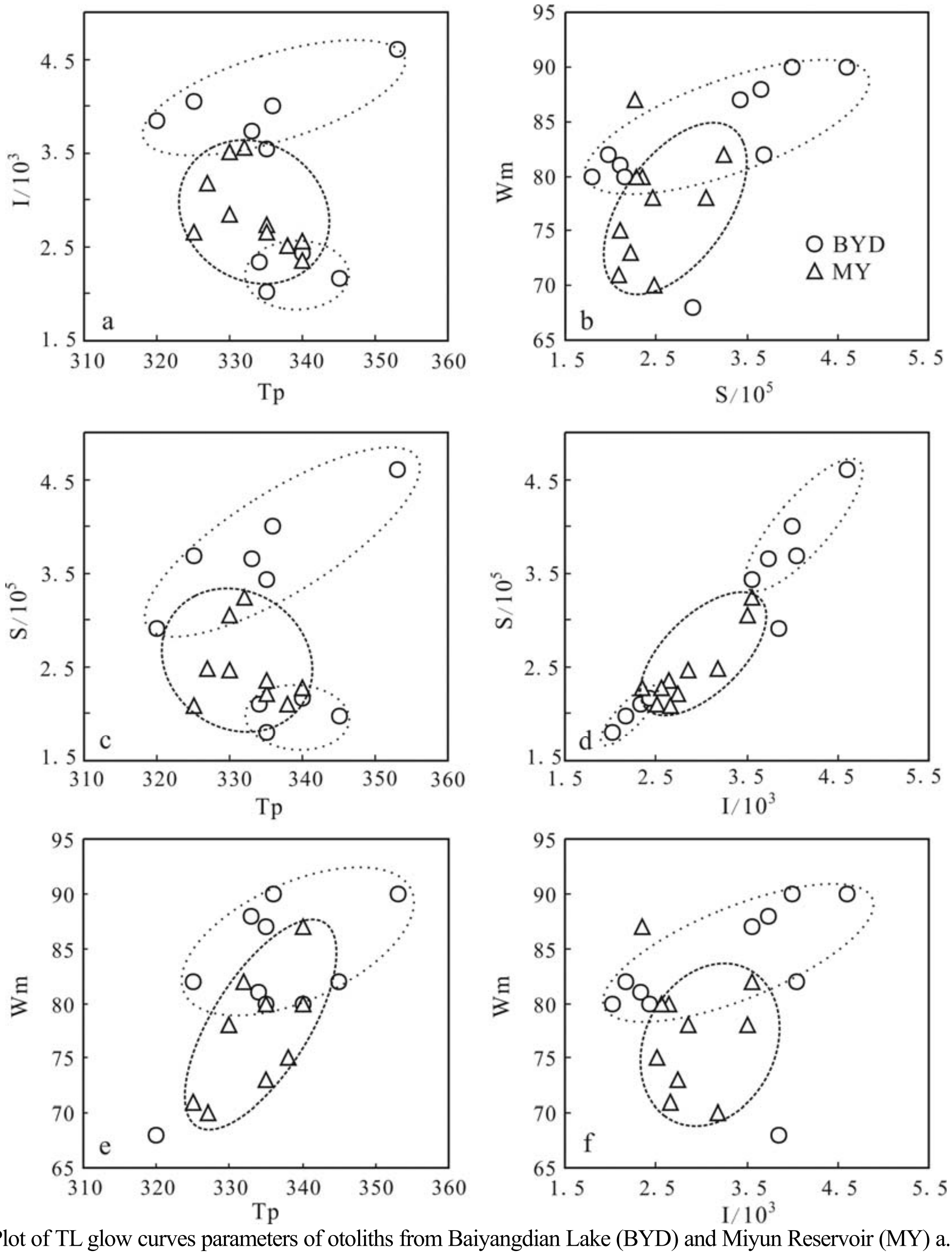

Figure 3. Plot of TL glow curves parameters of otoliths from Baiyangdian Lake (BYD) and Miyun Reservoir (MY) a. plot of the peak temperatures (Tp) vs. the luminous intensity (I); b. plot of the integrated intensity (S) vs. the middle with (Wm); c. plot of the peak temperatures (Tp) vs. the integrated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

5. CONCLUSION

Otolith TL analysis is an easy and low-cost method applied into assess monitoring 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 is shown that the otoliths from less contaminated and weaker change waters correlates with lower values of Tp, I, S, Wm, α, SEB and higher E value. It inferred that TL for fish otoliths is a feasible method to be applied into 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.

ACKNOWLEDGEMENTS

Funded by Chinese state basic research program ("973" project, 2007CB815604), National Natural Science Foundation of China (Grant No. 90914002, 40473044) and the 111 Project under the Ministry of Education and the State Administration of Foreign Experts Affairs, China (Grant No. B07011). Help from Dr. Gao Yongwen, Makah fisheries Management, USA, during the research and Dr. Chang Jianbo, Institute of hydrobiology, Chinese Academy of Sciences, are highly appreciated.

REFERENCES

Anderle, H., Steffan, I., Wild, E., Hille, P., Bermanec, V. & Sovegjarto, F., 1998. *Detection and dosimetry of irradiated biominerals with thermoluminescence, radiolyoluminescence and electron spin resonance measurements: comparison of methods.* Radiat. Meas., 29, 531-551.

Basun, S., Imbush, G.F., Jia, D.D. & Yen, W.M., 2003. *The analysis of thermoluminescence glow curves.* J. Lumi., 104, 283-294.

Calderon, T., Townsend, P.D., Beneitez, P., Guinea, J.G., Millan, A., Rendell, H.M., Tookey, A., Urbina, M. & Wood, R.A., 1996. *Crystal field effects on the thermoluminescence of manganese in carbonate lattices.* Radiat. Meas., 26, 719-731.

Chen, R., 1984. *Kinetics of Thermoluminescence Glow Peaks.* Cambridge University Press, Cambridge, pp.1-45.

Chen, R. & McKeever, S.W.S., 1997. *Theory of thermoluminescence and related phenomena.* World Scientific Press, Singapore, pp.1-162.

Christiane, S. & Henry, D., 2002. *Thermoluminescence analysis for detection of irradiated food luminescence characteristics of minerals for different types of radiation and radiation doses.* Lebensmittel-Wissenschaft und Technologie, 33, 431-439

Coy, Y.R., Calderon, T. & Aguilar, M., 1988. *Thermoluminescence and radioluminescence in aragonite.* Mineral. Petrol., 39, 39-53.

Cui, X.L., 1999. *The survey to the source of eutrophication of the water of Baiyangdian Lake.* Env. Sci., 16(S1), 17-18 (in Chinese with English abstract).

David, A. & Simon, R., 2001**.** *Sources and uptake of trace metals in otoliths of juvenile barramundi (Lates calcarifer).* J. Exp. Mar. Biol. Ecol., 264, 47-65.

Du, G.S., Meng, F.Y., Li, X.D., Zhang, W.H., Wang, J.T. & Wu, D.W., 1999. *Water quality and development trend of Miyun reservoir.* Env. Sci., 20, 110-112 (in Chinese with English abstract).

Ge, X.L., Liu, X.D., Pan, X.C., Li, Q. & Luo, S.K., 2003. *The geochemical characteristics of water body in Miyun reservoir.* Rock. Miner. Anal., 22, 44-48 (in Chinese with English abstract).

Charlet, J.M. & Quinif, Y., 1990. *Quartz thermoluminescence (TL) in gold exploration; some applications.* Mineral. Deposita, 25(Suppl), 13-20.

Guo, W., Pei, Y.S., Yang, Z.F. & Wang, C.H., 2011. *Assessment on the distribution and partitioning characteristics of polycyclic aromatic hydrocarbons (PAHs) in Baiyangdian Lake, a shallow freshwater lake in China.* J. Environ. Monitor., 13, 681-688.

Fekete, J.G., 2006. *Education, research and development tasks of environmental protection.* Carpathian Journal of Earth and Environment Sciences, 2, 5-12.

Halden, N.M., Mejia, S.R., Babaluk, J.A., Reist, J.D., Kristofferson, A.H., Campbell, J.L., Teesdale, W.J., 2000. *Oscillatory zinc distribution in Arctic char (Salvelinus alpinus) otolith: The result of biology or environment.* Fish Res., 46, 289-298.

Lenaz, D., Miletic, M., Pizzul, E., Vanzo, S. & Adami, G., 2006. *Mineralogy and geochemistry of otoliths in freshwater fish from Northern Italy.* Eur. J. Mineral., 18, 142-148.

Li, S.R., Luo, J.Y., Cao, Y., Yang, L.F., Gao, Y.H., Tong, J.G., Xu, H. & Shen, J.F., 2008. *New discoveries in the study of carp otoliths.* Geochim. Cosmochim. Ac., 72(12), A545.

Li, S.R., Du, F.Q., Yan, L.N., Cao, Y., Luo, J.Y., Gao, Y.H., Yang, L.F. & Tong, J.G., 2011**.** *The genetic mineralogical characteristics of fish otoliths and their environmental typomorphism.* Afr. J. Biotechnol, 10, 4405-4411.

Pannella, G., 1971. *Fish otoliths: daily growth layers and periodical patterns.* Science, 173, 1124-1126.

Rasheedy, M.S., 2005. *A new evaluation technique for analyzing the thermoluminescence glow curve and calculating the trap parameters.* Thermochim. Ac., 429, 143-147.

Sako, A. & O'Reilly, C.M., Hannigan, R., Bickford, N. & Johnson, R., 2005. *Variations in otolith elemental compositions of two clupeid species, Stolothrissa tanganicae and Limnothrissa miodon in Lake Tanganyika.* Geochem.- Explor. Env. Anal., 5, 91-97.

Travis, S.E. & Bronwyn, M.G., 2004. *Fish otolith chemistry influenced by exposure to multiple environmental variables.* J. Exp. Mar. Biol. Ecol., 313, 269-284.

Yang, L.F., Li, S.R., Luo, J.Y. & Cao, Y., 2008. *Mineral chemistry of carp otolilths reflecting water quality change.* Geochim. Cosmochim. Ac., 72(12), A1055.

Yang, L.F., Li, S.R. & Luo, J.Y., 2009. *Study on $CaCO_3$ crystal structure and its environmental information of carp asteriscus from Miyun Reservoir and Baiyangdian Lake.* Geochim. Cosmochim. Ac., 73(13), A1476.

Received at: 22. 08. 2011
Revised at: 08. 03. 2012
Accepted for publication at: 28. 05. 2012
Published online at: 01. 05. 2012