

# Uranium ( $^{238}\text{U}$ and $^{234}\text{U}$ ) and Thorium ( $^{232}\text{Th}$ and $^{230}\text{Th}$ ) Records in the Bottom

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# Uranium ( $^{238}\text{U}$ and $^{234}\text{U}$ ) and Thorium ( $^{232}\text{Th}$ and $^{230}\text{Th}$ ) Records in the Bottom Sediments of Lake Baikal, Siberia

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## Introduction

Lake Baikal in southeastern Siberia is located in a crucial area for reconstructing insolation-related, long-term climate changes, because the area is known to be highly sensitive to variation in solar insolation (Short et al. 1991; Kashiwaya et al. 2002). Reconstruction of the paleoenvironmental changes has been attempted with the appropriate approach by using physical, chemical and biological signatures inferred from the lake sediments (Kashiwaya et al. 1991; Takahara et al. 2000; Muller et al. 2002; Ochiai and Kashiwaya 2004; Sapota et al. 2004; Sakai et al. 2005). Studies so far made in sediment cores, mainly from the Academician Ridge in the central part of the lake, have revealed that some sensitive indicators are distributions of Bio-Si, organic matter and microelements, primarily uranium (Colman et al. 1995; Grashev et al. 1997; Goldberg et al. 2000; Prokopenko et al. 2001; Haraguchi et al. 2003; Watanabe et al. 2004). Diatomaceous algae are by far the dominant producers of Bio-Si in Lake Baikal, contributing to about 98% of all sedimentary silica (Mackay et al. 1997). The bottom sediments in Lake Baikal have been characterized by the increased contents of Bio-Si and organic carbon during the warm (interglacial) intervals and the decreased contents during cold (glacial) ones, and they are positively correlated with U contents (cf. Gavshin et al. 1994). The high U content in diatomaceous oozes with their high content of Bio-Si is explained by the increase in amount of U in dispersed organic matter, mainly in humic acids and phosphates (Gavshin et al. 1994; Zhmodik et al. 2001). Furthermore, direct association of U-bearing phosphates in sediments with diatomaceous oozes has been recently found (Zhmodik et al. 1999, 2003). However, more complete interpretation of these records is needed, because the relation between U and Bio-Si contents and U sedimentary behavior are, as yet, unknown.

We have investigated the depth distribution in the concentrations of U ( $^{238}\text{U}$  and  $^{234}\text{U}$ ) and Th ( $^{232}\text{Th}$  and  $^{230}\text{Th}$ ) isotopes, providing their own internal geochronometers, in the Lake Baikal sediments. Uranium-238 and  $^{232}\text{Th}$  are primordial radionuclides. In most places on earth they vary only within narrow limits, but in some locations there are wide deviations from normal levels. The uranium normally found in nature consists of three isotopes having mass number 234, 235 and 238. In the earth's crust,  $^{238}\text{U}$  is present in the amount of 99.28%, and is usually in radioactive equilibrium or near equilibrium with its daughter  $^{234}\text{U}$ . Uranium is a redox-sensitive and biologically-related element, and a small change to more reducing conditions may immobilize the soluble U(VI) to insoluble U(IV), while more oxidizing conditions have the reverse effect. Transfer of U from water to sediments is known to arise from adsorption and/or adhesion onto settling particles including organic matter. Additional transfer of U may result from diffusion into the sediments and reduction of U(VI) to U(IV) with precipitation of  $\text{U}(\text{OH})_4$  at the redox boundary. Thorium normally found in nature consists of three isotopes having mass number  $^{232}\text{Th}$  and  $^{228}\text{Th}$  in

$^{232}\text{Th}$  decay-series and  $^{230}\text{Th}$  in  $^{238}\text{U}$  decay-series. Thorium is an element mostly associated with terrestrial materials, and is well known as an immobile element. Thorium has an extremely low solubility in water and is conserved during chemical weathering processes. Therefore, Th is recognized as a proxy for terrestrial materials. Lake bottom sediments contain U and Th isotopes originating mainly from two sources: one is U(Th) fraction in soil itself derived from river and direct discharge (hereafter referred to as terrigenous U(Th)) and the other is U(Th) fractions which is formed mainly from a dissolved phase within the lake and its input rivers (hereafter referred to as authigenic U(Th)). Actually, the authigenic U in sediments seems to reflect the physico-chemical conditions of sedimentation and environmental changes and thus it is essential to separate the two U sources.

In this paper, we presented information on sedimentary behavior of U (and Th) using a sediment core (ca. 60 cm in depth) characterized by a relatively high sedimentation rate from the offshore bottom sediments of the Selenga Delta in Lake Baikal. We measured concentrations of U and Th isotopes ( $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{232}\text{Th}$  and  $^{230}\text{Th}$ ), as well as other physical and chemical parameters of sediments. The obtained data are discussed laying stress on sedimentary behavior of U, including the results of sequential leaching for the speciation of U in the sediment core. A part of the results on the core VER98-1-6 taken from the northern part of the Academician Ridge of the Lake Baikal will be discussed here, mainly related to the dating (sedimentation rate) using  $^{234}\text{U}$ - $^{238}\text{U}$  and  $^{230}\text{Th}$ - $^{238}\text{U}$  methods

## Study area

Lake Baikal is located in the center of the Asian continent, in southeastern Siberia, between  $51^{\circ}28'$ - $55^{\circ}47'$  N and  $103^{\circ}43'$ - $109^{\circ}58'$  E. It resulted from tectonic rifting of the land that occurred to over 30 Myr ago (Belova et al. 1983). Lake Baikal, is the deepest (1,642 m deep), largest volume ( $23,000 \text{ km}^3$  of fresh water)(Kozhov 1963) and oldest rift valley in the world. The bottom sediments of Lake Baikal are more than 7,000 m thick (Hutchinson et al. 1992). The lake consists of southern, central and northern basins which are separated by two structural highs. One is the Academician Ridge, which provides the boundary between the central and northern basins. Sedimentation rates are one or two orders of magnitude higher in the offshore bottom sediments of the Selenga Delta than in the Academician Ridge (Edgington et al. 1991). Past glaciations have had dramatic effects on the Lake Baikal area, i.e., hydrology, sedimentology, ecosystem and so on, but the lake itself has never been glaciated (Mackay et al. 1997). Its main water input is the Selenga River which accounts for more than 50% of the input out of more than 300 inflows to the lake. Concentration of soluble  $^{238}\text{U}$  in the Selenga River water is high ( $6\text{-}7 \text{ mBq l}^{-1}$ ), and about 80% of the U input to the lake, with a high  $^{234}\text{U}/^{238}\text{U}$  activity ratio of ca. 2, comes from this river. The Angara River is only one outlet. The water and U residence times in this lake are estimated to be as long as ca. 400 y and 270 y, respectively. (Weiss et al. 1991; Edgington et al. 1996)

## Experimental

### *Sampling*

Four sediment core samples (ca. 60 cm in depth, 5.2 cm in diameter) were taken in August 2003 by using a gravity corer. The core samples were immediately cut on the research ship into 1.0 cm segments beginning from the top. Only one sediment core No.4 (50°12'35" N, 105°59'54" E) from a depth at about 120 m in the offshore of Selenga Delta was used for this study. Lake water samples were also collected by using a Bandon sampler in order to get information on  $^{238}\text{U}$  concentrations and their  $^{234}\text{U}/^{238}\text{U}$  activity ratios at selected depths of the water column.

The VER98-1-6 composite sample was obtained from gravity (177 cm) and piston (906 cm) cores with a composite length of about 10 m from the Academician Ridge (53°44'46" N, 108°24'38" E) at a water depth of 320 m in the central part of lake Baikal in September 1998. The both cores were cut into 5 mm segments from the surface of sediment, and the samples obtained were preserved at 4°C till they were analyzed. The sampling sites are shown in Fig.1.

#### *Biogenic-SiO<sub>2</sub> content and grain size distribution of the sediments*

Biogenic-SiO<sub>2</sub> content in the sediments was determined by the method of Mortlock and Froelich (1989). About 50 mg of dry sample was weighed out. One ml of 10% H<sub>2</sub>O<sub>2</sub> solution and the sediment sample were put into a sample tube, and heated in a 60 °C water bath for 1 h while being shaken mechanically. Then, the sample was stood for 12 h at room temperature. After being centrifuged, the supernatant was decanted and the residue was washed well with distilled water and dried at 77 °C for 24 h. The weight loss of this dried residue was designated as organic matter fraction. Then, the residue was leached with 1M HCl for 20 min at room temperature. After centrifuging and decanting, this residue was washed well with distilled water and dried at 77 °C for 24 h. In this fraction, carbonates and Fe-Mn oxyhydroxides were decomposed. As there are not so much carbonates in the Lake Baikal, the decrease of this fraction was designated for convenience as Fe-Mn oxyhydroxides fraction. For extraction of Bio-Si, the residue was heated for 7 h at 85 °C with 2.4 mol kg<sup>-1</sup>-Na<sub>2</sub>CO<sub>3</sub> solution, and the sample tube was shaken for about 1 min every hour. A part (0.1 ml) of this solution was diluted with 7.8 ml of distilled water and 0.1 ml of 4M HCl, and then 0.2 ml of 3M H<sub>2</sub>SO<sub>4</sub> and 0.4 ml of 10% (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> were further added to this solution. After standing for 30 min, the absorbance was measured at 420 nm. This fraction was designated as Bio-Si fraction. The remaining fraction was designated as residual fraction. Grain size distribution in bulk samples and their mineral fractions were measured using a laser diffraction particle size analyzer (SALD-2000J, Shimazu Co. Ltd.). The mineral sample was obtained from the residue after the removal of organic matter, Fe-Mn oxyhydroxides and Bio-Si.

#### *Uranium and Th isotopes analyses*

The short sediment core from the offshore of Selenga Delta was at first dated by using excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  methods. The sediment samples (ca. 5 g) was packed into a plastic vessel, and after standing for 2-3 weeks, the sample was subjected to a non-destructive  $\gamma$ -ray spectrometric analysis. The spectrometer was calibrated with standards prepared from NBL (New Brunswick Laboratory, U. S. Department of Energy) reference material No. 42-1 (4.04 % uranium) and analytical grade KCl. The samples were measured for more than 2 days. For the VER98-1-6 taken from the northern part of the Academician Ridge of the Lake Baikal, dating (sedimentation rate) using  $^{234}\text{U}$ - $^{238}\text{U}$  and  $^{230}\text{Th}$ - $^{238}\text{U}$  methods was attempted because of its long core

Aliquots (ca. 1.0 g) of sample were calcinated overnight at 500 °C and then treated with a mixture of HNO<sub>3</sub>, HF and HClO<sub>4</sub> in a Teflon beaker. The residue remaining after the acid treatment

was further fused with  $\text{Na}_2\text{CO}_3$  in a platinum crucible and the melt was completely dissolved in diluted  $\text{HNO}_3$ . After spiking with a mixture of  $^{232}\text{U}$  and  $^{229}\text{Th}$  as yield tracers, U and Th were radiochemically separated and purified in accordance with the method described by Sakaguchi et al. (2004). The U analysis in water was performed using 20 liters. The sample was at first acidified with 50 ml of conc.  $\text{HNO}_3$ , with the addition of  $^{232}\text{U}$  as a yield tracer and  $\text{Fe}^{3+}$  (ca. 200 mg) carrier. Then, the U was coprecipitated with  $\text{Fe}(\text{OH})_3$  and separated and purified by an anion exchange resin column method (Sakaguchi et al. 2004). Finally,  $\alpha$ -activity of U or Th electroplated onto a polished stainless steel disc was determined by  $\alpha$ -ray spectrometry.

#### *Selective chemical leaching for the speciation of U in sediments*

The sequential leaching of U using 1 g of sediments sample was performed on the basis of Tessier et al. (1979) combined with the Bio-Si fractionation method of Mortrock and Froelich (1989). The initial procedure of washing with  $\text{MgCl}_2$  solution extracting the exchangeable U was omitted because previous experiment showed that dissolution of U was negligibly small.

For the partitioning of U, the following five fractions were selected according to the methods mentioned above:

- (1) U bound to carbonates; 1 g of sediment was treated for 5 h under continuous agitation at room temperature with 8 ml of sodium acetate solution (1 M NaOAc) adjusted to pH 5.0 with acetic acid (HOAc).
- (2) U bound to Fe-Mn oxyhydroxides; The residue from fraction (1) obtained after centrifugation (3500 rpm, 35 min), was treated for 6 h at  $96^\circ\text{C}$  with occasional agitation with 20 ml of 0.04M  $\text{NH}_2\text{OHCl}$  in 25% (v/v) HOAc (pH 2).
- (3) U bound to organic matter; The residue from (2) was treated for 2 h with occasional agitation at  $85^\circ\text{C}$  with a mixture of 3 ml of 0.02 M  $\text{HNO}_3$  and 3 ml of 30%  $\text{H}_2\text{O}_2$ . Then, a 5 ml aliquot of 30%  $\text{H}_2\text{O}_2$  was added and the sample was treated again at  $85^\circ\text{C}$  for 3 h. After cooling, 15 ml of 3.2M  $\text{NH}_4\text{OAc}$  in 20% (v/v)  $\text{HNO}_3$  were added, and the sample was diluted to 20 ml with distilled water and agitated continuously for 30 min.
- (4) U bound to Bio-Si; The residue obtained after (3) was treated at  $85^\circ\text{C}$  for 7 h under continuous agitation with 25 ml of 2M  $\text{NaCO}_3$ .
- (5) U in the residue; The residue from (4) was decomposed completely by fusion with  $\text{Na}_2\text{CO}_3$ .

After chemical separation described above, the U concentration in each fraction was determined by  $\alpha$ -ray spectrometry.

## **Results and Discussion**

### *1. The Sediment Core in the offshore of Selenga Delta*

#### *1.1. Characteristics of the sediment core*

The analyzed sediments showed vertical variation in composition, especially in Bio-Si and mineral contents, and in grain size (Fig. 2). The contents of organic and Fe-Mn fractions are rather low, i.e., 5-9 wt% and 2-5 wt%, respectively, and both gradually decrease with increasing depth. The sediments are dominated by mineral materials (70-85 wt%) derived mainly from the nearby Selenga River. In generally, the core is characterized by the Bio-Si-rich layers up to a depth of ca. 25 cm from the surface, followed by a decreasing content of diatom layers with fine grain sizes in

the 25-40 cm interval. The layer around 40 cm is Bio-Si-rich and the final 50-62 cm layer consists of diatom-barren sediment layers with relatively large grain size.

The relationship between the excess  $^{210}\text{Pb}$  and fallout  $^{137}\text{Cs}$  concentrations versus mass-depth for the sediment core is shown in Fig. 3. Providing that both the flux  $F$  ( $\text{Bq cm}^{-2} \text{ y}^{-1}$ ) of  $^{210}\text{Pb}$  to the sediment-water interface and the sediment accumulation rate  $S$  ( $\text{g cm}^{-2} \text{ y}^{-1}$ ) have remained constant in the undisturbed sediments, the excess (unsupported)  $^{210}\text{Pb}$  activity  $A_{\text{Pb-210}}$  ( $\text{Bq g}^{-1}$ ) on the mass-depth ( $\text{g cm}^{-2}$ ) obeys the constant flux-constant sediment accumulation rate model:

$$A_{\text{Pb-210}}(m(z)) = (F/S)\exp(-\lambda m(z)/S) \quad (1)$$

where  $\lambda$  is the radioactive decay constant for  $^{210}\text{Pb}$  ( $0.693/22.26 \text{ y}^{-1}$ ), and  $m(z)$  is the integrated mass of sediment above a depth( $z$ ) which is independent of density changes produced by physical compaction of the sediments. The sediment accumulation rate of  $24.2 \text{ mg cm}^{-2} \text{ y}^{-1}$  was estimated from the optimized least square fit for exponential decrease in concentration from the top to ca. 8 cm in depth. Providing that the sedimentation rate was constant, this core covers about 2 kyr. The observed sedimentation rate, which is not significantly different from rates obtained already from the surrounding area ( $22\text{-}34 \text{ mg cm}^{-2} \text{ y}^{-1}$ ), is remarkably high compared to the slow sedimentation rates (around  $3 \text{ mg cm}^{-2} \text{ y}^{-1}$ ) estimated for the Academician Ridge (Edgington et al. 1991). The  $^{137}\text{Cs}$  profile does not exhibit the sub-surface maximum deposition generally associated with maximum fallout in 1963. This may result from a long residence time of this nuclide in water.

The flux of excess  $^{210}\text{Pb}$  to the sediment and the sedimentary inventories of excess  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  were evaluated to be  $10.0 \text{ mBq cm}^{-2} \text{ y}^{-1}$ , and  $0.23$  and  $0.09 \text{ Bq cm}^{-2}$ , respectively. The  $^{210}\text{Pb}$  flux is close to the mean atmospheric  $^{210}\text{Pb}$  flux ( $11.2 \pm 3.0$ , ranging from  $7.9$  to  $15.5 \text{ mBq cm}^{-2} \text{ y}^{-1}$ ) estimated previously by us from the excess  $^{210}\text{Pb}$  accumulation in soil samples up to a depth of 30 cm collected around the lake. This indicates that most of the excess  $^{210}\text{Pb}$  in sediments directly came from the atmosphere. The  $^{137}\text{Cs}$  inventory ( $0.09 \text{ Bq cm}^{-2}$ ) in the sediments seems lower (mean:  $0.14 \pm 0.06 \text{ Bq cm}^{-2}$ , range:  $0.07\text{-}0.24 \text{ Bq cm}^{-2}$ ) than values evaluated from the above soil samples. However, the activity ratio ( $0.40$ ) of  $^{137}\text{Cs}/\text{excess } ^{210}\text{Pb}$  for inventory in the sediments lies within the values ( $0.37 \pm 0.12$ ) estimated from soil samples.

### *1.2. Uranium and thorium concentrations in water and sediments*

Dissolved  $^{238}\text{U}$  concentration in the lake water was as high as about  $6 \text{ mBq l}^{-1}$ , irrespective of the sampling positions and depths (Table 1). The observed values are several tens of times higher than the  $^{238}\text{U}$  concentrations (around  $0.1 \text{ mBq l}^{-1}$ ) which are usually observed in Japanese lakes (Sakaguchi et al. 2004). Additionally, U in the Lake Baikal water exhibited an excess of  $^{234}\text{U}$  relative to  $^{238}\text{U}$ , with a distinctly high  $^{234}\text{U}/^{238}\text{U}$  activity ratios of about 2, resulting from the recoil-enhanced mobility of  $^{234}\text{U}$  in the watershed surface and sub-surface. These values are similar to the data reported previously by Edgington et al. (1996): ca.  $190 \text{ fCi l}^{-1}$  ( $7 \text{ mBq l}^{-1}$ ) for  $^{238}\text{U}$  content and ca. 2.2 for  $^{234}\text{U}/^{238}\text{U}$  in water samples from the Selenga Delta. High  $^{238}\text{U}$  concentrations and high  $^{234}\text{U}/^{238}\text{U}$  ratios largely reflect the input of U from the Selenga River.

The  $^{238}\text{U}$  contents in bulk sediment samples exhibit a large variation of  $70\text{-}123 \text{ Bq kg}^{-1}$  ( $5.7\text{-}10 \text{ ppm}$ ) with a relatively narrow range from  $36\text{-}56 \text{ Bq kg}^{-1}$  ( $9.5\text{-}14.3 \text{ ppm}$ ) of  $^{232}\text{Th}$ . (Fig. 4). The  $^{232}\text{Th}/^{238}\text{U}$  ratios (ppm/ppm) were within the range of  $1.2\text{-}2.0$  which was lower than typical values of  $3\text{-}4$  for the Earth's crust (Taylor 1964). The  $^{234}\text{U}/^{238}\text{U}$  activity ratios exhibited a marked disequilibrium ranging from  $1.53\text{-}1.84$  with a mean value of  $1.71 \pm 0.07$ , which are greater than unity, demonstrating the presence of some authigenic  $^{238}\text{U}$  in the bulk sediments. There were clearly

oxidized layers, red-brown, within the 0-3 cm upper part of the core. If the diffusion is the dominant transfer mechanism of U from water to the bottom sediment, high  $^{238}\text{U}$  content must be observed at the redox boundary layer (Anderson 1997). However, there is little or no evidence for this mechanism from the  $^{238}\text{U}$  profile. Most of the  $^{238}\text{U}$  found in the sediments may be mainly attributed to the deposition by adsorption and/or adhesion onto the settling particles. Thorium-230 in the core was not in radioequilibrium with its grandparent  $^{234}\text{U}$ . The profile of the  $^{230}\text{Th}/^{238}\text{U}$  ratios is analogous to that of the  $^{232}\text{Th}/^{238}\text{U}$  ratios (Fig. 4). The distribution of  $^{232}\text{Th}$  concentration agrees well with that of the grain size median values for bulk samples (rather than for mineral fractions), while the distribution of the  $^{238}\text{U}$  concentration does not correlate well with that of grain size median values for bulk samples (Fig. 5). Chemical weathering is the most important way to fractionate elements between weathering products and parental bedrocks. Generally, Th tends to be enriched in fine grain size components. The fine-grained sediments have a larger surface area than the coarse-grained one. Hence, the distribution of  $^{232}\text{Th}$  in the sediments may reflect the changes in the sediment compositions of terrestrial materials inflowing into the lake through the rivers (Scott 1968).

### 1.3. Distribution of authigenic and terrigenous U in the sediment core

It is apparent from the  $^{234}\text{U}/^{238}\text{U}$  activity ratios in sediments that the bottom sediments are dominated by authigenic U derived from the lake water and/or rivers. Assuming that the  $^{234}\text{U}/^{238}\text{U}$  activity ratio in the dissolved phase ( $R_w = 2.0$ ) was constant during the period of the last 2 kyr, and taking into consideration that the time after the deposition was negligibly short compared with the half-lives of  $^{238}\text{U}$  ( $4.5 \times 10^6$  kyr) and  $^{234}\text{U}$  ( $2.5 \times 10^2$  kyr), the relative contributions of two different U sources (authigenic and terrigenous U) in sediments can be evaluated from the following mass balance equation:

$$x = (R_S - R_L) / (R_w - R_L) \quad (2)$$

where  $R_S$  is the observed  $^{234}\text{U}/^{238}\text{U}$  activity ratio at any depth in the core,  $R_L$  is the  $^{234}\text{U}/^{238}\text{U}$  activity ratio (1.0) assumed for the terrigenous  $^{238}\text{U}$  fraction, and  $x$  is the ratio of the authigenic  $^{238}\text{U}$  fraction to the observed total  $^{238}\text{U}$  content.

As much as 50-80% of the  $^{238}\text{U}$  in the bulk sediments is not hosted in terrestrial detritus, rather it is authigenic in origin, and its concentration with depth varies over the rather wide range of 40-90  $\text{Bq kg}^{-1}$  (Fig. 6). The above results indicate that even in the terrigenous material-dominated sediments, enrichment of authigenic U is significant. In contrast, the terrigenous  $^{238}\text{U}$  profile, whose concentrations vary within a relatively narrow range of 20-40  $\text{Bq kg}^{-1}$ , shows a quite similar pattern to that of  $^{232}\text{Th}$ . Most of the  $^{238}\text{U}/^{232}\text{Th}$  activity ratios for the terrigenous fraction are around 0.6 ( $0.65 \pm 0.14$  on average), suggesting that weathered materials are dominant and are of the same origin. The mean value ( $0.65 \pm 0.14$ ) is close to the value of  $0.54 \pm 0.05$  observed for interglacial periods found in the sediments from the Academician Ridge (Edgington et al. 1996). Since the terrigenous  $^{238}\text{U}$  concentrations and their  $^{232}\text{Th}/^{238}\text{U}$  activity ratios seem essentially constant for all layers, the distribution of  $^{238}\text{U}$  concentration found in bulk sediments is largely attributable to that of authigenic  $^{238}\text{U}$ .

The obtained distribution of authigenic  $^{238}\text{U}$  does not display any clear correlation with those of sediment components including grain size median. The correlation is particularly poor at 25-40 cm depth, which is dominated by an abundance of mineral contents. Together with increasing content of Bio-Si, the  $^{238}\text{U}$  content may be expected to increase if U is absorbed by diatom frustules from

water. However, the Bio-Si-poor layer between 25 to 40 cm below the sediment surface does not exhibit lower authigenic  $^{238}\text{U}$  values. On the other hand, the relatively high Bio-Si layers around 40 cm depth show high accumulation of authigenic  $^{238}\text{U}$  (Fig. 7). Thus, it is clear that the distribution of authigenic U does not necessarily coincide with that of Bio-Si (%) in the sediments studied. Therefore, adsorption of U by the sediments of the 25-40 cm layer may be either due to direct adsorption on fine-grained materials such as clay minerals or due to binding by organic matter associated with these fine-grained materials.

#### *1.4. Sequential leaching for the speciation of U in the sediments*

In order to achieve a better understanding of the enrichment of authigenic U, sequential leaching for the speciation of U was examined in samples from selected layers of the core (Fig. 8). Although the  $^{238}\text{U}$  in the Bio-Si fraction is the focus of this study, the enrichment of  $^{238}\text{U}$  in the carbonate and Fe-Mn oxyhydroxides fractions is clear. The  $^{238}\text{U}$  contents in carbonate and Fe-Mn oxyhydroxides fractions were ranging from 27-53% and 17-38%, respectively. The  $^{238}\text{U}$  content in organic fraction ranged from 6.2-14%. The Bio-Si fraction showed a very small  $^{238}\text{U}$  content (1- 4%), except for ca. 6% at the surface layer. This result is consistent with the conclusion of Goldberg et al. (1998) drawn from studies on U and other trace elements in bottom sediments of Lake Baikal which were separated into biogenic and clastic components by an aerodynamic method. The  $^{238}\text{U}$  content in the residual fraction ranged from 13-31%. Contrary to the  $^{238}\text{U}$  content, the  $^{234}\text{U}/^{238}\text{U}$  activity ratios for all the carbonates, Fe-Mn oxyhydroxides, organic and Bio-Si fractions show values close to or a little lower than 2.0 which is the value for the lake water. The ratio for the residual fraction is characterized by the radioactive equilibrium value of 1.0 that is typical of the Earth's crust.

The U variations in carbonate plus Fe-Mn oxyhydroxide fractions seem to reflect mainly the distribution of authigenic U amongst the sediment layers. It is well known that U adsorbs onto both inorganic and organic particles from natural waters (cf. Scott 1968; Langmuir 1978; Zhmodik et al. 2003). Previous studies have suggested that since the water in Lake Baikal is unsaturated with respect to calcite (Falkner et al. 1991), the precipitation of carbonate with U by the “within-lake” processes is unlikely to occur (Edgington et al. 1997). In fact, we tried to detect calcite in selected sediment layers of this core by X-ray diffraction analysis, but its presence was not recognized clearly. Therefore, it seems likely that most of the U found in the carbonate fraction is derived from the U adsorbed onto other components of sediments, including loosely bound U to the sediments. The Fe-Mn oxyhydroxides fraction is a less significant sedimentary component, yet the important role played by Fe oxyhydroxides in the adsorption of trace metals, including U, in soils and sediments has been strongly emphasized (Young and Harvey 1992; His and Langmuir 1985). Generally, the Fe and Mn contents in sediments are closely related to organic material and dependent on redox conditions. In fact, the organic-rich sediments including Fe-Mn oxyhydroxides exhibit high accumulation of uranium (Sakaguchi et al. 2004). Kanai et al. (1998) studied the behavior of U by the chemical leaching technique in weathered granitic conglomerate, and showed that the Fe-Mn oxyhydroxides fraction contained relatively large amounts of Fe, Mn, Mg, P, Zn, V and U.

The sediment core studied contains an abundant of terrestrial materials, and large amounts of suspended matter-rich, organic-rich and uranium-rich water come from the Selenga River through the delta. It is probable that a large fraction of the uranium finally deposited into the sediments was already adsorbed onto particles including organic matter and Fe-Mn oxyhydroxides before they

entered the lake. Our previous findings that suspended materials in rivers inflowing into Lake Biwa, central Japan, already adsorbed authigenic U before they entered the lake, support this hypothesis (Sakaguchi 2003). It seems to be reasonable to assume that the distribution of authigenic  $^{238}\text{U}$  in sediments can be mainly accounted for in terms of changes in terrestrial material components, including hydrology, from the Selenga River rather than "within-lake" processes.

## 2. The sediment core of VER98-1-6

### 2.1. Age estimation associated with each depth interval

The both cores, which partially overlapped, were at first combined by matching their Bio-Si content and median bulk grain size records. The distribution of these components in sediments is plotted in Fig. 9. The combined core showed intermittent diatomaceous silt and mineral layers and the distribution of Bio-Si content was counterbalanced by an increase in mineral. The diatom-rich sedimentary layers correspond to the interglacial intervals and the clay-rich layers to the glacial intervals (eg. Qui et al., 1993; Colman et al., 1995; Mackay et al., 1998; Horiuchi et al., 2001; Prokopenko et al., 2001, 2002; Goldberg et al., 2005).

The orbital tuning method has often been used for studies of glacial-interglacial-scale climate records (e.g., Imbrie et al., 1984; Shackleton et al., 1990). This method tunes the climatic signal containing Milankovitch cycles to the solar insolation fluctuation for age determination. We applied orbital tuning method to median bulk grain size fluctuations in core VER98-1-6. The target signal used here was the insolation curve at  $65^\circ\text{N}$  in July (Laskar et al., 1993). To establish a detailed age model, automatic orbital tuning method by using computer program was used (Ochiai and Kashiwaya., 2005), although this correlation does not ensure accuracy of dating of ever interval of the core. This method was based on the Genetic Algorithm (Holland, 1975), which is one of the optimization methods. The advantage of Genetic Algorithm is the ability to search many possible solutions in huge search spaces. The result is also shown in Fig. 10. The sediment core includes the last four interglacial stages covering the last 230 kyr. The sampling site is characterized by low sedimentation rate (ca. 4.32 cm/kyr) and its mean sedimentation rate is in good agreement with previously reported for sediments from the Academician Ridgete (Williams and Jenkins, 1993; Colman et al., 1995; Edgington et al., 1996; Horiuchi et al., 2000; Fagel et al., 2003; Chebikin et al., 2004).

### 2.2. Distribution of U and Th isotopes in the sediment core

The distributions in the concentrations of  $^{238}\text{U}$  and  $^{232}\text{Th}$  and the activity ratios  $^{234}\text{U}/^{238}\text{U}$ ,  $^{230}\text{Th}/^{238}\text{U}$  and  $^{230}\text{Th}/^{232}\text{Th}$  with depth in the core are shown in Fig. 11. The  $^{238}\text{U}$  concentration fluctuates by a factor of 9, ranging from 45.9 to 402.9 mBq/g. Generally, the  $^{238}\text{U}$  concentration displays the higher value during the warm intervals equivalent to MIS 1, 5 and 7, and, in contrast, the lower value during the cold intervals (MIS 4 and 6). The  $^{234}\text{U}/^{238}\text{U}$  ratios ranged from 1.9 at the surface to as low as 1.1, and its distribution is similar to that of  $^{238}\text{U}$  concentrations.

The  $^{238}\text{U}$  concentration in surface layers is considerably higher than that normally observed in the lake sediments (20-50 mBq/g, Sakaguchi 2003) and decreases abruptly by a factor of 3 at a depth of about 0.5 m. From a depth of approximately 2 to 5.5 m, there is a gradual increase in  $^{238}\text{U}$  concentration with a maximum at a depth of 550cm. Extremely high peak of  $^{238}\text{U}$  at the depth of 6 m is observed. Such high concentration of  $^{238}\text{U}$  have been already found for the core from the Academician Ridge by Zhmodik et.al.(1999, 2001, 2003), in which the age of depth observed is

different from our one. After this layer,  $^{238}\text{U}$  concentration abruptly decreases, and reaches a plateau with a low content. Finally, in a depth of approximately 8.5 m to the core bottom, there is a regular increase with two prolonged peaks.

Dissolved  $^{238}\text{U}$  concentrations in the lake water are as high as about 6 mBq/L, and the  $^{234}\text{U}/^{238}\text{U}$  activity ratios exhibit an excess of  $^{234}\text{U}$  relative to  $^{238}\text{U}$  with a distinctly high ratios equal to about 2 (Edgington et al., 1996; Sakaguchi et al., 2006). The high ratios are caused by preferential dissolution of  $^{234}\text{U}$  from mineral grains due to alpha recoil effect. The high  $^{234}\text{U}/^{238}\text{U}$  ratios in the sediments demonstrate the presence of some authigenic  $^{238}\text{U}$  in the bulk sediments. As a whole, the  $^{234}\text{U}/^{238}\text{U}$  ratios are also high during the warm intervals, while is low during the cold. These distributions primarily correlate that of the Bio-Si content.

The  $^{232}\text{Th}$  concentration varies between 37.1 and 107.7 mBq/g, only by a factor of 3. The distribution of  $^{232}\text{Th}$  displays the inverse correlation with that of  $^{238}\text{U}$ . The low  $^{232}\text{Th}$  concentration usually characterizes the diatom-rich intervals during the warm stages. Thorium is usually used as a cold stack based on the correlation with Bio-Si content (Goldberg et al, 2000). The distribution of  $^{232}\text{Th}$  concentration could be interpreted by a combination with the detrital input into the lake from the catchment basin and dilution with the accumulation of Bio-Si. The  $^{230}\text{Th}/^{238}\text{U}$  ratios at the surface layers gradually increase with depth, suggesting that a portion of  $^{230}\text{Th}$ , not initially in sediments, is supplied through decay of excess  $^{234}\text{U}$  and  $^{238}\text{U}$ . The in-growth of  $^{230}\text{Th}$  with depth is also observed from the distribution of  $^{230}\text{Th}/^{232}\text{Th}$  ratios.

### 2.3. Chronology using $^{238}\text{U}$ - $^{234}\text{U}$ and $^{238}\text{U}$ - $^{230}\text{Th}$ (Ionium) methods

Radionuclides in lake sediments may act as indicator of the sedimentation rate of particles on which they adsorbed. Uranium and Th isotopes provide their own internal geochronometers. Dating method established and/or establishing for lake and marine sediment are  $^{210}\text{Pb}$ · $^{137}\text{Cs}$ (present – ca 150 y),  $^{14}\text{C}$ (a few decades – ca. 30 kyr),  $^{10}\text{Be}$ · $^{26}\text{Al}$ (a few hundreds kyr – ca. tens Myr) and paleomagnetic (over a few hundreds kyr) methods, although it is not completely established the detail dating method for Pleistocene (B.P.10 kyr – B.P.1.7 Myr) sediment (Fig. 12). As appropriate dating methods for this age, the use of  $^{234}\text{U}$ - $^{238}\text{U}$  and ionium ( $^{230}\text{Th}$ - $^{238}\text{U}$  or  $^{230}\text{Th}$ - $^{234}\text{U}$ ) methods are proposed. These methods are usually used in the cases of simple composition such as coral and stalagmite, and of assurance for closed system after the burial of uranium from water. However, the applications of these methods to sediment are limited because of the difficulty for authigenic uranium and thorium estimation, and of assurance for closed system of these nuclides within sediment layer after the burial of settling particles from the water column. Edgington et al. estimated the sedimentation rate of core from Academician Ridge by using parameter- $\alpha$  (terrigenous  $^{238}\text{U}/^{232}\text{Th}$ ) with  $^{234}\text{U}$ - $^{238}\text{U}$  and ionium ( $^{230}\text{Th}$ - $^{238}\text{U}$ ) methods. Ku et al.(1984) applied isochrone dating method to sediments with diluted nitrate acid leaching from carbonate-rich lake in China. At any rate, dating in the time interval of about 50 to 1000 kyr BP is of vital importance in Quaternary and environmental geology. In order to obtain an accurate U-series date, authigenic  $^{238}\text{U}$ ,  $^{234}\text{U}$  and  $^{230}\text{Th}$  must be separated from bulk  $^{238}\text{U}$ ,  $^{234}\text{U}$  and  $^{230}\text{Th}$  found in the sediments which contain various amounts of detritus materials.

To apply the  $^{234}\text{U}$ - $^{238}\text{U}$  and  $^{230}\text{Th}$ - $^{238}\text{U}$  methods to the present data, we assumed that  $^{238}\text{U}$  and its progenies,  $^{234}\text{U}$  and  $^{230}\text{Th}$ , were in secular equilibrium for terrigenous materials. The isotope  $^{232}\text{Th}$  was used as a correction index for detrital origin. The  $^{230}\text{Th}/^{232}\text{Th}$  ratio (1.05 on average) found in the surface sediments, which in-growth of  $^{230}\text{Th}$  from adsorbed  $^{234}\text{U}$  seems to be negligibly small,

was further assumed to be retained in terrigenous materials throughout the core studied. The authigenic  $^{238}\text{U}$ ,  $^{234}\text{U}$  and  $^{230}\text{Th}$  concentrations in the sediments were calculated by subtracting the value of 1.05 times  $^{232}\text{Th}$  concentration at the corresponding depth from the  $^{238}\text{U}$ ,  $^{234}\text{U}$  and  $^{230}\text{Th}$  concentrations found at each depth of core.

The results obtained from above equations are shown in Fig. 13. Circle plots give authigenic  $^{234}\text{U}/^{238}\text{U}$  and triangle plots authigenic  $^{230}\text{Th}/^{238}\text{U}$ . Black and white plots are all data and selected data without outlier, respectively. These plots were applied to estimate the sedimentation rate using the following equations:

$$\text{Uranium-uranium method: } ^{234}\text{U}/^{238}\text{U} = 1 + (R_0 - 1) \cdot \exp(-\lambda_{234} \cdot D/S)$$

Ionium method

$$^{230}\text{Th}/^{238}\text{U} = [1 - \exp(-\lambda_{230} \cdot D/S)] + (R_0 - 1) [\lambda_{230}/(\lambda_{230} - \lambda_{234})] \cdot [\exp(-\lambda_{234} \cdot D/S) - \exp(-\lambda_{230} \cdot D/S)]$$

where  $\lambda_4$  and  $\lambda_0$  are decay constants (1/kyr) for  $^{234}\text{U}$  and  $^{230}\text{Th}$ , and D depth (cm) from the surface of the core.  $R_0$  gives the initial value ( $R_0=2.13$ , mean value of surface lake water found) for authigenic  $^{234}\text{U}/^{238}\text{U}$  activity ratio, with the assumption being constant during the dating period. The data from the cold intervals were removed because most of data gave negative ones. The value of the sedimentation rate realizing the best fit of these two equations was calculated using non-linear optimization techniques and estimated to be  $4.47 \pm 0.37$  cm/kyr (Fig. 13). It is very important to note that the obtained sedimentation rate is in good agreement with the mean sedimentation rate (4.32 cm/kyr) from the orbital tuning methods. The calculation indicates strongly that  $^{234}\text{U}/^{238}\text{U}$  ratio in lake water remains nearly constant at least during the warm intervals, although it is speculative during the cold. Further works are needed. Thus, the authigenic and terrigenous  $^{238}\text{U}$ , including  $^{232}\text{Th}$ , in sediments are potential indicators of long-term climate-sensitive processes, especially in catchment hydrology and their isotopes provide their own internal geochronometers.

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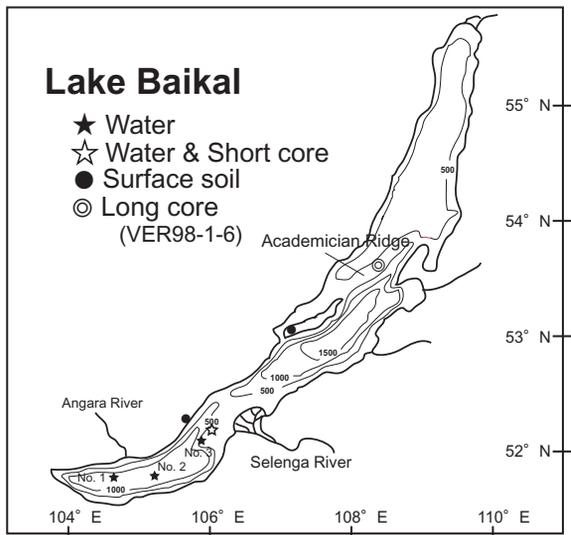


Fig.1. Map showing sampling locations in Lake Baikal.

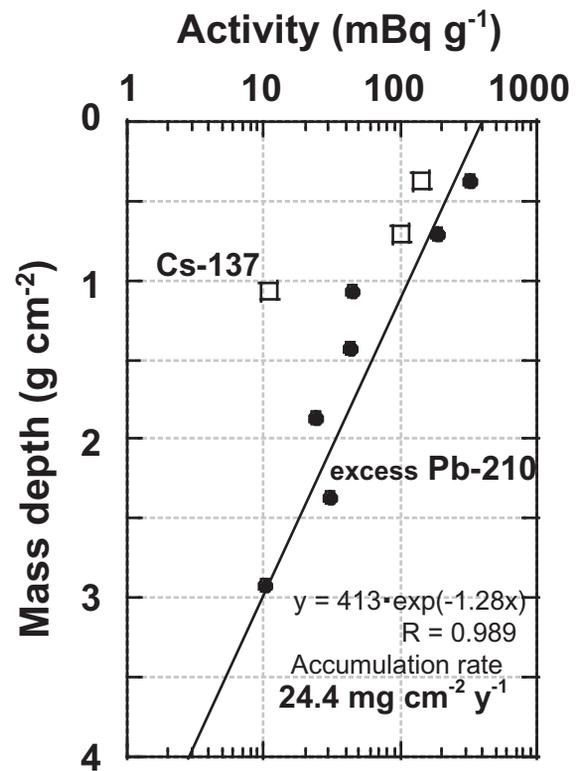


Fig. 3. Sediment accumulation rate in the studied sediment core estimated using excess-<sup>210</sup>Pb method.

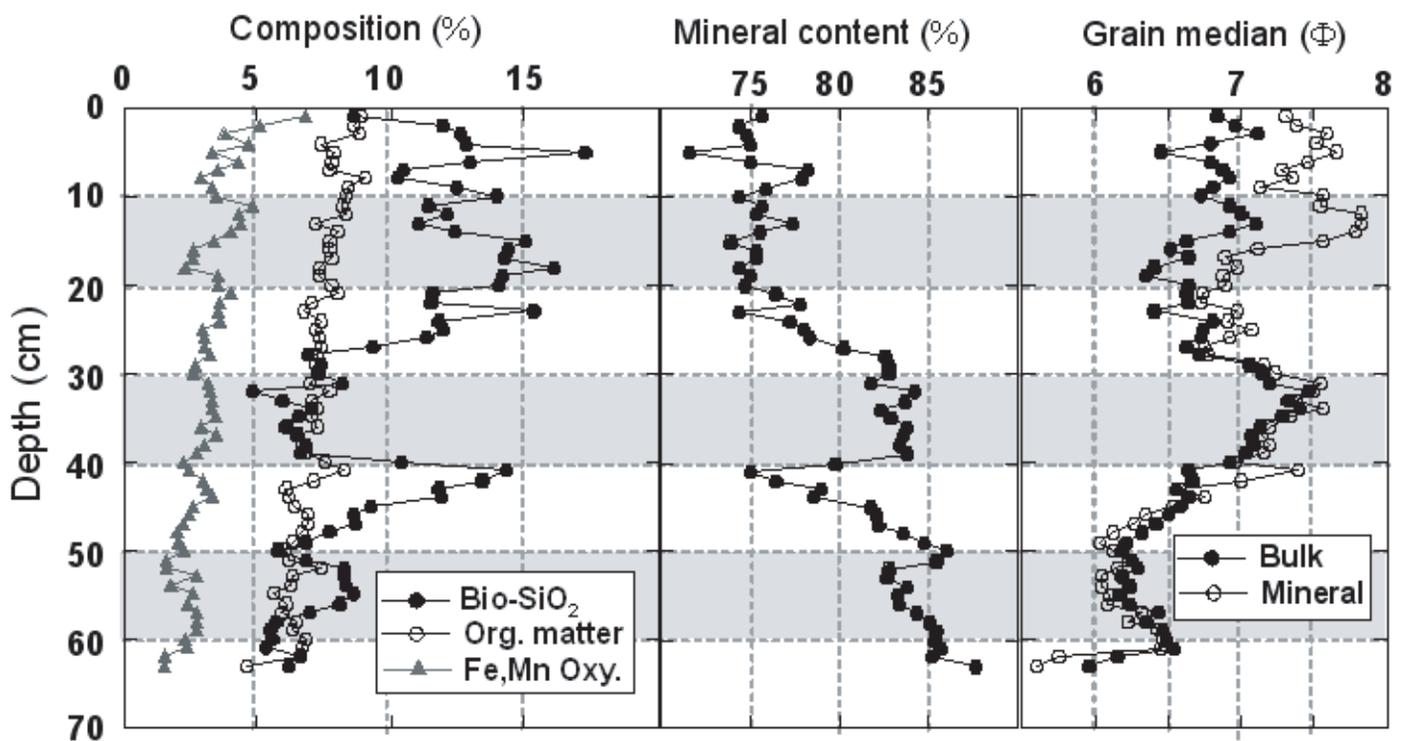


Fig. 2. Sediment composition and grain size median in bulk samples and their mineral fractions in the sediment core.

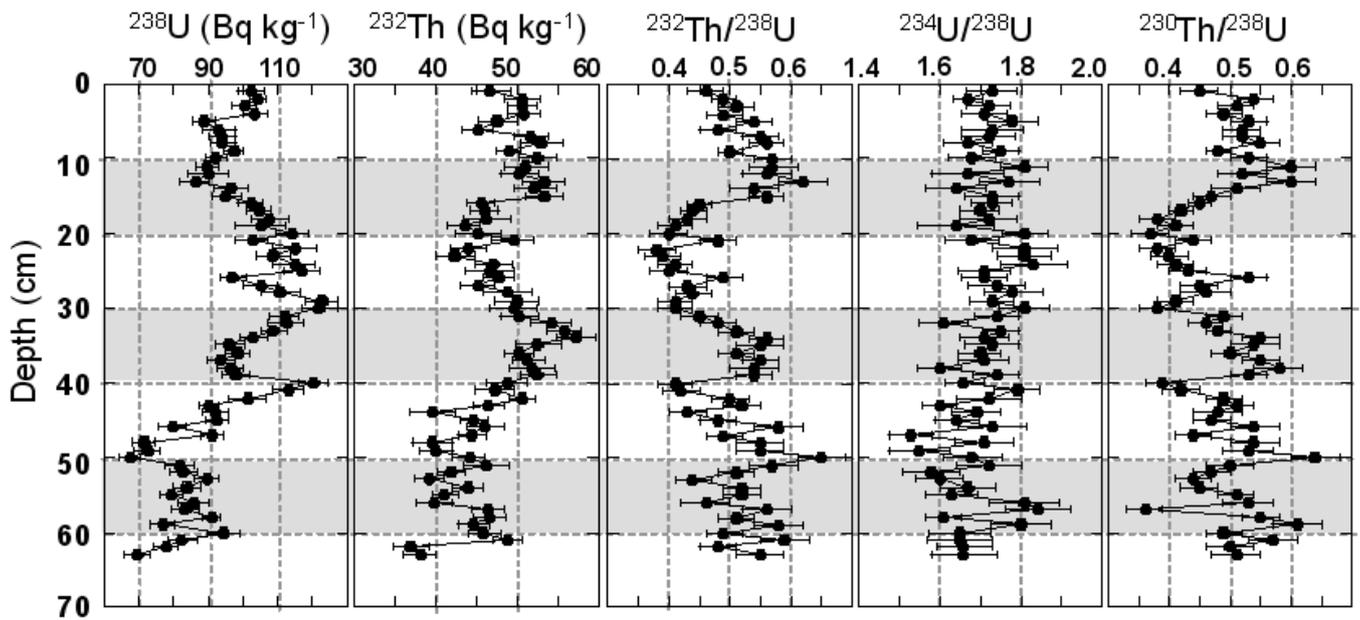


Fig. 4. Distribution of U and Th concentrations and their isotopic ratios in the sediment core.

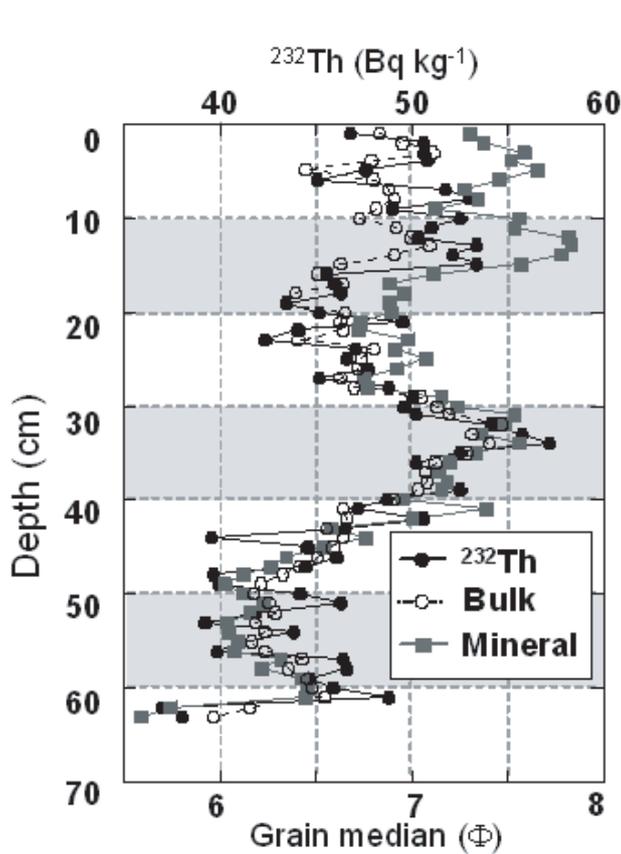


Fig. 5. Comparison of depth distribution between bulk (total)  $^{232}\text{Th}$  and size median (bulk sample and mineral fraction) in the sediment core.

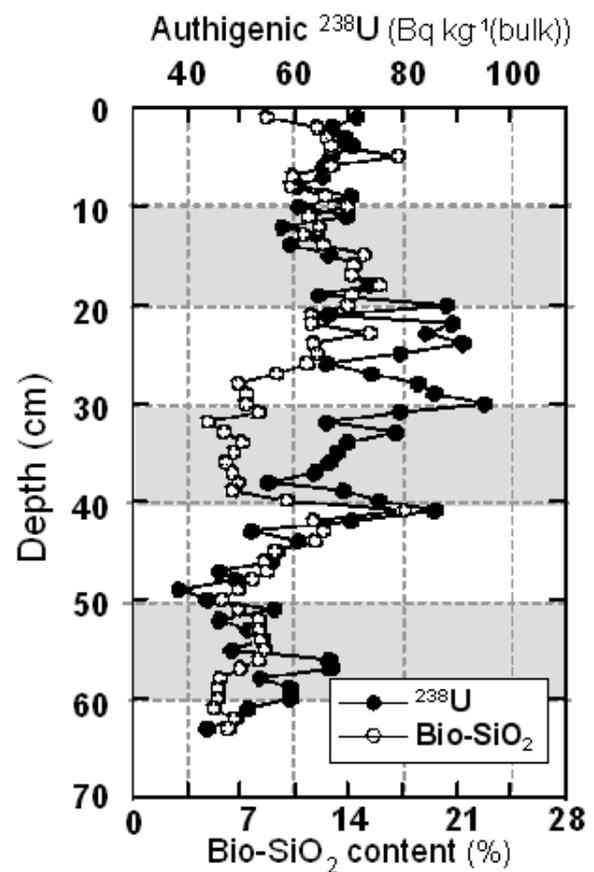


Fig.7. Comparison of depth distribution between authigenic  $^{238}\text{U}$  and Bio-Si contents in the sediment core.

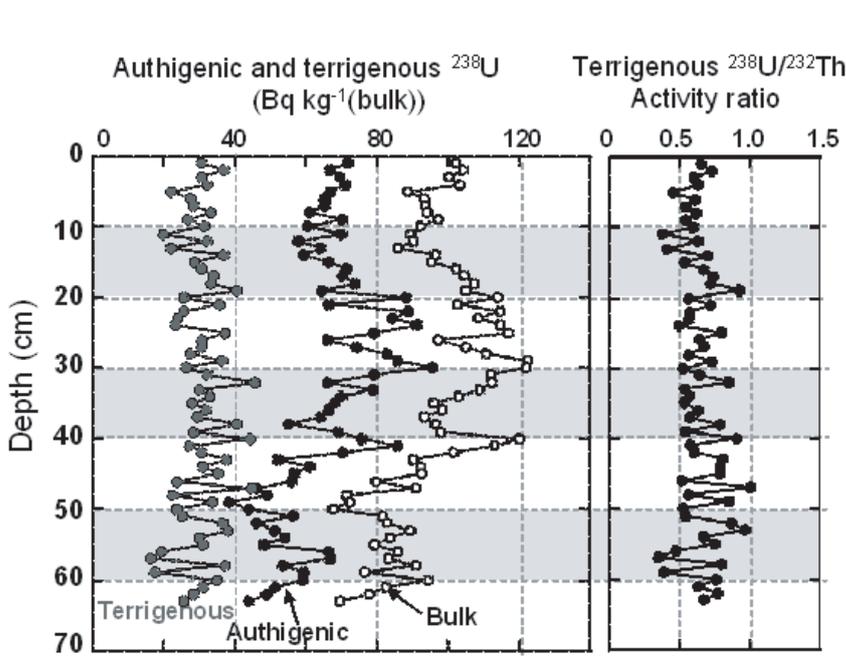


Fig.6. Depth profiles of authigenic, terrigenous and bulk (total)  $^{238}\text{U}$  fractions, and terrigenous  $^{238}\text{U}/^{232}\text{Th}$  activity ratios in the sediment core.

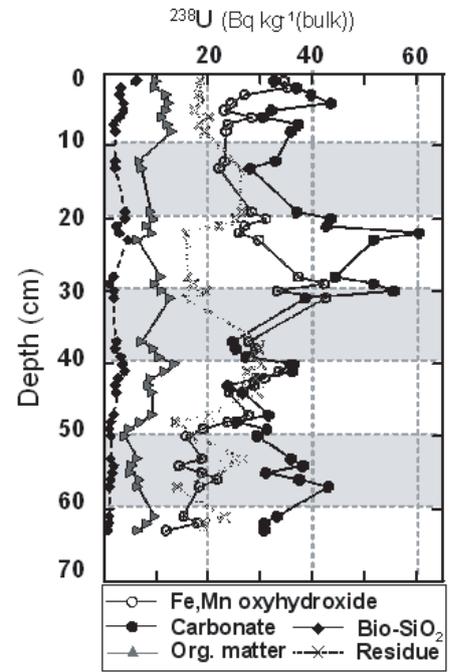


Fig. 8. Distribution of  $^{238}\text{U}$  in various sediment fractions obtained from sequential leaching for selected layers of the sediment core.

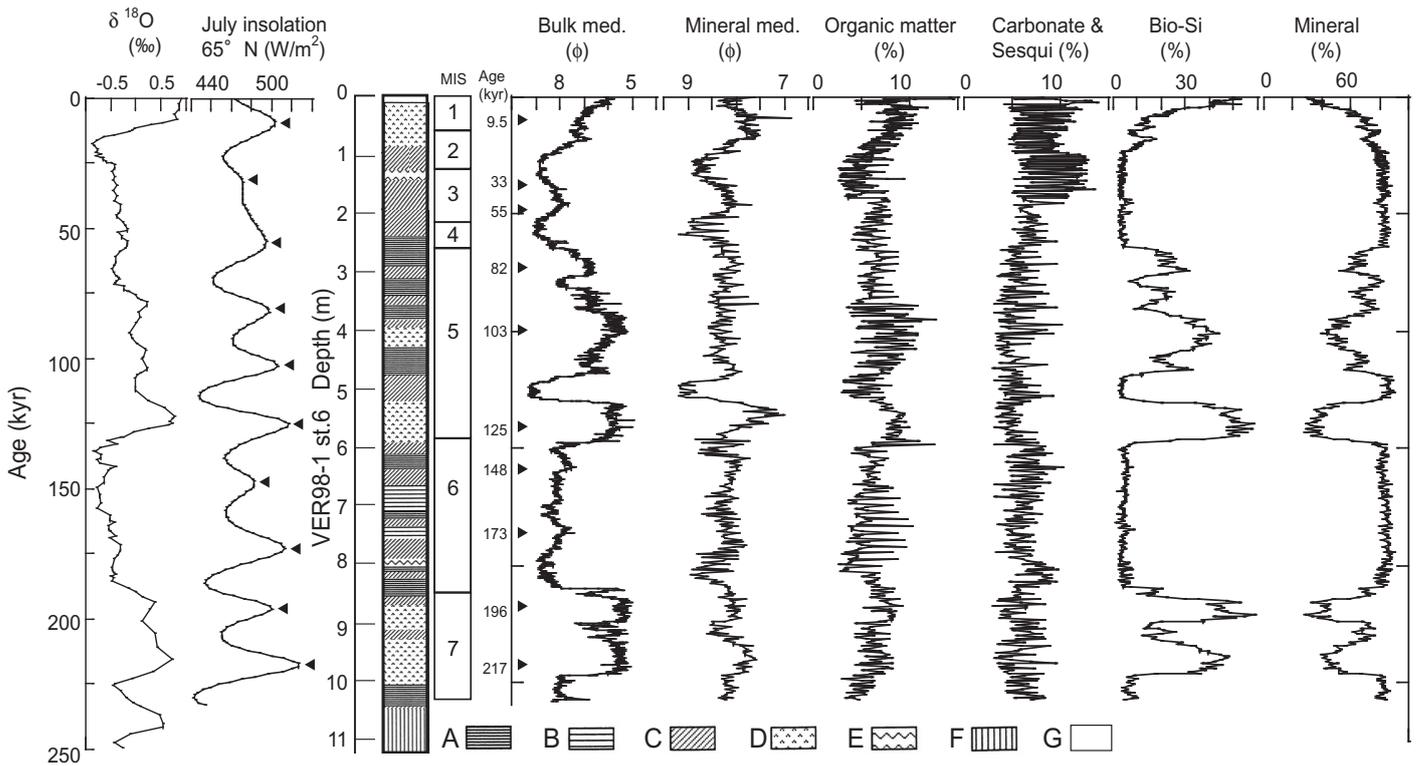


Fig. 9. Depth distributions for sediment composition and grain size median in bulk samples and their mineral fractions in VER98-1-6 core. Automatic orbital tuning method was applied to median bulk grain size fluctuations by using the insolation curve at  $65^\circ\text{N}$  in July (Laskar et al. 1993) as a target signal. Black arrows denote the corresponding peak between insolation curve and grain size as easily understanding. Normalized  $^{18}\text{O}$  record from open ocean sea (Martinson et al. 1989) is also shown for comparison. Marine isotopic stages (MIS) are represented on the side of lithologic cycle description. The symbols for the depth core indicate (A) laminated silty clay, clayey silt, silt, (B) faintly laminated silty clay, silt, (C) massive silty clay, clayey silt, silt, (D) diatomaceous silt, silty clay, (E) deformed sediment, (F) flow-in, (G) water-rich silty clay.

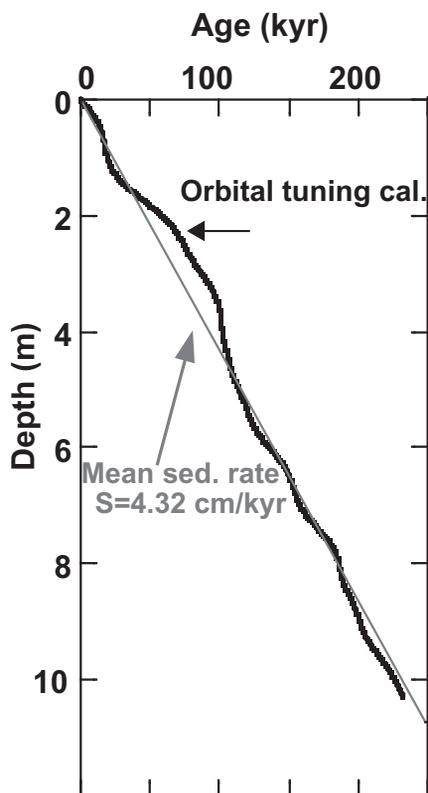


Fig. 10 Result dated by orbital tuning method for VER98-1-6 core.

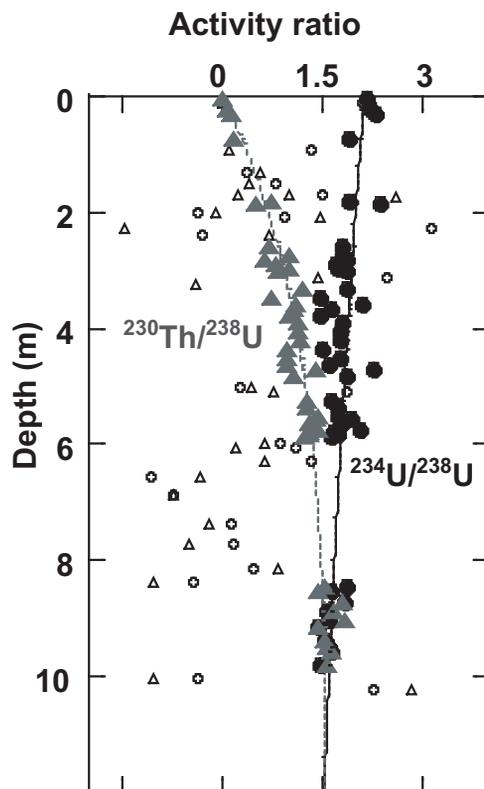


Fig. 13. Depth distributions of authigenic  $^{234}\text{U}/^{238}\text{U}$  and  $^{230}\text{Th}/^{238}\text{U}$  activity ratios in the sediment core. Circle and triangle plots give  $^{234}\text{U}/^{238}\text{U}$  and  $^{230}\text{Th}/^{238}\text{U}$ , and black and white colors mean all data and selected one without glacial period, respectively. By using  $^{234}\text{U}$ - $^{238}\text{U}$  and  $^{230}\text{Th}$ - $^{238}\text{U}$  dating methods, the data except for ones during the cold intervals were fitted using non-linear optimization techniques to obtain the mean sedimentation rate.

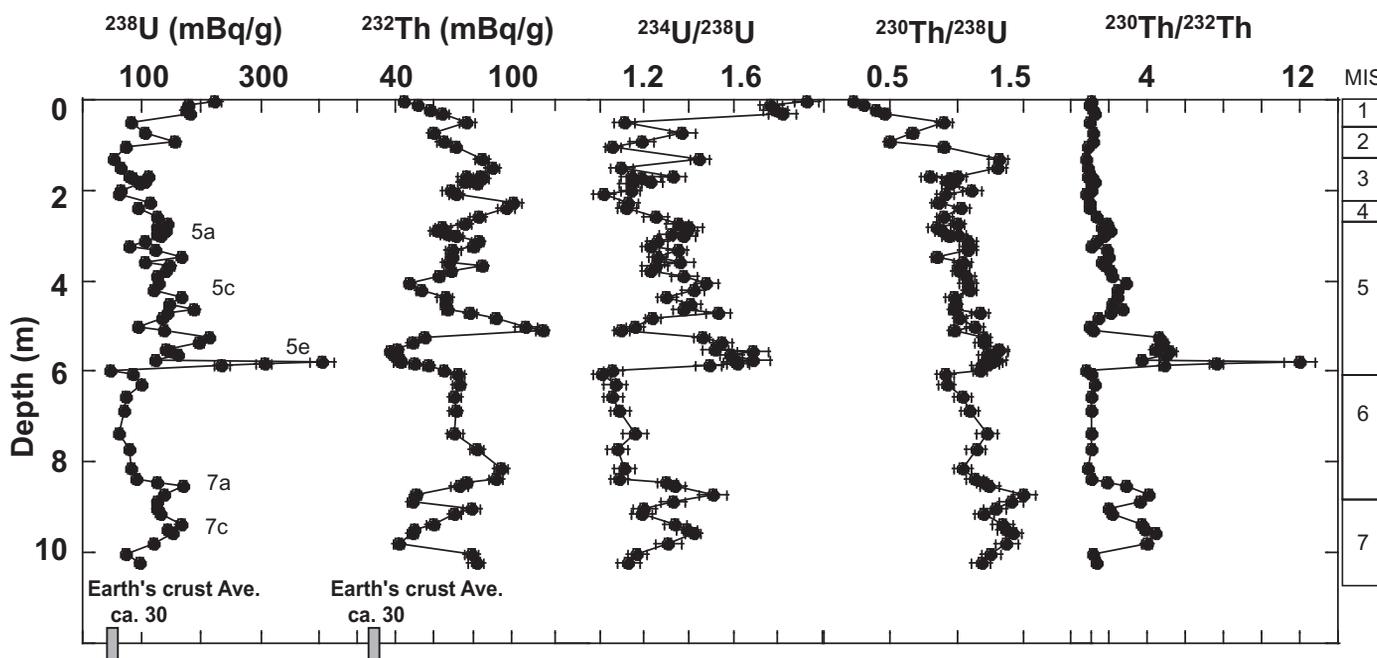


Fig. 11. Distribution of U and Th concentrations and their activity ratios in the sediment core. Earth's crust averages of U and Th were cited from Taylor (1964).

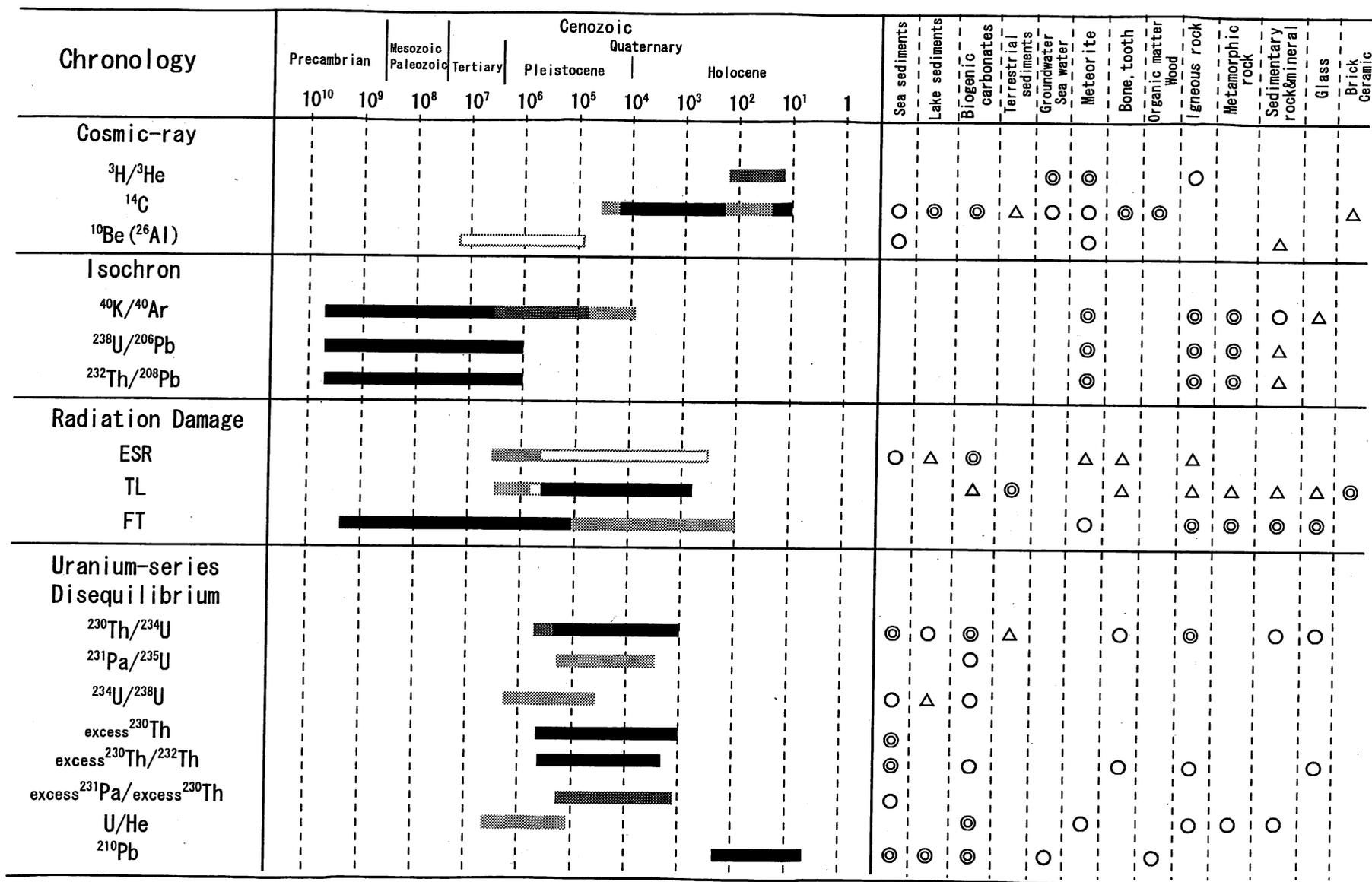


Fig. 12 Chronology using radionuclides or radiation damage.

Table 1. U-238 concentrations and  $^{234}\text{U}/^{238}\text{U}$  activity ratios in surface and bottom water samples from Lake Baikal.

Sampling position	N	E	Depth (m)	$^{238}\text{U}$ (mBq l <sup>-1</sup> )	$^{234}\text{U}/^{238}\text{U}$ activity ratio
No. 1	51 ° 42.020'	104 ° 35.396'	Surface	5.67 ± 0.20	2.01 ± 0.05
	51 ° 42.020'	104 ° 35.396'	1421	6.59 ± 0.33	1.87 ± 0.11
No. 2	51 ° 46.485'	105 ° 17.038'	Surface	6.61 ± 0.21	1.96 ± 0.04
	51 ° 47.817'	105 ° 19.200'	600	6.78 ± 0.15	1.95 ± 0.04
	51 ° 47.817'	105 ° 19.200'	1200	7.19 ± 0.24	1.80 ± 0.07
	51 ° 46.485'	105 ° 17.038'	1489	5.16 ± 0.31	2.20 ± 0.14
No. 3	52 ° 08.466'	105 ° 54.527'	Surface	7.02 ± 0.17	1.92 ± 0.03
	52 ° 08.618'	105 ° 54.934'	392	5.85 ± 0.30	2.16 ± 0.12
No. 4	52 ° 12.035'	105 ° 59.054'	Surface	6.94 ± 0.19	1.92 ± 0.03
	52 ° 12.035'	105 ° 59.054'	116	6.10 ± 0.32	2.13 ± 0.13