論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Clumped-isotope thermometry of natural carbonate: application to high temporal resolution of biogenic and pedogenic carbonates
著者(和文)	ﾜｼﾘｴﾌﾐﾊｲﾙ
Author(English)	MIKHAIL VASILEV
出典(和文)	学位:博士(理学), 学位授与機関:東京工業大学, 報告番号:甲第9262号, 授与年月日:2013年9月25日, 学位の種別:課程博士, 審査員:吉田　尚弘,山中　浩明,中村　恭志,豊田　栄,上野　雄一郎,野尻　幸宏
Citation(English)	Degree:Doctor (Science), Conferring organization: Tokyo Institute of Technology, Report number:甲第9262号, Conferred date:2013/9/25, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

Outlines of doctoral thesis

Clumped-isotope thermometry of natural carbonate: application to high temporal resolution of biogenic and pedogenic carbonates

A DISSERTATION
SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENT FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN SCIENCE

Presented by

Mikhail V. Vasiliev

Department of Environmental Science and Technology

Tokyo Institute of Technology

June, 2014

Abstract

Temperature is a key for understanding of climate changing processes in the history of Earth. Carbonate paleo-thermometry is a novel method, which has been examined in this work, based on "clumped-isotopes" and independent of oxygen isotopic composition in water and sensitive to growth temperature of carbonates. That makes a strong capacity to determine the temperature of local environment at the moment of carbonate formation and interprets the estimation of paleo-hydrology. The content of doctoral thesis covers application of "clumped-isotopes" technique for temperature reconstruction using carbonate materials inhered to different geo-chronological epochs. Here author focused on methodology in order to understand the processes which lead to temperature determination by promoting this research on detailed analysis of shells which have records of climate temperature variation within. Author believes that microanalysis of biogenic type of carbonate materials can be applied for high temporal resolution of season variability in the past.

Chapter 1 followed mainly about the basic steps in paleo-thermometry, its fundamental knowledge, materials and applications. Two methods (^{18}O thermometry and "clumped-isotopes" analysis) were applied and then compared in this work showing its benefits and limitations. In this chapter main historical events with achievements and some questions were established in order to frame the topic and open for further research. Fundamental calibration lines of Δ_{47}-T relationship for wide types of carbonates were performed in this study.

Chapter 2 discusses the technical devises which were used at the time of the study. The main focus is a description of tools for measuring $\delta^{13}C$, $\delta^{18}O$ and δ_{47} for better protocol of Δ_{47} establishment on analytical devices (Gas Chromatograph, Thermo Finnigan Delta^{plus}XP IRMS, Delta XL with coupled Gas Bench II IRMS). Also in the present study (published in the journal "Rapid Communication in Mass Spectrometry" with a title" Precision and long-term stability of clumped-isotope analysis of CO_2 using a small-sector isotope ration mass spectrometer) there were a description of method, technical comparison between the DeltaXP and MAT 253 IRMS for precise measurements on "clumped-isotope", correction of Δ_{47} parameter in absolute frame work, long-term external precision and the correlation between δ_{47} and Δ_{47} for two instruments. It is notable that *Abalone molluska* was analyzed on Kiel IV Carbonate Device coupled with MAT253 for automatically measured $\delta^{18}O$ and $\delta^{13}C$ of a small carbonate samples. Instruction of operating machine was done by adjunct researcher Suzuki Nozomi in the laboratory of Prof.

Saito, Division of Paleo-environment and Paleo-ecology, department of Geology and Paleontology, National Museum of Nature and Science, Tsukuba, Japan.

Chapter 3 relied on an important problem of temperature variability recorded within one single shell of marine or continental biogenic carbonates as one of the informative source of climate changes. High temporal resolution profiles were performed for better understanding of seasonality for *gastropod* marine and terrestrial shells, where it showed clear variability of Δ_{47} signature along the profile compared to a simple bulk temperature reconstruction. The manuscript "High resolution profile of *Euhadra* land-snail's shell as a tool for temperature reconstruction using clumped-isotopes analysis" was submitted to the "*Geochemical Journal*" and now is under review. *Abalone* gastropod sample was applied for reconstruction high temporal resolution profile of δ^{13}C, δ^{18}O, Δ_{47} and estimated calcification temperature and δ^{18}O of seawater. With assumption of δ^{18}O approximately to zero, the excursion peaks on the δ^{18}O carbonate profile were accepted for independent measurements of Δ_{47} signature. It gives us the seasonal temperature variability which was also compared to Kim and O'Neil theoretical temperature estimation and data from observed temperature of surface seawater. Examined *Abalone* species were collected from Oshika Peninsula, Tomarihama bay, Japan. Samples and monitored data of marine surface temperature at very high resolution (data for every 10 min for whole day from 2008 to 2010) were kindly provided from Prof. Nojiry laboratory, National Institute of Environmental Studies, Tsukuba, Japan.

Chapter 4 is mainly devoted to the application of "clumped-isotopes" techniques for paleo-temperature reconstruction using the fossil fragments of biogenic carbonates which were discovered in the cores, drilled from Khubsgul-lake and Dharhad paleo-basin, North Mongolia in order to reconstruct paleo-environment. The Darkhad basin in Northern Mongolia is close to lake Khubsgul and was occupied by a paleo-lake since the maximum of the Late Pleistocene territorially and contains valuable environmental information within a long sedimentary record. The fragments of mollusks from the cores Hodon-1 in Khubsgul lake and Darkhad basin were analyzed to reconstruct climate changes during last 15 ka. It is become possible for estimation of δ^{18}O in both regions where the mollusks exist. Core distribution and field work for Darhad drilling project was organized by Prof. Kawai, Kanazawa University and Dr. Krivonogov, Russian Academy of Science in Novosibirsk and other researchers from Republic of Korea, US. Shell fragments and research work data were provided by Prof. Kawai and Dr. Krivonogov.

Phanerozoic soil carbonates collected from Satpura Basin, central India were analyzed for paleo-temperature reconstruction. Carbonate samples correspond to different time period (290-80 Ma) when Indian Plate was migrated from low latitudes to equator. Novel method was used for soil carbonates during the time of precipitation, reconstruction of possible paleo-latitudinal migration and hydrology of Indian plate with its interpretation of temperature in atmosphere during last 300Ma. Samples were supplied by Dr. Ghosh from the Indian Institute of Science for Δ_{47} signature of Satpura basin formation. At this moment, the manuscript is under preparation.

Chapter.5 summarized the most important achievements and contributions of the doctoral thesis and conclusion to this current moment. Further prospects in carbonate paleo-thermometry were also noted to be done.

Here there were presented mainly establishment and application of this approach as a unique method for paleo-temperature proxy applying for different goals at wide range geo-chronological epochs. Focusing on detailed single sample or bulk measurements of Δ_{47} signature, author gives the information about the local climate changes records or interpretation of temperature variation through the long-term history in Earth. Moreover, determined temperature was applied for estimation of $\delta^{18}O$ for body water or ground water source.

Introduction

Climate change is a hot and discussable topic in the modern life. It is a fact the temperature is a key parameter and its variability on the surface of Earth affect on climate variation. Through the history of our planet climate has been changing for many times, sometimes dramatically dropped to global cooling and again warmed up, forming repeatable cycles. Recently, big impact of global warming has been discussing among scientists and media which affected by human activity in Earth. Locally, it could be clearly seen, although global cycles of temperature variability has been occurring through the whole geological epochs. To solve that question the study on paleo-thermometry has been established to reconstruct the temperature changes and interpret big events which had happened in that epoch.

Basically ^{18}O method of carbonate paleo-thermometer has been used to reconstruct the temperature of environment by analyzing of $\delta^{13}C$ and $\delta^{18}O$ in carbonate materials which had precipitated in the lithosphere. The principal of this method is isotope exchange fractionation between oxygen in carbonate and precipitate water, which equilibration depends on temperature of environment. That linear relationship is a paleo-thermometry proxy for various marine calcitic carbonates and speleothems. Limitations of this tool is providing independent research on determination of $\delta^{18}O$ signature in water where the carbonate grew up what make a problematic to work with a samples from older then a Holocene. It is also known that fractionation factor between water and aragonitic carbonates or terrestrial land-snails differs from calcific form of carbonates (Kim et al., 2007).

Recently new developing method of carbonate paleo-thermometer based on “clumped-isotopes” analysis can solve some problems of climate reconstruction in ancient geological epoch. This new technique can direct reconstruct the calcification temperature at the time of formation without knowledge of $\delta^{18}O$ water and allows estimating the paleo-hydrology situation where the species were formed. Fundamental works on establishment of this method were done by Eiler in his work (2007) defining phenomena of “clumped-isotopes”, description of isotopologues, mechanism of fractionation and application in paleo-thermometry. Ghosh et al., 2006 provided the calibration curve between defined Δ_{47} parameter and temperature of calcification (Ghosh et al, 2006). Theoretical models on effect of acid fractionation during carbonate dissolution by phosphoric acid (Guo et al., 2009), analytical methods, calculation procedure, error propagation and technical limitation (Yoshida et al, 2013; Huntington et al., 2009) were also performed during last 10 years. Studies in atmospheric chemistry were continued by Affek (2008) in atmospheric CO_2 to distinguish sources of respiration and combustion on seasonal and diurnal variation in stratospheric CO_2. Recently there is no one unique calibration curve line for every types of carbonate describing dependency between Δ_{47} of carbonate and its temperature that makes a complication in achieving the accuracy of temperature reconstruction. Numerous studies (Ghosh et.al. 2006, 2007; Guo et al. 2009; Dennis et al, 2010) provide their own calibration curves mostly differ from each other, depending on materials which were applied.

In this research the author focused on establishing and application of “clumped-isotope” technique of inorganic and biogenic carbonates from continental and marine environment from different geo-chronological periods. For the first time, a high resolved study on different parts of an individual land-snail shell was examined to obtain substantial information about current and the past climate. Using clumped-isotope technique, more accurate analysis for temperature variability reconstruction was inducted. Thereby, interpretation of the data obtained from the whole bulk and from specific parts of the shell should be differentiated. In this work, there were demonstrated different sections of a land-snail shell (*Euhadra Quaesita Bradybaenidae*) to obtain high temporal resolution profiles.

Main statements which author put in this doctoral thesis are making the protocol for precise Δ_{47} analysis on Delta^{plus}XL IRMS in comparison to MAT253 IRMS. An absolute reference frame was plotted for standard calibration results. High temporal resolution profile of calcification temperature within a single shell records temperature variability. That information might help for detailed estimation of local climate where the specie lived. Paleo-latitudinal reconstruction of Indian plate was performed during its migration for 200 Ma and atmospheric temperature interpretation from pedogenic carbonates using “clumped-isotopes” techniques.

Author believes that contribution on “clumped-isotopes” analysis will be significant for scientific society. High temporal profile performs periodical fluctuation of temperature which is interpreted as the seasonal variation in the local place where the specie lived. Thus calculation of $\delta^{18}O$ of body water and possible the age estimation of material could be done.

Chapter 1. General introduction and thesis overview

^{18}O method vs “clumped-isotope” technique

The^{18}O method of paleo-thermometry is based on isotope exchange reaction between oxygen in HCO_3^- of carbonate and water where is precipitated. That fractionation achieves equilibration in depending on temperature of environment. Linear relationship is used between temperature and difference between δ^{18}O in carbonate and water for paleo-thermometry proxy. Firstly, the weak point of this approach is dependency from variation of δ^{18}O in water. It is become problematic to use this proxy when the carbonates have age older then Holocene because of complication of independent δ^{18}O estimation in water. Secondary, that linear relationship has been proved for marine and some speleothems carbonates where the δ^{18}O almost has the same value. Terrestrial carbonates, both calcite and aragonite which precipitated in rivers, lakes or in soil have a variable and difficult to determine δ^{18}O in water which depends on many environmental factors.

Recently, a novel method for carbonate paleo-thermometry has been established. The temperature reconstruction clumped-isotopes technique is based on the sensitivity of predominance of ^{13}C-^{18}O bonds in the carbonate minerals with temperature is used to pursue the temperature reconstruction. The Δ_{47} parameter is determined by Eiler, 2007 and defined as:

$$\Delta_{47} = \left[\left(\frac{R_{47}}{R_{47*}} - 1\right) - \left(\frac{R_{46}}{R_{46*}} - 1\right) - \left(\frac{R_{45}}{R_{45*}} - 1\right)\right] \times 1000 \qquad \text{(Eq. 1-1)}$$

where R_{47}, R_{46}, R_{45} – abundances ratios of mass-47, 46 and 45 relative to mass 44 and where R_{47*}, R_{46*}, R_{45*} are corresponding ratios in the sample if it had stochastic distribution and calculated as:

$R_{45*} = R^{13} + 2\,R^{17}$

$R_{46*} = 2\,R^{18} + 2\,R^{13}\,R^{17} + (R^{17})^2$

$R_{47*} = 2\,R^{13}\,R^{18} + 2\,R^{17}\,R^{18} + R^{13}\,(R^{17})$

where R^{13}, R^{17} and R^{18} are the abundances ratios ^{13}C/^{12}C, ^{17}O/^{16}O and ^{18}O/^{16}O of the sample.

To a provide Δ_{47}-T relationship between the clumped isotopes (Δ_{47}) distributed in the calcite minerals and their temperature of calcification, a calibration line of inorganic precipitated carbonate has been already constructed (Ghosh et al. 2006; Ghosh et al. 2007; Thiagarajan et al., 2009; Tripati et al., 2010 Dennis, 2010; Daeron et al., 2011) (Fig 1-1).

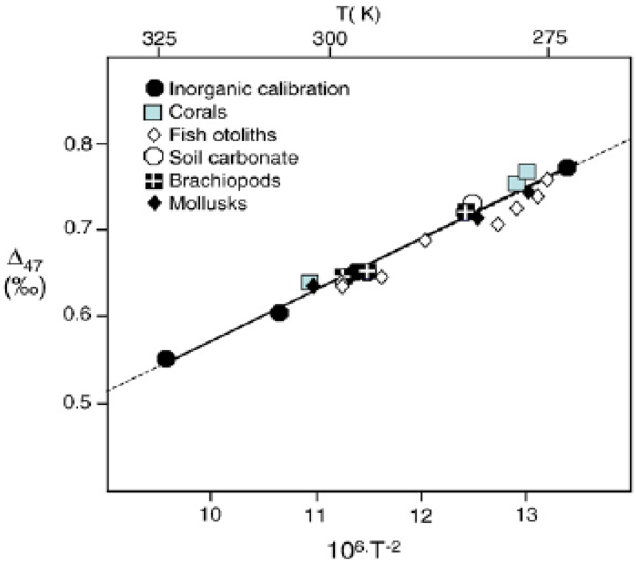

Fig. 1-1 Calcite calibration curve between Δ47 and temperature of precipitated inorganic carbonates at controlled temperature, examined with different types of carbonates (marine and terrestrial mollusks, corals, fish otholiths). Experimental temperature range is from 1 to 50°C (from Eiler, 2007).

Thus “clumped-isotope” technique has a direct approach to determine temperature and independent from variability of $\delta^{18}O$ in water where the carbonate grew up.

This method is still developing and it has some limitations. There is no universal calibration line for between temperature and Δ_{47} (Fig.1-2). These lines were built for inorganic calcite, aragonitic fish otholith, foraminifera and carbonites independently. And reason of discrepancy is not yet solved.

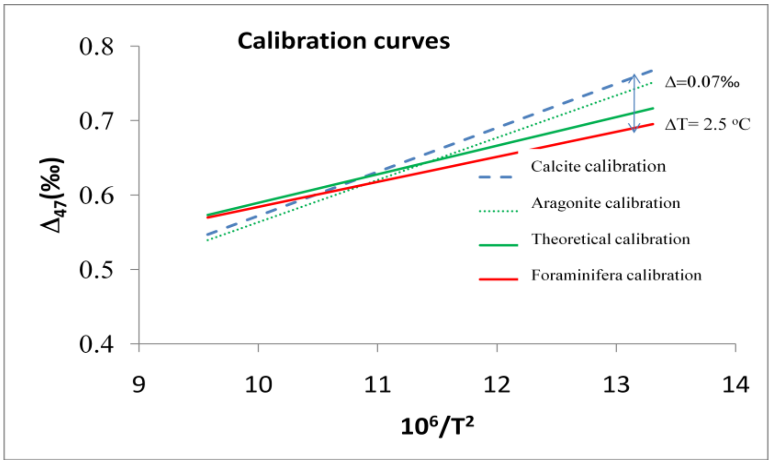

Fig. 1-2 Calibration curves series between Δ47 and temperature for different types of carbonates. Data were taken from published.

One of possible explanation of different slop is vital effect could be affect on aragonitic carbonates or deep sea corals. Vital effect is frequently observed in biogenic carbonates as a result of offsets from the equilibrium of the $\delta^{13}C$ and the $\delta^{18}O$ that lead to increase the Δ_{47} values (Thiagarajan et al., 2011). Numerous works (Ghosh et al., 2006; Thiagarajan et al., 2011) report Δ_{47} enrichment of deep-sea corals due high calcification rate. Other mechanisms of the metabolic process such hydration/ hydroxylation, diffusion and kinetic effect could lead to deviation of Δ_{47} and $\delta^{18}O$ in aragonitic carbonates (Guo et al., 2009). Terrestrial gastropods have a shell structure mainly composed of aragonite which could be altered depending o the environment and life style of the specie (eg. diet) although investigation on that process has not been published yet.

Objectives

Here we performed mainly application of doubly-substituted isotopologues of mass-47 ($^{13}C^{18}O^{16}O$) for reconstruction of temperature calcification of different carbonaceous materials at different locations and time of Earth. This method solves numerous problems for geochemistry interests. High temporal resolution of temperature profiles and temperature average reconstruction will be performed to show the reader benefits and limitation of this method. This ability could be useful for the estimation of $\delta^{18}O$ in water and paleo-hydrology reconstruction.

Two methods were compared with it benefits and limitations. “clumped-isotopes” technique seems have a privilege to apply for its capacity for direct temperature estimation and independent to $\delta^{18}O$ water composition. Despite on it will be beneficial to work with both of approaches in order to have absolute results.

Chapter 2. Tools feasibility to “clumped isotopes” analysis

Routine experiments

To approach successful and scientifically valuable data, high precised technology should be operated for. Three basic steps of sample treatment were used in order to achieve research results: (i) CO_2 production from carbonate material, (ii) purification sample from contaminant, (iii) it is measurements for $\delta^{13}C$, $\delta^{18}O$ and δ_{47} main parameters for Δ_{47} calculation. Depending on analytical device, some procedure may have some minor differences. In above, there were briefly shown the sample treatment work for mass-47 isotopologues analysis on Delta^{plus}XP IRMS.

(i) CO_2 released from carbonate by reaction with anhydrous phosphoric acid was kept in the bath at 25°C for two hours to achieve complete reaction. Note temperature could be change at the reaction time but in that case fractionation factor of $\delta^{18}O$ between reaction product in water and dioxide carbon should be considered. It is common used that the fractionation factor for carbonate material at T=25°C is taken for 1.01.

(ii) CO_2 was attached to the steel pipe evacuation line constructed in Yoshida lab in order for purification from water, oxygen compounds by freezing under liquid nitrogen in the trap. And then released from water, CO_2 with helium flow transported through the line to gas-chromatographer to purified from hydrocarbon components at fixed -10°C.

(iii) Purified sample attached to Delta^{plus}XP IRMS and operate to measure $\delta^{13}C$, $\delta^{18}O$ and δ_{45}, δ_{46}, δ_{47}, δ_{48} and δ_{49} isotopologues of CO_2 in dual inlet mode with standard (reference gas) which determined for $\delta^{13}C$ and $\delta^{18}O$ values. Cycle of analyses, integration time and ion beam intensity on mass-44 were set up on the PC and then he measurements were started.

Heated gas

Δ_{47} parameter calculated from the measured isotope ration mass-47 ($^{13}C^{18}O^{16}O$), mass-46 ($^{12}C^{18}O^{16}O$) and mass-45 ($^{13}C^{16}O^{16}O$) of isotopologues divided on same mass achieved at random stochastic distribution between all isotopologues of CO_2 (Eq.1-1) has linear dependency with temperature of calcification (Fig. 1-1). To achieve that random stochastic distribution, in Yoshida laboratory we heat CO_2 in the oven for 2 hours at temperature 1000°C. After that procedure we repeat our measurement of CO_2 on Delta^{plus}XP IRMS. That difference of calculated Δ_{47}

at temperature of reaction and heated gas is used to apply for a calibration line in order to reconstruct the temperature (Fig.1-1). Heated gas (HG) periodically was analyzed on Delta^{plus} XP mass-spectrometer from 2007 to 2011 and has a value which equal to -1.070‰ with standard error 0.019 (published in Yoshida et al., 2013). Quasi-seasonal variability was discovered for Wako in laboratory standard which routine work was done since 2007 to 2011 with unknown reason (Fig.2-1). One possible explanation is high humidity in the experimental room in summer which may affect on background of analytic machine during its measurement. Therefore combined δ^{18}O in air with analyzed CO_2 give uncertainty at Δ_{47} calculation which requires ratio^{18}O/^{16}O to be known (Eq.1-1).

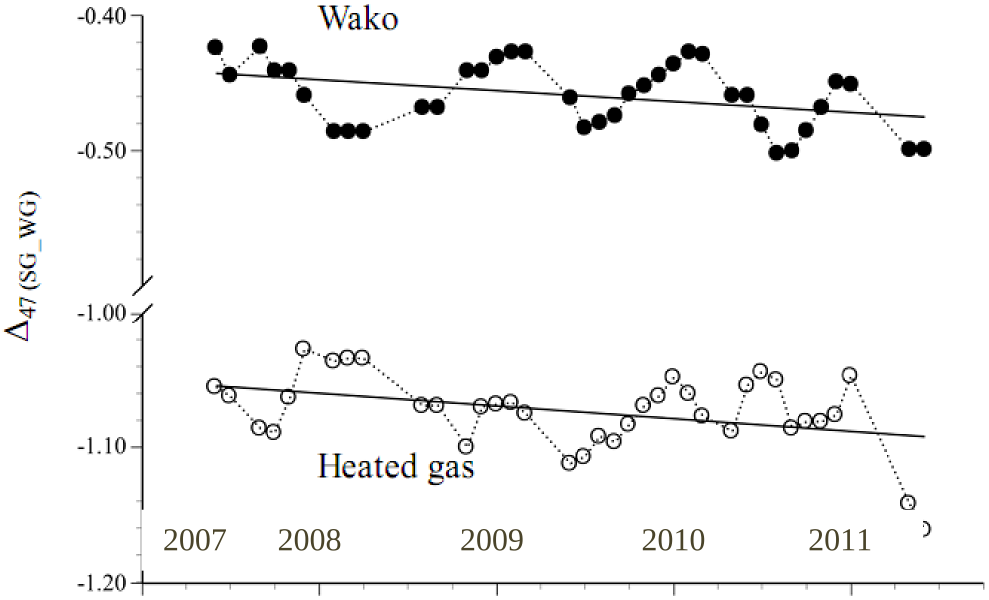

Fig.2-1 Long term stability of Wako (intra-laboratorial) standard measured on Delta^{plus}XP IRMS for calculation Δ_{47} from temperature from and reaction and heated at 1000°C during period from 2007-2011.

Precision of temperature determination

Standard error of calculated Δ_{47} determines accuracy of calcification temperature. Huntington et al. 2009 provided relationship between Δ_{47} standard error and temperature accuracy and showed that at 25°C Δ_{47} standard errors =0.01‰ established 2°C of temperature accuracy. Thus our calculated Δ_{47} values should have a minimum standard error in order for precise temperature reconstruction. What does make uncertainties to have place?

- Amount of sample. Signal beam on mass-44 during program installation shows intensity, which depends on a total amount of analyzed sample, of ions of CO_2 isotopologues transferring from ion source to cups collector. For proper measurements 12V or higher signal intensity should be set up.
- HG long term stability. Heated gas is used for measurements of CO_2 isotopologues which achieved a random stochastic distribution. Long-term variability data of HG from 2007 to 2011 were performed in Yoshida et al., 2013 and shows quasi-seasonal variability through the years (Fig. 2-1).

Correction

As was written above Δ_{47} heated gas uncertainties negatively effect on determined temperature accuracy. To solve that problem “true” line correction were performed (Fig. 2-2). It was formed from published data: (i) calculated value of CO_2 heated gas by Wang et al. 2004 which is equal to 0.0292, (ii) published data of NBS-19 by Dennis et al., 2011 and equal 0.392 and then compared to measurements which were run in Yoshida laboratory for HG and NBS-19 (Yoshida et al., 2013). For the calibration Eq. 2-1 were used:

$$\Delta_{corrected} = \frac{(\Delta measured\_scr + 1)\cdot(\Delta^{*}_{NBS-19\_HG} + 1)\cdot(\Delta_{HG\_WG} + 1)}{(\Delta_{NBS-19\_WG} + 1)} - 1 \qquad \text{(Eq. 2-1)}$$

where the ’measured_SCR’, ’NBS-19_HG’, ’NBS-19_WG’ and’HG_WG’ represent the Δ_{47} value of measured sample with respect to the stochastic distribution, the NBS-19 value with respect to heated CO_2, the NBS-19 value with respect to Oztech reference CO_2 and the heated CO_2 value with respect to Oztech reference CO_2, respectively. Superscript * represents the calibrated Δ_{47} value. It is notable that HG measured compared to calculation HG by Wang et al., 2004 on Delta^{plus}XP IRMS is equal to -1.01 with variability through years. The reason for such specific number for our machine was not yet understood although it would be expected to be closed to zero.

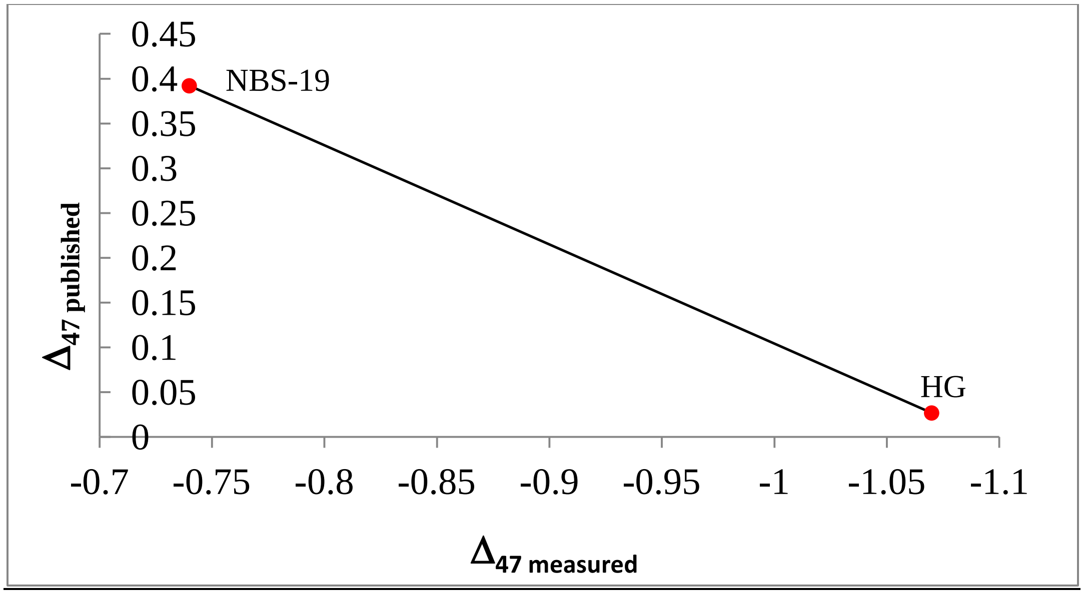

Fig.2-2 Plot of "true" line correction between Δ_{47} published values for HG (heated gas) CO_2 and NBS-19 vs Δ_{47} calculated at temperature of reaction measured on Delta^{plus}XP IRMS where HG is calculated value of heated CO_2 by Wang et al., 2004 (Δ_{47}=0.0292) vs heated CO_2 in Yoshida lab (Δ_{47} = -1.070) and NBS-19 international standard published by Dennis et. al. 2011 (Δ_{47} =0.392) vs NBS-19 analyzed in Yoshida lab. (Δ_{47}= 0.740). *Data from Yoshida lab. were taken from Yoshida et al., 2013.

Comparison of two mass-spectrometers

A striking feature of clumped-isotope analysis using the MAT 253 was a strong δ_{47}-dependency of the Δ47 values (Huntington et al. 2009; Dennis et al.2010). According to the definition of Δ_{47} (Eq. 1-1) and generally wider variation in δ_{45} and δ_{46} values relative to the Δ_{47} value, the δ_{47} value is approximately equal to (δ_{45} + δ_{46}). It is therefore related to the value of ($\delta^{13}C+\delta^{18}O$). The values measured using the MAT253 generally show positive relationships between the δ_{47} and Δ_{47} values. And opposite, that correlation was not discovered for Delta^{plus}XP IRMS (Fig. 2-3). Yoshida et al. 2013 showed comparison data in resolution and sensitivity between two mass-spectrometers and found that it is approximately equal in those parameters for MAT253 and Delta^{plus}XP IRMS. Therefore, daily measurements of the reference material and heated CO_2 gas might be necessary to achieve higher reproducibility when using the Delta XP. Nevertheless, it is advantageous for Delta XP-based analysis that the strong dependence of δ_{47} values on Δ_{47} values commonly found in the MAT 253 were not found in this study.

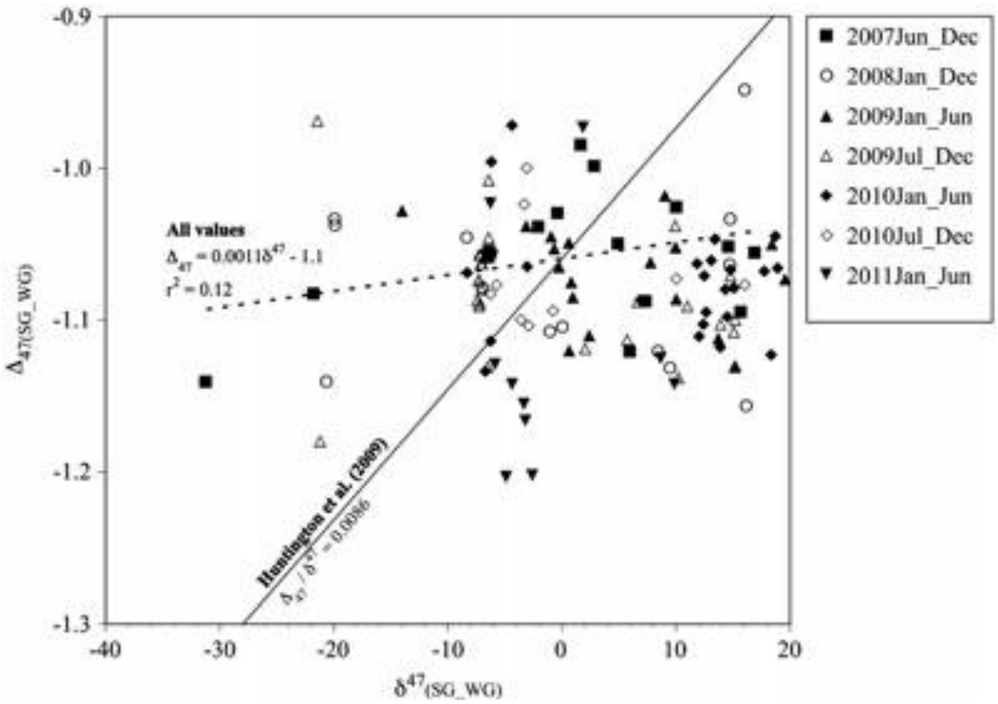

Fig.2-3 Plot of calculated Δ_{47}vs δ_{47} heated gas showing independency in Delta^{plus}XP IRMS with opposite same relationship for MAT253 IRMS (presented by Huntington et al., 2009).

In conclusion of chapter 2 short-term and long-term stability of analyzed Wako in-lab standard were performed on Delta^{plus}XP mass-spectrometer with sensitivity and resolution approximately equal to MAT253 IRMS. It is advantageous for Delta XP-based analysis that the strong dependence of δ_{47} values on Δ_{47} values commonly found in the MAT253 were not found in this study.

Chapter 3. Temperature variability records on marine and terrestrial mollusk's shell

High temporal resolution profiles for terrestrial shells

In this chapter, a high resolved study on different parts of an individual land-snail shell could be useful to obtain substantial information about current and the past climate. Using "clumped-isotopes" technique, more accurate analysis for temperature variability reconstruction can be inducted. Thereby, interpretation of the data obtained from the whole bulk and from specific parts of the shell should be differentiated. In this work, we analyze different sections of a land-snail shell (*Euhadra Quaesita Bradybaenidae*) to obtain high temporal resolution profiles (Fig.3-1). There were evaluated the variability of $\delta^{18}O$, $\delta^{13}C$ and Δ_{47} to reconstruct the calcification temperature throughout the snail's life cycle. The values obtained are discussed along with the isotopes data of meteoric water.

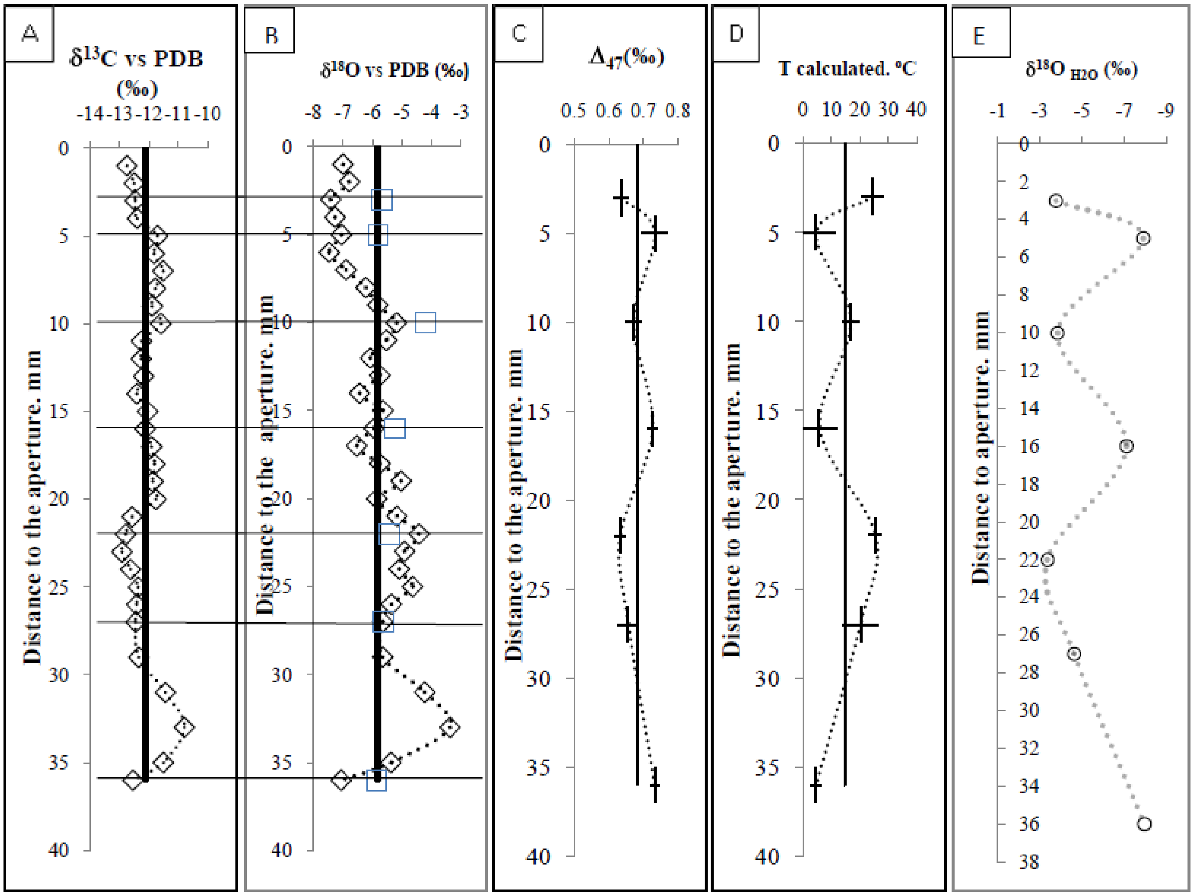

Fig.3-1 High temporal resolution profile of $\delta^{13}C$ (A), $\delta^{18}O$ (B), Δ_{47}(C), calcification temperature (D), and estimated $\delta^{18}O$ body water *Euhadra* land-snail shell among growing from aperture (0 mm of distance) to the apex (36 mm).

The central vertical lines drawn in Fig. 3-1 (A-D) correspond to their respective average meaning. In the case of Fig.3-1 (D), the average temperature, obtained from the high temporal resolution analysis of Δ_{47}, is calculated to be 12±9 ^{o}C and it should correspond to the whole bulk. The deviation of the other points significantly varies through all the shell and they represent the variability of the recorded temperature.

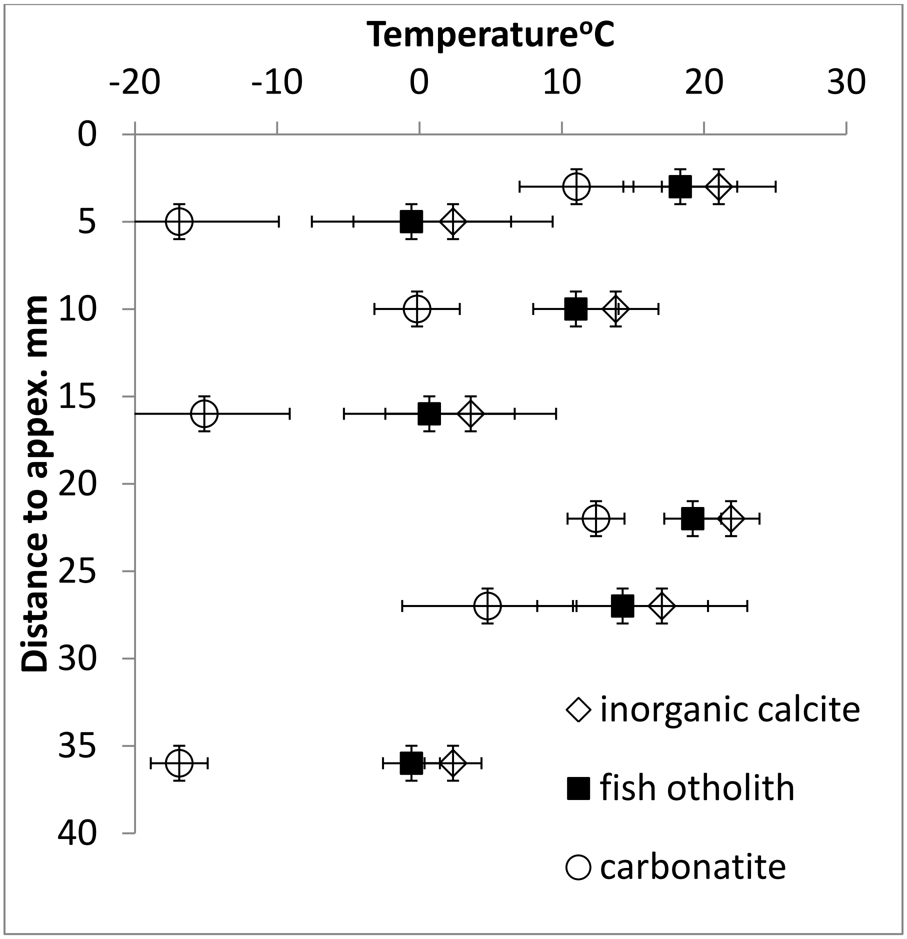

Fig. 3-2 Reconstruction of calcification temperature of Euhadra shell using equations from different calibration lines: for inorganic calcite (Ghosh et al., 2006), fish otholith (Ghosh et al., 2007) and carbonatite (Dennis et al., 2010).

Although disequilibrium during precipitation on δ^{13}C and δ^{18}O has been reported on deep-sea corals (Thiagarajan and et al., 2011), a re-calibrated Δ_{47} signature as a function of temperature reported by Dennis and Scharg (Dennis, 2010, 2011). That discrepancy could be influenced by a kinetic effect at low range of temperatures and lead to significant differences in the calcite calibration curves provided by Ghosh (Ghosh, 2006; 2007) (Fig. 3-2). Curiously, in the case of fish's otolith, the calibration curves seem to fit very well despite a slightly deviation which is probably caused by some uncertainty in the temperature estimation of the fish habitat (Ghosh et al., 2007).

Abalone molluska temperature estimation

Upper part shell of Abalone mollusk was analyzed for high temporal resolution profile in order to establish “clumped-isotopes” technique for seasonal variability records. With assumption to $\delta^{18}O = 0$, temperature of environment was estimates using $\delta^{18}O$ carbonate from fundamental ^{18}O method of paleo-thermometry (Fig. 3-3). Seasonal variability shows four year life cycle for that specie. That was confirmed by researcher who supported that specie. Δ_{47} was analyzed on curve peaks in order to approve estimated temperature. In additional estimated temperature from Fig. 3-3 was compared to obtain surface temperature of ocean where the sample was collected.

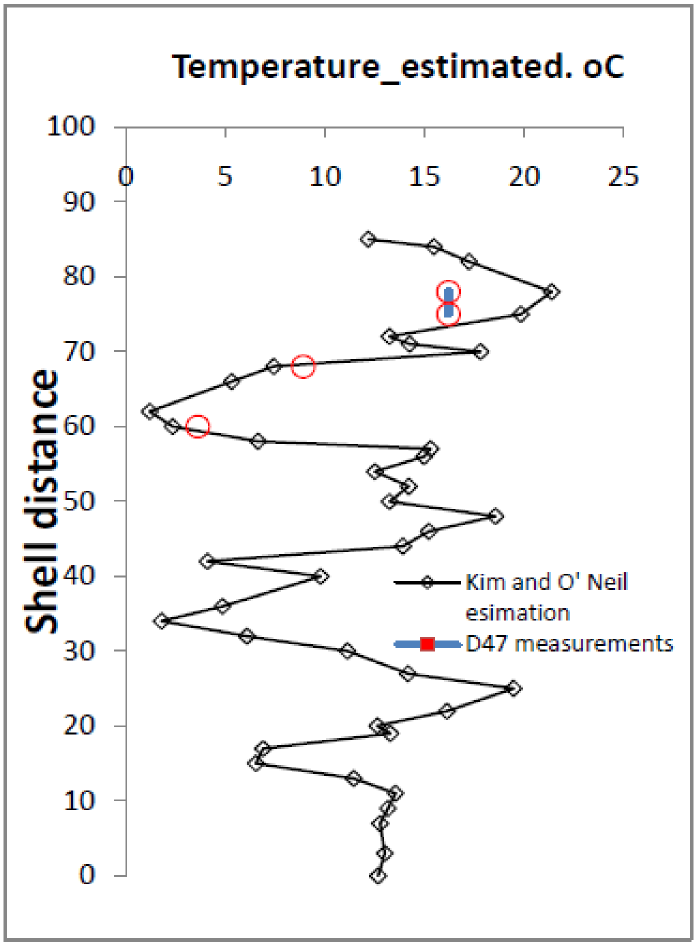

Fig.3-3 Estimated temperature by ^{18}O method of paleo-temperature reconstruction during growth shell of *Abalone* molluska and reconstructed calcification temperature using “clumped-isotope” technique.

In conclusion chapter 4 high temporal resolution profiles of *Euhadra* land-snail's shell and *Abalone mollusks* were performed and the $\delta^{13}C$, $\delta^{18}O$, Δ_{47} and calcification temperature were reconstructed during its life time. For the first time, calcification temperature variations are measured within one single shell. The periodical variation of the temperature is interpreted as the seasonal variation in the local place where the specie lived. The calcification temperatures varied in the range 2^oC to 22 ^oC, which is consistent to the real mean monthly temperature in the Kanagawa Prefecture, Japan. We suggest that high resolution temperature profile calculated from clumped-isotopes is high informative for the reconstruction of the temperature variation recorded in a snail shell. Although the current work requires more measurement for Δ_{47} values, this technique seems promising for temperature reconstruction.

Chapter 4. Paleo-temperature and paleo-hydrology reconstruction at different geological epochs

Darkhad paleo-lake reconstruction

This trip was planned as a part of the International Darhad Drilling Project (DDP) launched in 2010 by four countries: Mongolia, Japan, Korea, and Russia as a continuation of the successful Baikal and Hovsgol Drilling Projects (1990-2000 and 2001-2009, correspondingly). The reason of field work could be described in the main goals obtaining samples for dating key sections of the Darhad paleolake sediments and basalts:

1. Sampling of the Hodon Gol outcrop for ^{14}C and OSL dating.
2. Sampling of the Talyn Nuur outcrop for ^{14}C and OSL dating.
3. Sampling of the Shishhid Gol basalt terrace for Ar/Ar or K/Ar dating.

Core analysis profile was analyzed for climate changes proxy (Fig. 4-1). Shell fragments were discovered from different layers, probably corresponding warmer period for growing of mollusks. Calcification temperature from bulk measurement was reconstructed covers for 12 m core distance corresponding to 15ka.

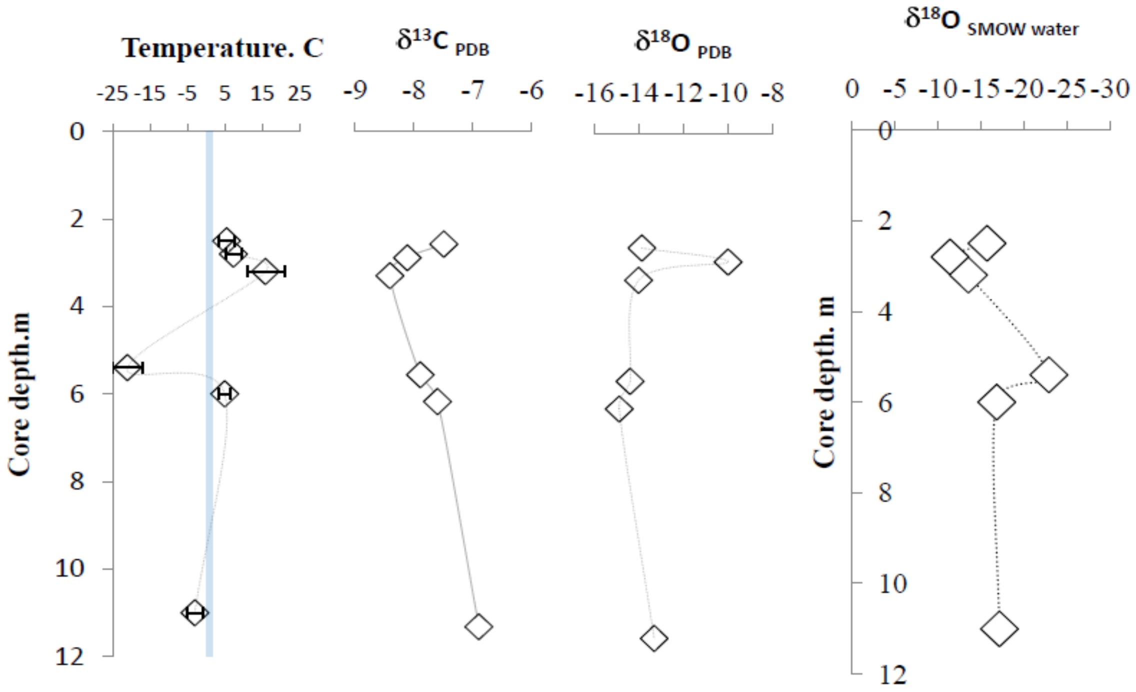

Fig.4-1 Core profile from Darhad paleo-lake of δ^{13}C, δ^{18}O, calcification temperature and estimated paleo-water δ^{18}O.

Paleozoic paleo-climate reconstruction of Indian plate

Indian plate passed different latitudes, and it may tell us the temperature situation during its whole path. Estimated values of $\delta^{18}O$ for each formation during the time traveling of Indian plate were put on the graphic (Fig.4-2) latitude vs $\delta^{18}O$ were the data of rain fall covering all latitude. We assume that $\delta^{18}O$ of rainfall should represent the similar values based paleo-magnitude re-construction. Thus, we can see the movement of Indian plate in this plot from south to equator. The values of Δ_{47} parameter will help us to tell about the temperature of rock formation, also di-genetic imprints and possible paleo-latitudinal reconstruction of Indian plate during Phanerozoic time scale (275 till 80 Ma).

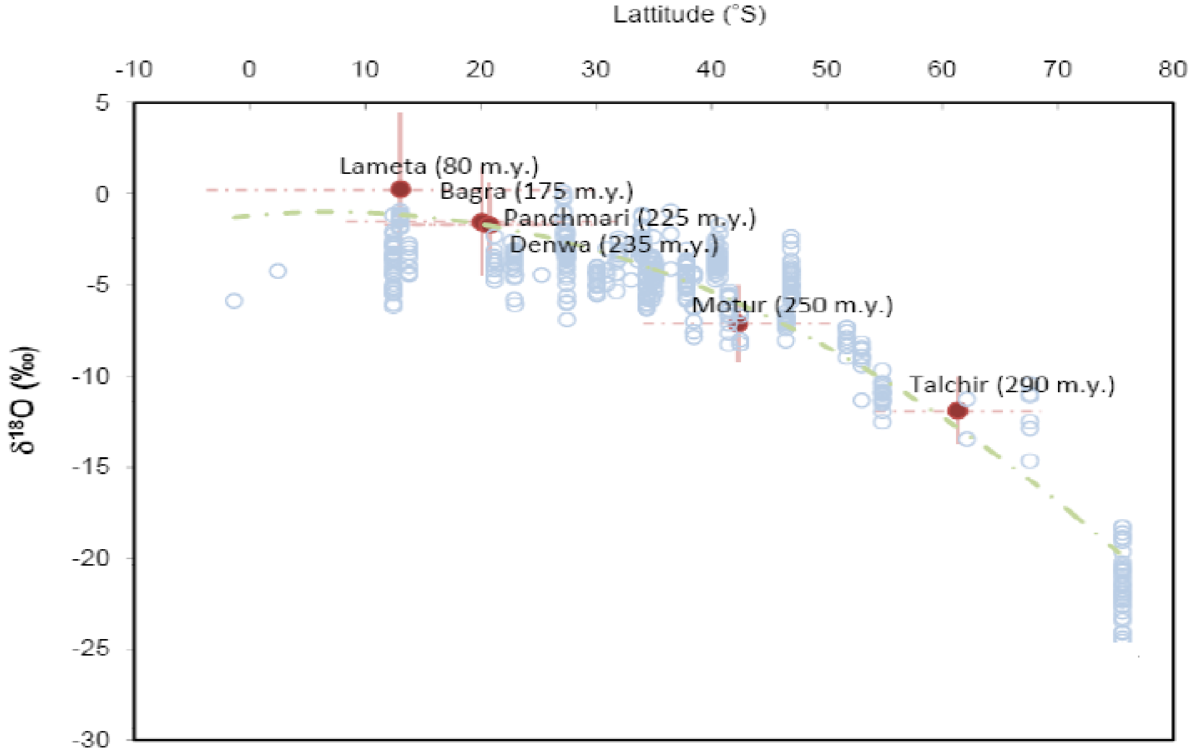

Fig. 4-2 Reconstruction of meteoric $\delta^{18}O$ through paleo-migration of Indian plate from the periods 290 to 80Ma

Chapter 5. Summary and concluding remarks

In this doctoral thesis author presents “clumped-isotopes” techniques which applied for paleo-temperature proxy. For that purpose Δ_{47} signature was calculated from analyzed isotopologues of CO_2. The Δ_{47} calibrates with calcification temperature in a linear relationship where slop is depending on various type of inorganic/ biogenic, marine and terrestrial carbonates. Each line of Δ_{47}-T relationship calibrated for different carbonates independently has an angle slop which insignificant varied at 25^{o}C. Although at lower temperature, near to 1-2^{o}C, angle slop grows larger what lead to temperature uncertainty reaching up to 2.5^{o}C. Currently there is no universal calibration line corresponding to all types of carbonates and it is still open for debate which line is appropriate to use. Although numbered works were published for a new calibration lines for foraminifera, mollusks, carbonatites, deep sea corals.

The protocol of analyzed CO_2 was performed in this study for precise Δ_{47} calculation after measurement on mass-spectrometry. Two instruments Delta^{plus}XP and MAT253 IRMS were examine for optimum condition on operating systems. Both short-term and long-term external precision obtained from replicate analyses of standards on Delta^{plus}XP performed good stability and accuracy, approximately equal to MAT253 IRMS. Nevertheless, it is advantageous for Delta XP-based analysis that the strong dependence of δ_{47} values on Δ_{47} values commonly found in the MAT253 IRMS were not found in this study. It is notable to add that MAT 253 device more expensive than Delta^{plus}XP analog.

High temporal resolution profiles of *Euhadra* land-snail’s shell were performed with δ^{13}C and δ^{18}O and the calcification temperature recorded within one single shell for life time. The periodical variation of the temperature is interpreted as the seasonal variation in the local place. The temperatures varied in the range 5^{o}C to 25 ^{o}C, which is consistent to the real temperature in the Kanagawa prefecture, Japan. The estimated δ^{18}O values of the body water in the shell could be used for hydrological records. Compared to bulk measurements of whole shell high resolution temperature profile calculated from clumped-isotopes is high informative for the reconstruction of the temperature variation recorded in the shell. Although the current work requires more precise measurement for Δ_{47} values, this technique seems promising for temperature reconstruction.

Analysis of pedogenic carbonates taken from Sapura Basin, Central India were done in order to reconstruct calcification temperature and estimated continental water during the time of migration Indian plate from low latitudes to equator allowing paleo-hydrology reconstruction for 200Ma. Determined calcification temperatures which have more than 40 ^{o}C are reasonable to be explained as digenesis which cause re-crystallization in mineral lattice. Metamorphic proceed could be detected by measuring Δ_{47} although it is problematic to determine original temperature of calcification of the material.

Future prospects

It is still unknown to build the universal Δ_{47}-T calibration curve for all types of carbonates. Carbonatites are metamorphic rock containing carbonates with re-crystallized structure in mineral under temperature and pressure and have a different slop compared to original inorganic calcite calibration line (Ghosh et al., 2006). This is calcification temperature which is determined from that line and also corresponds to the temperature of metamorphism. Currently there is no study on different terrestrial carbonate such as precipitated siderite.

High temporal resolution profiles were performed for marine and terrestrial shell. It is clearly showing the temperature variability along the shell growth. But accuracy of sample extraction was not completely satisfied due to small amount of sample which is not good enough to repeat the measurements and hard condition for proper drilling the thin shell in the core. Probably bigger sample like *Acatina* can be used. Nevertheless, author has strong evidence that the high temporal resolution profile is a high informative method to detailed study of climate change for biogenic carbonaceous shell.

Many aspects from doctoral thesis were discussed on international and domestic conferences. Author participated on ISI (International Symposium on Isotopomer) and GSJ (Geochemical Society of Japan) presenting oral and poster presentations. The manuscript “Precision and long-term stability of clumped isotope analysis of CO_2 using a small sector isotope ration mass spectrometer” was published in *Rapid Communication in Mass Spectrometry*, **2013**, 27, 207-215. Recent paper “High temporal resolution profile of *Euhadra* land-snail’s shell as a tool of temperature reconstruction using clumped-isotope analysis.” is submitted to *Geochemical journal* and is under review.

References

[1] Affek, H. P., Bar-Matthews, M., Ayalon, A., Matthews, A. and Eiler, J. M. (2008) Glacial/interglacial temperature variations in Soreq cave speleothems as recorded by 'clumped isotope' thermometry. *Geochim. Cosmochim. Acta.* 72, 5351–5360.

[2] Eiler, J. M. (2007) 'Clumped-isotope' geochemistry – The study of naturally-occurring, multiply-substituted isotopologues. *Earth Planet. Sci. Lett*. 262, 309 – 327.

[3] Daeron, M., Guo, W., Eiler, J., Genty, D., Balmart, D., Boch, R., Drysdale, R., Maire, R., Wainer, K. and Zanchetta, G. (2011) $^{13}C^{18}O$ clumping in speleothems: observations from natural caves and precipitation experiments. *Geochim. Cosmochim. Acta.* 75, 3303–3317.

[4] Dennis, K. J. and Schrag, D.P. (2010) Clumped isotope thermometry of carbonates as an indicator of diagenetic alteration. *Geochim. Cosmochim. Acta.* 74, 4110 – 4122.

[5] Dennis, K. J., Affek, H. P., Passey, B. H., Schrag, D. P. and Eiler. J. M. (2011) Defining an absolute reference frame for 'clumped' isotope studies of CO_2. *Geochim. Cosmochim. Acta*. 75, 7117 – 7131.

[6] Ghosh, P., Adkins, J. , Affek, H., Balta, B., Guo, W., Schauble, E. A., Schrag, D. and Eiler, J. M. (2006) ^{13}C-^{18}O bonds in carbonate minerals: A new kind of paleothermometer. *Geochim. Cosmochim. Acta.* 70, 1439 – 1456.

[7] Ghosh, P., Eiler, J. M., Campana, S. E. and Feeney, R. F. (2007) Calibration of the carbonate 'clumped isotope' paleothermometer for otolith. *Geochim. Cosmochim. Acta.* 71, 2736 – 2744.

[8] Grossman, E. L. and Ku, T.-L. (1986) Oxygen and carbon isotope fractionation in biogenic aragonite: temperature effects, *Chemical Geology (Isotope Geoscience Section)*, 59, 59 – 74.

[9] Guo, W., Mosenfelder, J. L., Goddard III, W. A. and Eiler, J. M. (2009) Isotopic fractionations associated with acid digestion of carbonate minerals: Insights from first-principles theoretical modeling and clumped isotope measurements. *Geochim. Cosmochim. Acta.* 73, 7203 – 7225.

[10] Huntington, K. W., Eiler, J. M., Affek, H.P., Guo, W., Bonifacie, M., Yeung, L. Y., Thiagarajan, N., Passey, B., Tripati, A., Daeron, M. and Came, R. (2009) Methods and limitations of 'clumped' CO_2 isotope (Δ_{47}) analysis by gas-source isotope ratio mass spectrometry. *Journal of Mass Spectrometry*. 44, 1318 – 1329.

[11] Kim, S.-T., Mucci, A. and Taylor, B. E. (2007) Phosphoric acid fractionation factors for calcite and aragonite between 25 and 75 °C: Revisited. *Geochemical Geology*. 246, 135 – 146.

[12] Thiagarajan, N., Adkins, J. and Eiler, J. (2011) Carbonate clumped isotope thermometry of deep sea corals and implications for vital effects. *Geochimica et Cosmochimica Acta*. 75, 4416 – 4425.

[13] Tripati, A. K., Eagle, R. A., Thiagarajan, N., Gagnon, A. C., Bauch, H., Halloran, P. R. and Eiler, J. M. (2010) ^{13}C-^{18}O isotope signatures and „clumped isotope‟ thermometry in foraminifera and coccoliths. *Geochim. Cosmochim. Acta.* 74, 5697–5717.

[14] Wang, Z. G., Schauble, E. A. and Eiler, J. M. (2004) Equilibrium thermodynamics of multiply substituted isotopologues of molecular gases. *Geochim. Cosmochim. Acta*. 68, 4779–4797.

[15] Yoshida, N., Vasiliev, M., Ghosh, P., Abe, O., Yamada, K. and Morimoto, M. (2013) Precision and long-term stability of clumped-isotope analysis of CO_2 using a small-sector isotope ration mass spectrometer. *Rapid Commun. Mass Spectrom.* 27, 207 – 215.

[16] Zaarur, S., Olack, G. and Affek, H. P. (2011) Paleo-environmental implication of clumped isotopes in land snail shells. *Geochimica et Cosmochimica Acta.* 75, 6859 – 6869.