STABLE CARBON AND OXYGEN ISOTOP OF FRESHWATER MOLLUSK FOR SEASONAL AND CLIMATE CHANGE'S INDICATOR

Nur Rohmatin Isnaningsih* **& Simon Troelstra****

ABSTRACT

Fossil shells use to tell what the climate might have been like in the past. Stable isotope value of biogenic carbonate material including mollusk shell has become an important tool to evaluate environmental variable such as temperature, δ18 O and δ 13C. These biologic archives are particularly interesting because shell or skeletal carbonate is often deposited continually over the lifetime of the organism and isotopic compositions recorded in the carbonate can potentially be used to reconstruct past conditions. This information is important and useful to predict seasonal changes in the future. Carbonate samples took from Adult and Embryo Gastropod (Pachychilidae : Tylomelania) and Bivalve (Unionidae). Inner layer shell gastropod was drilled by hand-drill along the ribs. Sections of bivalve shell were mounted on glass slides. Using a computer assisted MERCHANTEK EO – Micromill, sequential samples were milled parallel to growth banding from the shell.Oxygen and carbon isotope was measured using Finnigan Delta mass spectrometer connected with GasBench II and equipped with CTC Combi PAL Autosampler device. The Unionidae oxygen isotopes vary on the range -8,34‰ to -5,59‰ More maximum values among the oxygen isotope exhibit the isotopic composition closer to dry conditions. It can define at least 10 maximum peaks for $\delta^{18}O$ Unionidae. It worse assumed that the Unionidae pass 10 dry seasons equal with 10 years along their life. $\delta^{18}O$ values of adult Tylomelania range from -6,88‰ to -6,21‰ and $\delta^{13}C$ values range for -8,82‰ to -7,65‰. Whereas, embryo $\delta^{18}O$ vary between -7,71‰ to -6,52‰ and $\delta^{13}C$ is about -15,05‰ to -8,49‰. Unfortunately, the $\delta^{18}O$ and $\delta^{13}C$ data from both adult and embryo of Tylomelania were not quite significant. More carbonate sample along their growth line complete with the information regarding their life cycle, nursing care period, and also ecological data was needed to explain $\delta^{18}O$ and $\delta^{13}C$ composition record of the embryo.

Keywords: *Stable isotope, gastropoda, bivalvia, seasonal changes*

INTRODUCTIONS

Stable isotope values have been used to characterize environmental conditions. As knowing on Paleoclimatology, biogenic carbonite use to tell what the climate might have been like in the past. This is done by comparing the biologic archive with their living relatives of today by noting where they live such as in warm or cold, and wet or dry climates. Stable isotope value of biogenic carbonate material has become an important tool to evaluate environmental variable such as temperature, δ18 O and δ 13C (Wurster and Patterson,2001). These biologic archives are particularly interesting because skeletal carbonate is often deposited continually over the lifetime of the

* Museum Zoologicum Bogoriense, Zoology Div-Research Center for Biology, Indonesian Institutes of Sciences. *e-mail ish_naningsih@yahoo.com*

** Department of Paleoclimatology and Geomorphology Faculty of Earth and Live science, Vrije University Amsterdam - Netherland

organism and isotopic compositions recorded in the carbonate can potentially be used to reconstruct past conditions (Shanahan et al, 2005).

Aquatic mollusks which preserved in sea, lakes or rivers sediment are one of potentially important source of paleoenvironmental information (Oswald, 2006). Carbonates in the shell of mollusk provide information on temperature variability in the past.

In this study we present freshwater bivalve and gastropod as proxy for temperature variability. These freshwater mollusks fulfill the prerequisites of environmental archives because they grow by periodic accretion and produce annual and daily growth increment. They also record environmental information during growth as variable increment widths in their shells. Carbon and oxygen isotope ratios in the shells of the freshwater mollusks yield information on the isotopic composition of the water in which the shell was formed, which in turn relates to climatic conditions prevailing during the mollusk's life (Leng et al, 1999). For this reason, bivalve and gastropod may be very useful for climate reconstructions.

MATERIALS AND METHODS

Carbonate Sample Preparations

Carbonate samples took from Adult and Embryo Gastropod (Pachychilidae : *Tylomelania*) and Bivalve (Unionidae and Corbiculidae : *Polymesoda*). Gastropoda was taken from Lake in Sulawesi. Unionidae came from Prambutan River - Central Java, whereas *Polymesoda* was from Pangandaran-West Java. Bivalve samples were taken during the field trip on August 2006.

Inner layer shell gastropod was drilled by hand-drill along the ribs. To avoid carbonate contamination between ribs, tip of the drill was immersed successively in 10 % HCL, water and ethanol.

Sections of bivalve shell were mounted on glass slides ± 1, 9 mm thickness (Fig.1). Using a computer assisted MERCHANTEK EO – Micromill sequential samples were milled parallel to growth banding from the shell. Sampling began at the interior margin of the shell (portion of latest growth) with 20-70 µm milling depth and progressively removed 0,005 mm^3 carbonate each scan. Drill movement through the coordinates provides digitized paths that represent growth features, between which intermediate paths were interpolated. The computer controlled stage moved along sample path as a micro burr mills carbonate parallel to growth banding.

Oxygen and Carbon Isotope Analysis

Oxygen and carbon isotope was measured using Finnigan Delta mass spectrometer connected with GasBench II and equipped with CTC Combi PAL Autosampler device at Mass Spectrometer Laboratory – Vrije Univ. 20 µg sampel were then enclosed in glass tube and the device measured mass/charge ion Helium was flowed toward the glass tube to create homogeny vacuum condition and keep on 90-140 ml/min during 6 minutes per sample. A needle sequentially punctures each glass tube, injecting phosphoric acid into glass tube containing carbonate material. The carbon dioxide that is evolved during acid digestion of the carbonate material enters a side port in the same needle and passes through a water trap prior to mass spectrometer. In the mass spectrometer carbon dioxide was ionized and the positive ions produced were accelerated into a high vacuum which is exposed to electric and magnetic fields. Different types of ion sorted via a detector into a mass spectrum. The mass spectrum consists of peaks of varying intensity to which mass/charge values can be assigned, and from which molecular structure can be deduced. The evolved carbon dioxide is analyzed by comparing its stable isotopic composition to that of reference carbon dioxide repeatedly during 5 samples analysis.

The standar deviation of the measurements for both isotope ratio's was approximately 0,1 ‰. All δ isotope results are reported in permil notation with respect to the V-PDB scale. Several carbonate standards GICS and NBS 18, 19, and 20 were also analyzed between samples.

RESULT AND DISCUSSIONS

Bivalve

The Unionidae oxygen isotopes vary on the range -8,34‰ to -5,59‰ and their seasonal changed can be showed throughout those data (Graphic.1). More maximum values among the oxygen isotope exhibit the isotopic composition closer to dry conditions. In the tropic, there is much water vapour during the dry season brings up the light (^{16}O) isotope. This make the water deplete with light oxygen isotope and enrich with heavy (^{18}O) oxygen isotope which indicated by the high values of $\delta^{18}O$. In contrast, during the rainy season, light oxygen isotope enriches the water together with rain condenses and makes $\delta^{18}O$ decreased. We can define at least 10 maximum peaks for $\delta^{18}O$ Unionidae. It worse assumed that the Unionidae pass 10 dry seasons equal with 10 years along their life.

Unionidae carbonates record trend reveal that $\delta^{18}O$ increasing gradually continued with the rapidly decreasing. This phenomenon is likely in the rainy season water debit in river become abundant very fast bringing a lot of light oxygen isotope. But in a dry season, river become dry slowly that makes the $\delta^{18}O$ increase gradually.

For the *Polymesoda*, the maximum $\delta^{18}O$ values is -2,60 ‰ whereas the minimum values is -6,26 ‰. We find about 6 maximum peaks (Graphic 2) based on $\delta^{18}O$ fluctuation, but we are not sure that it reflected annual seasons. The more likely explanation is that only monthly signal considering that the *Polymesoda* sample still in the juvenile stages. *Polymesoda* living in brachis-water where characterized by salinity level on between freshwater and sea-water. In addition, this area also influence by sea tide. This make *Polymesoda* spends a considerable portion of its life exposed to air transfer to brackish-water in mangrove swamps where salinity fluctuates greatly. Monthly spring tide phenomenon may have contribution to depend carbon oxygen isotope value that record on *Polymesoda* shell.

Several number of carbonate sample took along the growth-line where organic compound accumulate (which characterized by darker line). In fact, generally those accumulations are imposed on higher value of carbon-oxygen isotope. Darker line develops when forming of shell grow very slowly because of certain inhibits factors such as environmental changed. However, this cannot fully explain but it believed related with salinity and spring tide phenomenon also.

Carbon Isotope $\delta^{13}C$ values on both bivalve specimens fluctuate on the range -13,79‰ to -7,67‰. Unionidae have $\delta^{13}C$ vary between -13,79‰ and -7,67‰, while the $\delta^{13}C$ *Polymesoda* is about -12,65‰ to -8,91‰. In the first growing of unionidae, $\delta^{18}O$ and $\delta^{13}C$ values looks unequal, but herein after, both values go equally. For

Polymesoda, $\delta^{18}O$ and $\delta^{13}C$ values seem like concomitant. However, we cannot define whether there are any correlations between $\delta^{18}O$ and $\delta^{13}C$ values.

The $\delta^{13}C$ values have a limitation for explaining temperature and seasonal changed. It likes to perform more on metabolic CO2 composition which effected by physiologist condition and dietary along the animal life. The differences $\delta^{13}C$ values can also reflect the type of a photosynthesize process of a particular plant consumed by this animal (DeNiro and Epstein, 1978).

Gastropod

Tylomelania patriarchalis (fig.2) which belongs to family Pachycilidae is an endemic species in old lakes in Sulawesi. Shell turriform, with 9,8 cm in length and 5 cm in width, often corroded at top. This species characterized by sculpture consisting of axial and spiral ribs with multispiral round operculum. The most noticeable feature of *Tylomelania patriarchalis* together with others species in same genus *is* its nursing care strategy witches retains eggs and embryos in the pallial oviduct. Within the uterine brood pouch the offspring is surrounded by amounts of nutritive material produced by a very large albumin gland and the embryos are produced continuously and hatching complete shelled juveniles. This combination of reproductive features in *Tylomelani*a, characterized by a high amount of maternal investment, is considered to be ovoviviparous, rendering its brooding strategy unique also among other gastropods.

This embryonic shell was also remarkable throughout the isotopic studies. During the nursing care in maternal body, embryo did not have any direct contact with environments of which generates inquisitiveness on what is being carried out by oxygen carbon isotope values of embryo subsequently.

Grafik 3 shows that $\delta^{18}O$ values of adult *Tylomelania* range from -6,88‰ to -6,21‰ and $\delta^{13}C$ values range for -8,82‰ to -7,65‰. Whereas, embryo $\delta^{18}O$ vary between -7,71‰ to -6,52‰ and $\delta^{13}C$ is about -15,05‰ to -8,49‰. Unfortunately, the $\delta^{18}O$ and $\delta^{13}C$ data from both adult and embryo of *Tylomelania* were not quite significant. Moreover, many factors such as the vital effect and ontogenetic factor can also be affective on the isotopic character of the shells. For example, commonly heavy isotope (13C) values of shell structure in juvenile stage having high rate of growth and metabolic activations is frequently recorded (Varol,2004). More carbonate sample along their growth line complete with the information regarding their life cycle, nursing care period, and also ecological data was needed to explain $\delta^{18}O$ and $\delta^{13}C$ composition record of the embryo.

CONCLUSION

The Unionidae oxygen isotopes vary on the range -8,34‰ to -5,59‰ More maximum values among the oxygen isotope exhibit the isotopic composition closer to dry conditions. It can define at least 10 maximum peaks for $\delta^{18}O$ Unionidae. It worse assumed that the Unionidae pass 10 dry seasons equal with 10 years along their life. $\delta^{18}O$ values of adult Tylomelania range from -6,88‰ to -6,21‰ and $\delta^{13}C$ values range for -8,82‰ to -7,65‰. Whereas, embryo $\delta^{18}O$ vary between -7,71‰ to -6,52‰ and $\delta^{13}C$ is about -15,05‰ to -8,49‰. Unfortunately, the $\delta^{18}O$ and $\delta^{13}C$ data from both adult and embryo of Tylomelania were not quite significant. More carbonate sample along their growth line complete with the information regarding their life cycle, nursing care period, and also ecological data was needed to explain $\delta^{18}O$ and $\delta^{13}C$ composition record of the embryo.

ACKNOWLEDMENT

This study was funded by NWO-WOTRO. The authors would like to thank Susan Verdegaal, Emma Versteegh and Martin for their readiness in giving knowledge and information; Lia Auliaherliaty and all staffs at Department of Paleoclimatology and Geomorphology, Faculty of Earth and Live science, Vrije University Netherlands for their help and nice cooperation during this program

REFERENCES

DeNiro M.J. and S. Epstein. 1978. Influence of Diet on the Distribution of Carbon Isotopes in Animals. *Geochemica et Cosmochimica Acta.42,495-506.*

Leng M.J, A.L. Lamb, H.F. Lamb and R.J. Telford. 1999. Palaeoclimatic Implications of Isotopic Data from Modern and Early Holocene Shells of the Freshwater Snail *Melanoides tuberculata*, from Lakes in

the Ethiopian Rift Valley. *Journal of Paleolimnology* **21:** 97–106.

Oswald W.W. 2006. Mollusks in Holocene Lake-sediment Core from the Arctic Foothills of Northern Alaska. *The Nautilus.120(1),30-33.*

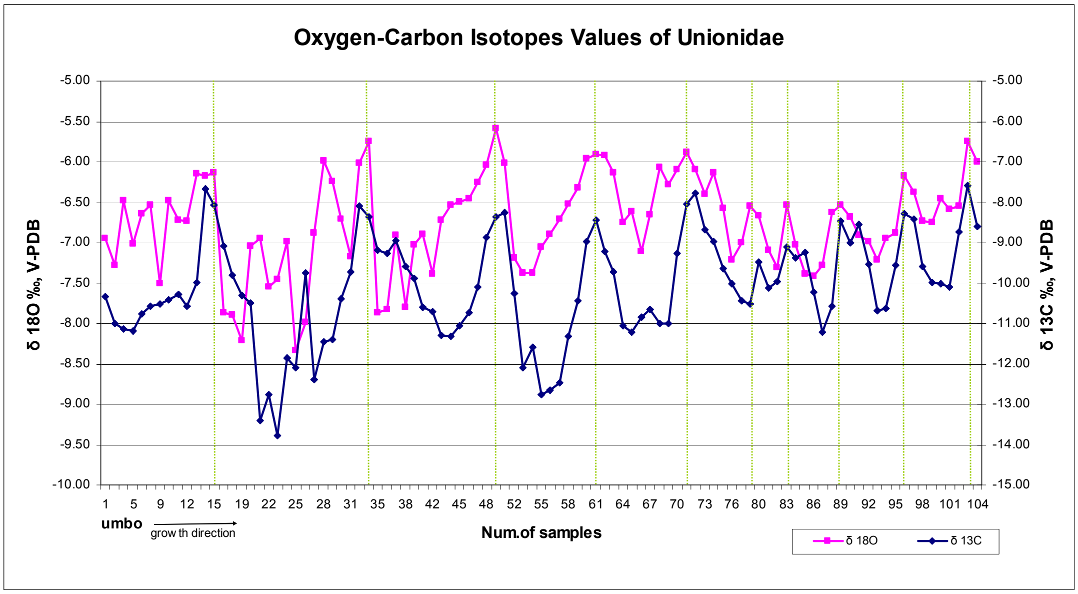
Shanahan T.M, J.S. Pigati, D.L. Dettman, and J.Quade. 2005. Isotopic Variability in the Aragonite Shells of Freshwater Gastropods Living in Spring with Nearly Constant Temperature and Isotopic Composition. *Geochemica et Cosmochimica Acta.69(16),3949-3966.*

Varol B. 2004. Stable Isotopes ($\delta^{18}O$, $\delta^{13}C$) of Mollusk Shells in Environmental Interpretations; an Example from Sinop Miocene Succession (Northern Turkey). Mineral Res Expl. Bull., 128, 49-60.

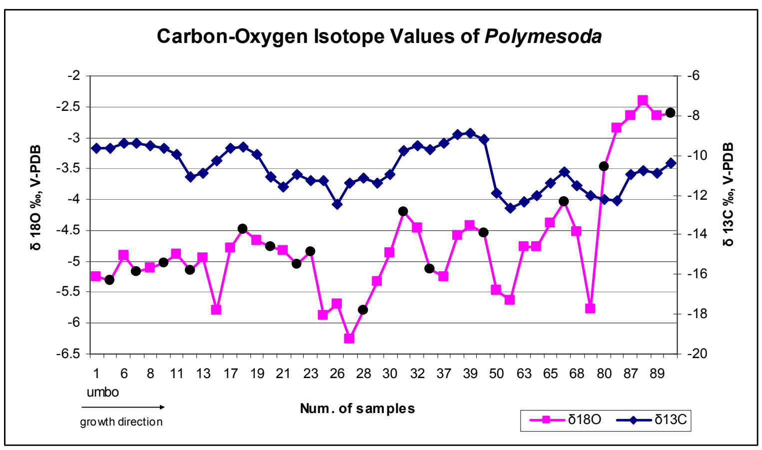
Wurster C.M. and W.P. Patterson. 2003. Seasonal Variation in Stable Oxygen and Carbon Isotope Values Recovered from Modern Lacustrine Freshwater Mollusk : Paleoclimatological Implication for Sub-weekly Temperature Records. *J.Paleolimnol.26(2),205-218.*

APENDIX

Fig 1. Thin section of shell Unionidae (40X) show growth-line in which carbonate sample collected

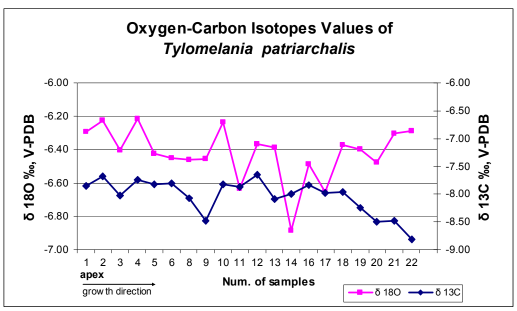


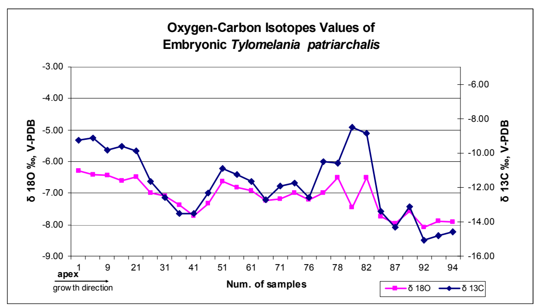
Graphic 1. Carbon-Oxygen Isotope of Unionidae. In the first growing, δ^{18} and $\delta^{13}C$ value looks unequal but herein after, both values go equally.



Graphic 2. Carbon-Oxygen Isotope of *Polymesoda*. Black mark on $\delta^{18}O$ curve indicated accumulation of organic compound

Fig 2. Shell of *Tylomelania patriarchalis* and two embryonic individu





Graphic 3. Carbon-Oxygen Isotope of adult *Tylomelania patriarchalis* (left)
and the embryo (right)