

Review on the Usefulness and Constraints of Paleotemperature Equations for the Late Quaternary Paleoclimatic Studies

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제4기 後期 古氣候復元을 위한 古溫度 方程式의 有用성과 限界성에 관한 考察

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要 約

제4기 후기의 古氣候 研究에 있어서 古環境을 復元하는데 炭酸鹽鑛物을 構成하고 있는 酸素同位元素의 測定은 매우 많이 使用되는 地化學의 方法중의 하나이다. 본 論文에서는 여러 가지 古溫度 方程式들의 特性을 發展성과 有用성에 基礎하여 記述하였다. 또한, 古海洋學과 古氣候學 研究에 있어서 古溫도의 計算이 보다 正確하고 確實하게 提供되기 위한 限界성을 說明하였다.

ABSTRACT

This review gives an information on the oxygen isotopic composition of carbonate and utility of paleotemperature equations to reconstruct the paleoenvironment in the late Quaternary paleoclimatic studies. The introduction of various paleotemperature equations is described with respect to the development and usefulness. In addition, the calculation of paleotemperature in the paleoceanographic and paleoclimatic research is constrained to provide more precise and correct approach in the interpretation of paleotemperature.

INTRODUCTION

The possibility of significant climatic warming of the global environment because of the rapid increase in anthropogenic production of "greenhouse" gases has led to the realization that a better understanding of past climate changes is necessary to determine what is happening and to predict what may happen if warming continues. Paleoclimate records and reconstructions have become a critical facet of climate modeling because accurate predictions require a comparison of present and predicted conditions with analogs from the climatic history.

Recently, the introduction of light stable-isotope mass spectrometer enhanced the paleoclimatic studies using the stable oxygen and carbon isotopes from fossil carbonates in Korea (Woo, 1989; Park and Lee, 1994; Park et al., 1994). Such isotopic studies allow a quantitative assessment of temperature ranges and a comparison with previous paleotemperature estimates (Paik et al., 1992; Woo et al., 1994, 1995a, 1995b; KORDI, 1995). Most of recent works in Korea reported the possible and preliminary calculation of paleotemperatures in various geologic events, however, the more detailed constraints would be necessary for the better interpretation of paleoenvironmental reconstructions.

This article reviews the information of paleotemperature equation with the oxygen isotope ratios (i.e., $^{18}\text{O}/^{16}\text{O}$) from fossil biogenic carbonate in the late Quaternary paleoclimate studies. It focuses on the development of equation and usefulness with

constraints on the precise calculation of paleotemperatures.

DEVELOPMENT OF PALEOTEMPERATURE EQUATIONS

Notation and Equations

By convention, oxygen isotopic composition of carbonate has been expressed in standard permil (‰) δ -notation as the ratio of $^{18}\text{O}/^{16}\text{O}$ in the sample relative to the standard as follow (Craig, 1957).

$$\delta^{18}\text{O} = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{standard}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} \right] \times 1000$$

There has been a developing consensus among carbonate stable isotope studies to explicitly use the V-PDB and V-SMOW nomenclature (vs PDB and SMOW), which has specific meaning in terms of the standards used (NBS-19 and V-SMOW) and the calibration procedure (Coplen, 1994).

All the paleotemperature equations are generally expressed by the form of $T = a + b(\delta^{18}\text{O}_c - \delta^{18}\text{O}_w) + c(\delta^{18}\text{O}_c - \delta^{18}\text{O}_w)^2$, where T is the temperature ($^{\circ}\text{C}$), corresponding to a value of $\delta^{18}\text{O}_c$ for the $\delta^{18}\text{O}$ values of carbonate precipitated from ambient seawater ($\delta^{18}\text{O}_w$) of oxygen isotopic composition (Table 1). Values of $\delta^{18}\text{O}_c$ and $\delta^{18}\text{O}_w$ are given in a PDB system. The isotopic composition reported for water is, in fact, the isotopic composition of CO_2 gas equilibrated with water at 25°C referred to CO_2 liberated by acid decomposition of a standard carbonate at 25°C . Therefore, the PDB values must be cor-

rected by -0.22‰ (Friedman and O'Neil, 1977) to the SMOW scale equivalent, and a similar correction (-0.26‰) was given by Coplen et al. (1983) for V-SMOW scale.

Development of Equations

The theoretical basis for oxygen isotope paleothermometry was pioneered by Urey (1947). He established the thermodynamic properties of isotopes that the distribution of the isotopes ^{16}O and ^{18}O in biogenic carbonate is controlled by the $^{18}\text{O}/^{16}\text{O}$ ratio of the ambient seawater and the temperature at the time of deposition. As the seawater cools, proportionally more ^{18}O is concentrated into the shell carbonate than at higher temperatures. In some cases where disequilibrium isotopic fractionation has been observed, the measured ^{18}O lev-

els (^{18}O) have been lower than equilibrium values, which is generally attributed to "vital effect" involving kinetic fractionation and $\delta^{18}\text{O}$ depletion by various metabolic pathways (for example, for corals, brachiopods etc).

The temperature-dependent fractionation was first empirically determined by McCrea (1950) based on inorganically precipitated calcium carbonate. Table 1 summarizes the various isotope paleotemperature equations available from different studies. Epstein et al. (1951, 1953) developed an empirical paleotemperature equation (the Epstein equation), which is the most widely utilized relationship, based on the isotopic composition of biogenic calcite from living mollusks grown in controlled experiments. Craig (1965) subsequently made a slight

Table 1. Various forms of paleotemperature equations for calcite water and aragonite-water $\delta^{18}\text{O}$ equilibrium.

All the equation has the form of $T = a + b(\delta^{18}\text{O}_c - \delta^{18}\text{O}_w) + c(\delta^{18}\text{O}_c - \delta^{18}\text{O}_w)^2$

Source	a	b	c	material used
McCrea(1950)	16.0	-5.17	0.09	inorganic calcite
Eqstein et al.(1953)	16.5	-4.30	0.14	bivalve(calcite)
Craig(1965)	16.9	-4.20	0.10	bivalve(calcite)
O'Neil et al.(1969)	16.9	-4.38	0.10	inorganic carbonate
Horibe and Oba(1972)	13.85	-4.54	0.04	mollusk(aragonite)
Horibe and Oba(1972)	17.04	-4.34	0.16	mollusk(calcite)
Shackleton(1974)	16.9	-4.0	?	benthic foraminifera
Killingley and Newman(1982)	22.14	-4.37	0.07	barnacle(calcite)
Grossman(1982)	20.19	-4.56	0.19	mollusk(aragonite)
Erez and Luz(1983)	17.0	-4.52	0.03	planktonic foraminifera
Jones et al.(1983)	19.88	-4.00	0.08	mollusk(aragonite)
Grossman and Ku (1986)	20.6	-4.38	0	foraminifera(aragonite)
Grossman and Ku(1986)	21.8	-4.69	0	mollusk(aragonite)
Grossman and Ku(1986)	20.6	-4.34	0	foraminifera and mollusk

modification to the Epstein equation by correcting for a systematic error in the mass spectrometer analyses. Craig (1965) also showed that the paleotemperature equation should be expressed as a quadratic formula based on the theoretical estimation of temperature-dependent fractionation.

A similar paleotemperature equation developed for the planktonic foraminifera *Globigerinoides sacculifer* grown in culture (Erez and Luz, 1983) adds confidence that oxygen isotope equilibrium is attained by some planktonic foraminifer, but is at variance with some field data suggesting disequilibrium. All of the equations are similar enough in slope so that relative temperature changes predicted from downcore data are not significantly different for the various equations. Thus, any of the standard temperature equations yields acceptable results for planktonic foraminifera within the range of 15 to 25°C. In spite of the vast amount of data on stable isotopic compositions in planktonic foraminifera, little attention was given to the fact that the paleotemperature equation was tested.

Questions about validity of the basic equilibrium assumption were first asked when it was found that different benthic foraminifera have different specific isotopic fractionation. Benthic foraminifera, however, grow in the deep sea, where seawater temperature are commonly less than 5°C. The absolute differences in the equations at cold temperatures are large enough that significant errors may occur when the freezing point of seawater is used as a constraint for interpretation of

downcore records. In the case of these conditions the various equations can yield temperature as much as 3°C (Craig, 1965 vs Erez and Luz, 1983) to 5°C in difference (McCrea, 1950 vs Craig, 1965). Shackleton (1974) evaluated paleotemperature equations in this range, using core-top benthic foraminifera with assumption of relatively stable deep-sea temperature and no contamination with glacial-age foraminifera for his samples. Because deep-sea sediments are bioturbated, however, the core-tops used for this analysis contained foraminifera dating from the present to several thousand years old. For more rigorous consideration of temperature effects in benthic foraminifera, further work on the calibration of isotopic temperature equations at low temperatures is necessary.

In an experiment designed to show differences in equilibrium fractionation between the two minerals, aragonite precipitated inorganically at 25°C was determined to be 0.6‰ heavier in ¹⁸O than calcite (Tarutani et al., 1969), which is consistent with the theoretical calculation of a 0.8‰ enrichment. The different fractionation between the two minerals may be attributed to the differences in the vibrational frequencies of the carbonate ions in the dimorphs (Schroder et al., 1962). Thus, the Epstein equation that is specific for calcite mineral is not appropriate for calculating paleotemperatures from aragonite.

Horibe and Oba (1972) developed a paleotemperature relation using a cultured aragonitic mollusk *Anadara broughtoni* and calcite crystal of *Patinopecten*

yessoensis but their results contradicted the previous measurements that aragonite was enriched in ^{18}O . Grossman (1982) and Grossman and Ku (1986) described more systematically the equilibrium oxygen isotope fractionation in aragonite and generated two aragonite paleotemperature equations in a quadratic and a linear forms. The main cause of divergence between the equations is the kinetic fractionation factor (2nd-order term) of the quadratic equation. For studies in temperate and subtropical regions, using either equation is acceptable, as no distinct differences are produced among the expected values. However, in a high-latitude region, a critical uncertainty is the use of the appropriate equation because the published paleotemperature equations were developed from limited data. For example, the lowest temperature represented by the mollusk data of Grossman and Ku (1986) is 4.5°C. Later, Jones et al. (1983) added more isotopic data on the Grossman's (1982) equation to refine the paleotemperature equation. Recently, in general, the linear equation (Grossman and Ku, 1986) has been known to supersede the quadratic equation (Grossman, 1982). Among three relationships (foram data only, mollusk data only, or combined data; Table 1) the combined set is more widely useful because of more data (pers. comm., Ethan Grossman).

USEFULNESS AND CONSTRAINTS OF PALEOTEMPERATURE EQUATION

According to the paleotemperature equa-

tion, the oxygen isotopic composition of biogenic carbonate depends upon both the temperature during precipitation and the oxygen isotopic composition of the ambient seawater. In turn, seawater $\delta^{18}\text{O}$ generally covaries with salinity (Epstein and Mayeda, 1953; Khim and Krantz, 1996) and changes through time with fluctuations in global ice volume (Shackleton and Opdyke, 1973). Emiliani (1955) first measured variations of oxygen isotopes in the planktonic foraminiferal tests from deep-ocean cores and demonstrated quasi-periodic fluctuations of paleotemperature during the Pleistocene. This application would become a valuable tool for marine stratigraphy and lead to the development of paleoceanography as a subdiscipline. Of the measured glacial-interglacial $\delta^{18}\text{O}$ range of about 1.8‰ in Caribbean planktonic foraminifera, Emiliani (1955) attributed about 0.4‰ to the ice-volume effect. This was equivalent to 100 m of sea-level change, assuming glacial ice had a mean $\delta^{18}\text{O}$ of -15 ‰, leaving the bulk of the signal, about 1.4‰, to be explained by glacial/interglacial temperature change, amounting to about 6°C in the Caribbean.

Emphasizing that benthic foraminifera have essentially the same downcore change as planktonic, Shackleton (1967) argued that the ice-volume effect dominated the record and that the temperature played a relatively minor role. He inferred that deep-water temperatures would not have raised more than about 2 to 3°C and that the ice-volume effect changed global seawater $\delta^{18}\text{O}$ values by 1.4 to 1.6‰. Nevertheless, in the forty

years since Emiliani's pioneering work, deep-ocean isotope records have become a keystone in our understanding of the global climate system. In particular, considerable effort has gone into separating from the isotope records the signals of temperature and global ice volume (Mix and Ruddiman, 1984), which relates directly to sea level (Shackleton, 1987). Resulting from glacio-eustatic fluctuations in sea level, oxygen isotopic composition of seawater has been estimated at ca 0.1‰ for every 10-m sea level change.

In Korea, recently, Woo et al. (1995) measured the oxygen isotopic composition of the mollusk shells obtained from the Pleistocene Seoguipo Formation (Cheju Island). They also calculated the paleotemperature, in which two different oxygen isotope values of the Pleistocene seawater were assumed because of nothing on information of Pleistocene seawater. Under these conditions, they reported two sets of paleotemperature data from the oxygen isotope values of shell carbonate. Considering the range of oxygen isotope obtained from mollusk shell carbonate, the difference between two sets of seawater $\delta^{18}\text{O}$ values is comparatively large as much as half the range in the variation of calculated paleotemperatures. Such a relatively big offset seems to result from the lack of information on recent oceanographic environment. Thus, the assumption must be based on the recent environment including any variation happened at that time.

Finally, the underlying complication of paleotemperature calculation in any paleoenvironmental reconstruction employ-

ing the oxygen isotopes is that seawater $\delta^{18}\text{O}$ values cannot be assumed to be constant or even closer to that of today. As mentioned, during the glacial-interglacial cycles of the Quaternary, seawater $\delta^{18}\text{O}$ values varied by as much as 1.6‰ in the extremes. These variations are caused by the preferential removal of isotopically light water (H_2^{16}O) from the ocean to form continental ice sheets, which leaves the oceanic reservoir enriched with H_2^{18}O . Consequently, it is definitely necessary to estimate or constrain as closely as possible the seawater $\delta^{18}\text{O}$ value when interpreting isotope paleotemperatures for a particular period of geological time. At the same time, before reconstructing the paleoenvironment, the recent marine environment must be satisfied to provide any kind of information enough to make assumption in the calculation of paleotemperature.

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