Evaluation of foraminiferal MG/Ca,Sr/Ca and δ18O as paleotemperature and salinity proxies : Comparison of experimental results and measurements in nature

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THESIS

Evaluation of foraminiferal Mg/Ca, Sr/Ca and δ^{18}O as paleotemperature and salinity proxies: Comparison of experimental results and measurements in nature.

有孔虫殻中のMg/Ca比，Sr/Ca比と酸素同位体比を組み合わせた古水温，古塩分指標の評価 ： 飼育実験と野外の比較

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Evaluation of foraminiferal Mg/Ca, Sr/Ca and $\delta^{18}O$ as paleotemperature and salinity proxies: Comparison of experimental results and measurements in nature.

Abstract

Seawater temperature and salinity are fundamental information to represent oceanographic environments. Many proxies have been established which attempted to estimate quantitative paleoenvironmental factors.

Foraminiferal Mg/Ca and Sr/Ca are promising proxies for temperature, because Mg and Sr uptake depend on the ambient temperature during foraminiferal chamber formation. Many studies tried to especially establish quantitative paleo-temperature proxy with these elements with the specimens, grown under natural environments. It is possible for natural specimens to experience biased variation in temperature, salinity and other environmental factors. Hence, it is necessary to compare elemental composition of foraminifera and environmental factors more accurately and directly. The excellent control of environmental parameters of temperature and salinity in culture studies makes it possible to determine precisely the correlation between temperature and uptake of elements.

Oxygen isotopic composition of foraminifera is also related to temperature. However, this relation is difficult to consider as temperature index, because foraminiferal oxygen isotopic composition is also affected by fluctuation of seawater oxygen isotopic composition, which again related to salinity. Conversely, now, oxygen isotopic compositions of water can be estimated from oxygen isotopic composition of foraminifera and combine to form double proxies with temperature estimated from Mg/Ca or Sr/Ca

The purpose of this study is to compare directly the foraminiferal Mg/Ca, Sr/Ca and $\delta^{18}O$ value with temperature, salinity and water $\delta^{18}O$ values through culture experiments. Chemical components of benthic foraminiferal tests such as Mg/Ca, Sr/Ca and $\delta^{18}O$ value both from cultured and natural environments were measured in order to evaluate temperature and salinity proxies for paleoceanographic reconstruction. Five species of shallow water benthic foraminifera, *Ammonia beccarii* forma 1, *Elphidium crispum*, *Rosalina bradyi*, *Planoglabratella opercularis* and *Quinqueloculina yabei*, were cultured under well-controlled temperature (10°C-30°C) and salinity (18‰-40‰) conditions.

All species show linear correlation between Mg/Ca and ambient water temperature, even though temperature sensitivity was different in each species. Salinity did not show significantly influence test Mg/Ca ratio. Although the Sr/Ca of some species changed with temperature, a direct, correlation between Sr/Ca and temperature was not apparently observed. Oxygen isotopic composition of foraminifera indicate clearly linear relation with temperature. Oxygen isotopic composition of ambient seawater changed foraminiferal $\delta^{18}O$ value proportionally. However, foraminiferal oxygen isotopic composition is not affected by quantity of ions (salinity).

Heterogeneous micro-distribution of Mg were observed measured within single chamber, calcified under well-controlled temperature condition with electron probe micro analyser (EMPA). Mg/Ca at outer part of a chamber showed lower value than those of middle or the inner part.

The chemical and oxygen isotopic composition of specimens grown under natural environments were also measured during this study.

Mg/Ca of natural specimens varied in response to sea surface temperature through the year.

Foraminiferal Mg/Ca have positive relationship with measured temperature. However, the foraminiferal Mg/Ca were different from values predicted from experimental relationships. It's possible that the foraminiferal Mg contents may indicate specific ecological character of each species (e.g. growth rates, suitable temperatures, life span).

EPMA measurement revealed that Mg/Ca of chambers have different values within single test. Each camber may have specific Mg content that relates to the ambient temperature during the chamber formation. Mg/Ca ratios of whole chamber is the averaged value of all single chambers.

Sr/Ca ratios of natural population were compared with measured temperature. Sr/Ca of natural population have no clear relationship with measured temperature as culture experiments.

I compared oxygen isotopic composition of foraminifera from natural populations with measured ambient temperature. They indicated weak positive relation with temperature. It is difficult to consider that the $\delta^{18}O$ value of natural population were controlled only by temperature, since $\delta^{18}O$ value of foraminifera will be affected not only by temperature but also $\delta^{18}O$ value of water. Therefore, foraminiferal $\delta^{18}O$ values are not suitable to apply as temperature proxy, although strong relationship between temperature and foraminiferal $\delta^{18}O$ values.

Mg/Ca thermometry was calibrated for five species that were cultured in this study. I tried to apply these temperature equations to natural populations. However, some problems were observed when these temperature proxies were applied to shallow water foraminiferal specimens. The temperatures estimated from foraminiferal Mg/Ca for natural populations differ from the temperatures which observed at the nearest meteorological stations or tidal stations. The calculated temperatures from *P. opercularis* and *Q. yabei* were slightly lower than measured sea surface temperature. In contrast, *R. bradyi* showed higher temperature than measured temperature. The reason for such discrepancy can be attributed to the time integrated Mg/Ca variation of foraminiferal test for natural population during the life span of the specimen. Therefore, foraminiferal Mg/Ca thermometry will lead to the accurate paleotemperature estimation, if ecological information such as growth rate of the species, the timing of chamber formation, life cycle, microhabitat and others, are well understood.

I also established both temperature and salinity double proxies by combining foraminiferal Mg/Ca thermometry and oxygen isotopic composition. These double proxies were applied to natural population. Salinity which calculated from these double proxies were comparable results to observed salinity in natural environments. More accurate salinity can be estimated by the repeated measurements of same size specimens, having similar growth history.

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1. Introduction

Seawater temperature and salinity are fundamental information to represent oceanographic environments. Mathematical computing simulation models of modern oceanic environments are constructed mainly as a function of temperature and salinity. This information could also be available for paleoceanographic reconstruction. Many proxies have been established for estimating the quantitative paleoenvironmental factors.

Transfer functions using population statistics of planktonic species is the one of the classical paleoenvironmental indices (e.g. Imbrie and Kipp, 1971). Transfer function, which proxies for past temperature, salinity and nutrient conditions, is calculated on the basis of planktonic microfossils assemblage. In this method, the relationship between the assemblage and specific environment is calculated statistically on the assumption that the fossil assemblage changed in proportion to one of the specific environmental factors. Many studies have applied this method to reconstruct the Quaternary environments, even though it is essential to identify all the species of fossil. However, there are several problems to apply transfer function to paleoceanographic reconstruction of the Tertiary strata. For instance, there is no proof whether or not extinct species keeps same relationship between environmental variability and populational growth. Selective preservation is also another problem to solve. This is why transfer function has theoretical limit to apply for all geologic age.

The oxygen isotopic compositions of marine biogenic carbonates are in equilibrium with the oxygen isotopic composition of seawater (Urey, 1947). The isotopic composition becomes heavier when ambient water temperature decrease. The relationship between oxygen isotopic composition of biogenic carbonate and ambient temperature were measured for several taxa of mollusks (Epstein *et al.*, 1951, 1953). The correlation between $\delta^{18}O$ of calcitic tests and ambient temperature was calibrated using the following equation:

$$\text{Temperature (°C)} = 16.5 - 4.3(\delta^{18}O_{C} - \delta^{18}O_{w}) + 0.14(\delta^{18}O_{C} - \delta^{18}O_{w})^2$$

where $\delta^{18}O_{C}$ and $\delta^{18}O_{w}$ are the oxygen isotopic compositions of calcite and seawater, respectively. Craig (1965) modified this equation to account for ^{17}O and equipment inaccuracies:

$$\text{Temperature (°C)} = 16.9 - 4.2(\delta^{18}O_{C} - \delta^{18}O_{w}) + 0.13(\delta^{18}O_{C} - \delta^{18}O_{w})^2$$

These equations are consistent with the experimental data on inorganic calcite (McCrea, 1950, O'Neil *et al.,* 1969). Emiliani and Edwards (1953) reconstructed Tertiary ocean bottom temperature variation based on Epstein's equations to benthic foraminiferal tests collected from deep-sea sediment core. However, Emiliani (1955) pointed out these oxygen isotopic variation reflected not only temperature but also the fluctuation of oxygen isotopic ratios of seawater. Therefore, this oxygen isotopic thermometer of biogenic carbonate can apply to the situation when the seawater isotopic values are known. Further, oxygen isotopic composition is also influenced by oxygen isotopic composition of seawater. Seawater oxygen isotopic composition changes in relation to amount of ice-sheet on both polar regions as ^{18}O depleted water concentrates into ice sheet. Therefore, oxygen isotopic values of seawater can fluctuate among glacial-interglacial environmental changes. The local fresh water input from river or rain fall also cause changes in seawater isotopic composition.

Horibe and Oba (1972) found that the proposed the formula so called as Horibe and Oba's formula which represent the relationship between temperature-oxygen isotopic values. Isotopic compositions of calcite and aragonite are differently affected by ambient water temperature and water oxygen isotopic composition as stated above. The experiments were carried out with cultured mollusks of *Anadara brougtoni* (aragonite) and *Patinopecten yesoensis* (calcite). They formulated two quadratic equations for temperature and oxygen isotopic composition for each carbonate species,

for calcite:

$$\text{Temperature (°C)} = 13.85 - 4.54(\delta^{18}O_{calcite} - \delta^{18}O_{water}) + 0.04(\delta^{18}O_{calcite} - \delta^{18}O_{water})^2$$

and for aragonite:

Temperature (°C) = $17.04 - 4.34(\delta^{18}O_{aragonite} - \delta^{18}O_{water}) + 0.16(\delta^{18}O_{aragonite} - \delta^{18}O_{water})^2$.

This scale can be applied to calculate both water oxygen isotopic composition and calcification temperature simultaneously. Horibe and Oba (1972) applied these equations to the fossil *Neptunea arthritica* of late Pleistocene Kioroshi Formation. This species secretes both calcite and aragonite at the same time as molluscan test consists of two layers. The results indicate that the fossil shell precipitated at 9 °C and a water oxygen isotopic composition of –1.45‰ (SMOW). However, only few works applied this method, although this is very sophisticated method. One of the reason is that this method can be adopted to the test which precipitate both calcite and aragonite shells simultaneously under isotopic equilibrium. Only few marine invertebrates are known to precipitate both calcite and aragonite in an individual hard tissue.

Oxygen isotopic thermometer of biogenic carbonate needs accurate seawater isotopic values to reconstruct paleotemperature. Conversely, water oxygen isotopic compositions can be estimated from oxygen isotopic composition of biogenic carbonate, if calcification temperature is known. The calcification temperature can be calculated from the temperature proxy which is independent from other environmental factors.

U^k_{37} alkenone thermometer can be used as another independent temperature index. The alkenones are a product of coccolithophorid cells. There are diunsaturated and triunsaturated alkenones among alkenone groups. The [c37:2-c37:3] ratio has empirically linear relationship with temperature (Brassel *et al.*, 1986). U^k_{37} alkenone thermometer can be used to calculate sea surface temperature. Coccolithophorids calcify very small (~1μm) coccolith made of calcite. If the cocolith of single species can divide from sediments, the oxygen isotopic composition of seawater can be calculated with the alkenone thermometer and oxygen isotopic composition of cocolith. However, cocolith is too small to extract from sediments at this moment. Oxygen isotopic composition of calcareous materials can measure with other biogenic carbonates (e.g. planktonic foraminiferal tests). However, other biogenic carbonates should carry problems of differences due to seasonal change in productivity, living depth and life span (e.g. Nürnberg, 2000). Therefore, alkenone thermometer is not the best method to calculate seawater isotopic composition with oxygen isotopic composition of carbonate.

Mg/Ca and Sr/Ca of biogenic carbonates have been used as a paleothermometer (e.g. Smith *et al.*, 1988; De Deckker and Corrège, 1992; Mitsuguchi *et al.*, 1996; Klein *et al.*, 1997). Many invertebrates formed their own hard tissues as calcium carbonate crystals precipitated. These carbonates should uptake many trace elements from seawater with correspond to partitioning coefficients. Both Magnesium (Mg) and Strontium (Sr) has long residence time in seawater for a long time. The residence time of each element is estimated to be 13Ma for Mg, 1.1Ma for Ca (Broecker and Peng, 1982) and 2.5Ma for Sr (Palmar and Edmond, 1989). Such stable elements in the seawater are called as "conservative elements". Partition coefficients of these elements between carbonate and seawater show linear relations with ambient temperature, and thus, can be used as paleothermometer. However, the relations need to be calibrated for a particular species, because the partition coefficient may vary depend on the organic species.

Many organisms which possess calcareous skeletons, such as coral, foraminifera, coccolithophorids, bivalves, ostracods, and others, are used to reconstruct paleoenvironments. Foraminifers are one of the most important organisms for this purpose, because they are widely distributed in most of oceanic environments, from low latitude to high latitude, from coastal environments to the open sea and from shallow water to deep sea. Further, large numbers of foraminiferal tests are well preserved in sediment as fossils. These fossils should record paleo-environment of respective geological times. Therefore, foraminiferal tests are commonly used in paleoceanographic studies, and hence it is important to establish paleothermometer and paleo seawater oxygen isotopic ratio double proxies with foraminiferal tests.

The relationship between Mg contents of biogenic carbonate and temperature was first reported by Chave (1954). Dodd (1965) suggested that Sr contents of biogenic calcareous skeletons depend on ambient seawater temperature. Savin and Douglas (1973) compared foraminiferal Mg content and oxygen isotopic temperature estimates of six planktonic foraminiferal species, *Groborotalia truncatulinoides*, *G. tumida*, *G. menardii*, *Globigerinoides conglobatus, G. sacculifer* and *G. ruber.* They recognized a positive relationship between foraminiferal Mg content and isotopic temperature. Cronblad and Malmgren (1981) indicated that Mg and Sr contents of *Globigerina bulloides* and *Globorotalia inflata* show close relations with the Quaternary climate indices (total fauna, percentage of sinistral of *N. pachyderma* and foraminiferal $\delta^{18}O$). Izuka (1988) found that the variation of Mg contents with depth of *Cassidulina subglobosa* and *C. oriangulata* were proportional with water temperature. Nürnberg (1995) compared sea surface temperature, salinity and the sedimentation depth to measured Mg content of *N. pachyderma* sinistral, collected from core top sediments of high latitudinal regions. According to his results Mg contents had strong relation to sea surface temperature, whereas salinity effect was minor on foraminiferal Mg contents. Nürnberg *et al.* (1996) evaluated Mg contents directly a paleotemperature proxy with cultured specimens of *G. sacculifer* grown under controlled temperature and salinity condition. Mg/Ca of *G. sacculifer* increased linearly with culturing temperature. However, drastic variations in salinity conditions change uptake amount of Mg. A salinity increase from 35‰ to 45‰ is affected by 110% increase of Mg uptake. They concluded that salinity change affect biological and physiological activities. Therefore, Mg uptake was enhanced at higher salinity condition. Recently, the relationship between foraminiferal Mg/Ca and temperature was examined with culture experiments on two planktonic foraminifera *G. bulloides* and *Orbulina universa* (Mashiotta *et al.* 1999, Lea *et al.*, 1999). Lea *et al.* (1999) also revealed that Sr/Ca of both *G. bulloides* and *O. universa* changed with temperature similar to Mg/Ca. A strong relationship between Mg/Ca and temperature was also observed in natural benthic foraminiferal samples. (Rathburn and DeDeckker, 1997, Rosenthal *et al.*, 1997). Sr/Ca also changed in relation to temperature (Rathburn and DeDeckker, 1997) and hydraulic pressure (Rosenthal *et al.*, 1997). However, there is no culture experiments with controlled environmental factors on benthic foraminifera.

In last coupled of years, attempts were made to reveal past temperature and oxygen isotopic composition of seawater using the foraminiferal Mg/Ca with its oxygen isotopic composition. Lear *et al.* (1999) reconstructed past water $\delta^{18}O$ with deep sea benthic foraminiferal Mg/Ca and $\delta^{18}O$. In their studies, Mg/Ca thermometer was established on the assumption that bottom temperatures at deep sea are assumed to be constant. Mashiotta *et al.* (1999) assessed Mg/Ca thermometer of *G. bulloides*, combining both Mg/Ca and temperature equation of foraminiferal $\delta^{18}O$ (Shackleton, 1974) to reconstruct both sea surface temperature and $\delta^{18}O$ values of surface water records of subantarctic Pacific Ocean. Elderfield and Gansson (2000) established planktonic foraminiferal Mg/Ca thermometer from Shackleton's oxygen isotopic thermometer for eight species of planktonic foraminifera which were collected from sediment surface. Both seawater $\delta^{18}O$ record and sea surface temperature was reconstructed from Mg/Ca thermometry and foraminiferal $\delta^{18}O$ equation. In all the three works mentioned above seawater isotopic composition was calculated using equation of Shackleton (1974) for $\delta^{18}O$-temperature relations. However, the relationship between foraminiferal $\delta^{18}O$ and seawater temperature some species-wise deviation from equilibrium (Erez and Luz, 1983; Bouvier-Soumagnac and Duplessy, 1985; Bemis *et al.*, 1998). Therefore, $\delta^{18}O$ -temperature equation for each taxonomic group should be adopted to estimate oxygen isotopic composition.

Many relationships between foraminiferal test chemical composition and environmental factors have been observed in natural populations that grew under biased environments. In some cases environmental proxies were proposed to compare compositions with recorded environmental factors. However, it is difficult to estimate the environmental effect except monitored environments. Boyle (1988) pointed out general problems of chemical proxies. He suggested that culture experiment under well-controlled environments in the laboratory is effective method to get direct proof of any kind of proxies. Culturing study is a better way to compare directly the relation between foraminiferal chemical or isotopic composition with well-controlled environmental factors. Several such studies have been carried out on planktonic foraminifera, which suggested Mg/Ca, Sr/Ca and $\delta^{18}O$ as environmental proxies (Nürnberg *et al.*, 1996; Mashiotta *et al*, 1999; Lea *et al*, 1999; Erez and Luz, 1983; Bouvier-Soumagnac and Duplessy, 1985; Bemis *et al.*, 1998). However, no attempt has been made on benthic foraminifera.

The purpose of this study is to compare directly the foraminiferal Mg/Ca, Sr/Ca and $\delta^{18}O$ with temperature, salinity and water $\delta^{18}O$ values through culture experiments. In this study, cultured foraminiferal specimens were grown under the well-controlled temperature, salinity and oxygen composition of water. The cultured specimens were grasped them history. During this study, I measured Mg/Ca, Sr/Ca and $\delta^{18}O$ values of the tests for five species of benthic foraminifera which were grown under well-controlled temperature, salinity and $\delta^{18}O$ of culture waters. From these experimental results, the Mg thermometer for five species was calibrated. Further, temperature and salinity double proxies was established using Mg/Ca and $\delta^{18}O$ for two species. In addition, I also measured chemical components of the test from natural foraminiferal populations. Natural specimens were collected along the coast of the Sea of Japan from north to south during spring and fall. Measurements were also conducted on the natural samples which collected from permanent station at Omaezaki cape, Shizuoka Prefecture. In order to evaluate the established temperature and salinity proxies, they were applied on natural samples. This effort of evaluation shed light on the practical problem of application of foraminiferal chemical proxies to shallow benthic and planktonic foraminiferal assemblage.

2. Materials and Methods

2.1 Foraminiferal species

Six species of shallow water benthic foraminifera were selected for this study. They are *Ammonia beccarii* (Linné), *Cibicides lobatulus* (Walker and Jacob), *Elphidium crispum* (Linné), *Planoglabratella opercularis* (d'Orbigny), *Rosalina bradyi* (Cushman) *and Quinqueloculina yabei* Asano. This study focused to compare foraminiferal chemical proxies and physico-chemical environmental factors with culture experiments. Culture experiments were undertaken with *A. beccarii, E. crispum, P. opercularis, R. bradyi* and *Q. yabei.* These shallow water species live in very biased environments, in particular, temperature and salinity. This is the reason why I used these shallow benthic species for this study.

The culture specimens of *A. beccarii* were collected from lake Hamana (Shizuoka Prefecture)(Figure 1). The other species for culture experiments were collected from tide pools at Omaezaki Cape and at the rocky shore at Okuzure (Shizuoka Prefecture)(Figure 1).

Here, I describe both chemical characters and ecological information of each species. *Ammonia beccarii* forma 1 has low Mg calcite test (Blackmon and Todd, 1959). *Ammonia beccarii* live under very large range of salinity and temperature conditions (Bradshaw, 1957). *Cibicides lobatulus* is a species which has close phylogenetic relation to genus *Cibicidoides. Cibicidoides* is a deep-sea genus which is used as good paleoenvironmental indicator. *Elphidium crispum* is a common species at rocky shore environments (Kitazato, 1994). This species often forms largest percentage of assemblage. *Planoglabratella opercularis* precipitates high-Mg calcite. One life cycle takes about 50 days (Tsuchiya, 2000MS). This is considerably shorter than those of other species (Kitazato, 1998). *Rosalina bradyi* has a large test for enough amounts for measurement of Mg/Ca and Sr/Ca with single specimens. *Quinqueloculina yabei* belong to family milliolid, which have porcellaneous test of high-Mg calcite. Milliolid species have very different calcification mechanism than hyaline species

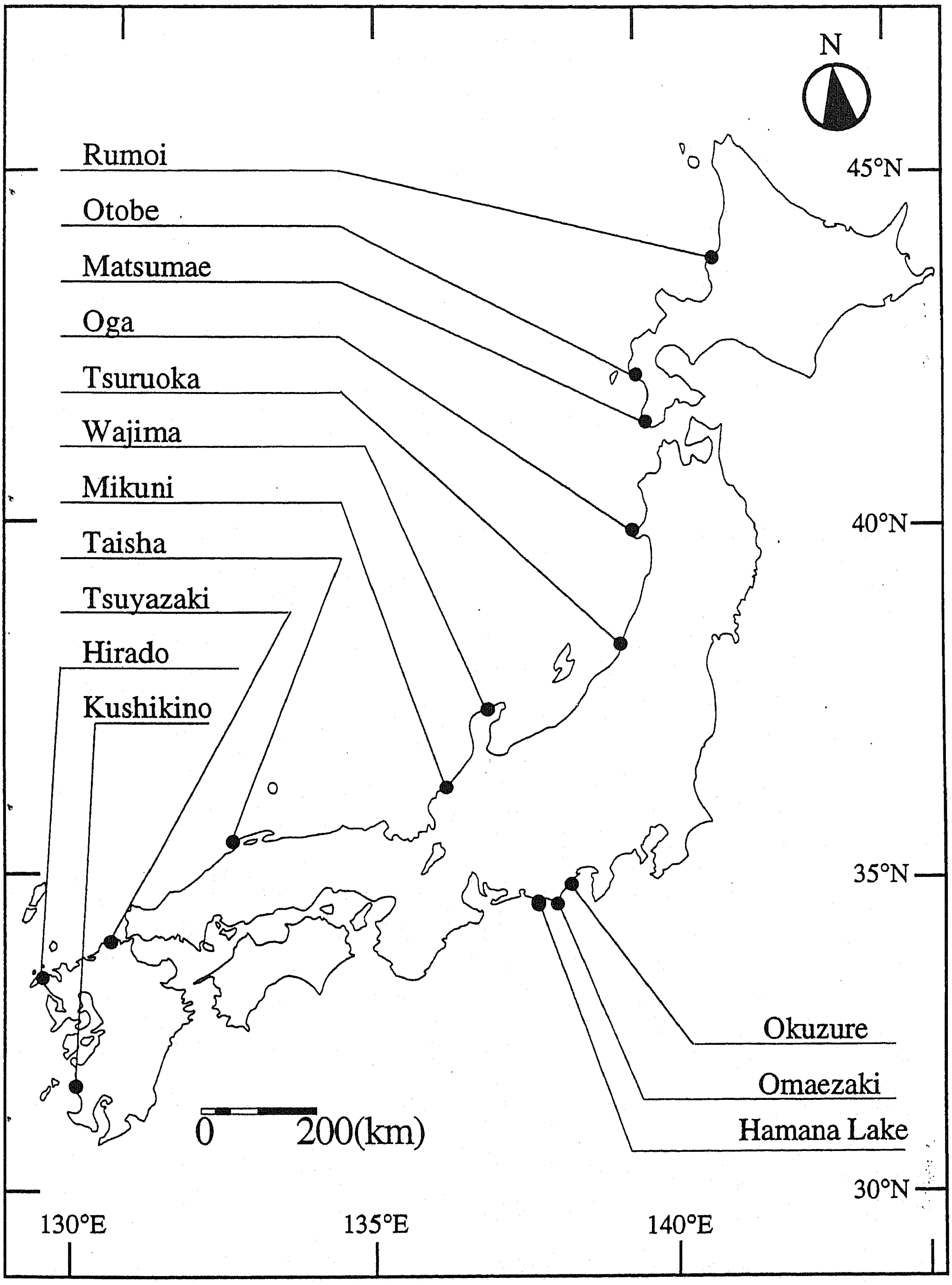


Figure 1: Map of sampling localities.

(Berthold, 1976).

Three species of foraminiferal specimens, living *Pararotalia nipponica* Asano, living *Q. yabei* and fossil *Globigerinoides sacculifer* (Brady) were used to estimate roasting effect to $\delta^{18}O$ values. *Pararotalia nipponica* and *Q. yabei* were picked from Omaezaki cape as culture specimens. *G. sacculifer* were picked from Last Glacial Maximum layer of NGC 34 sediment core. Core NGC34 was drilled from 2188m water depth at 141°29E, 3°48N on the Eauripik Ridge, which is located at eastern part of the West Caroline Basin.

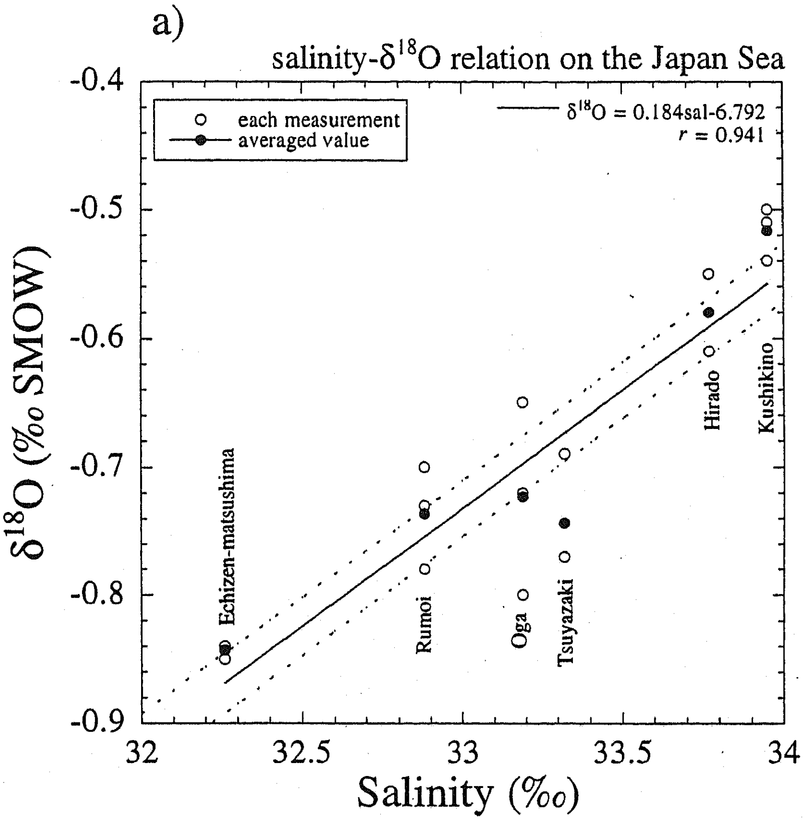
2.2 Culture experiments

In this study, culture experiments were carried out following the method of Kitazato (1994). Individuals were cultured until asexual reproduction had taken place. Juveniles reproduced from asexual reproduction are expected to have little genetic variability. Genetically less variable specimens were used for the culture experiments. Juvenile specimens were cultured in petri dishes with open-ocean surface water. Culture experiments were started a few days after asexual reproduction has taken place, even though the juvenile specimens already formed three or four chambers. The amount of calcite of juvenile specimen was not significant in comparison to the total amount of test. Test diameters of every specimen were measured at the end of culture experiment. Temperature, salinity and oxygen isotope values of culture water were controlled at several conditions for comparing chemical compositions both of foraminiferal test and ambient environments. The culture temperature for *Q. yabei* was measured by thermometer everyday. The culture temperatures recorded automatically every 30 min. by a temperature logger (Ondotori, T&D Co. Ltd.) for other species. The experimental seawater was filtrated with 0.2μm membrane filter (TOYO Advantec Co. Ltd.). The salinity and oxygen isotope ratio was adjusted by either dilution of filtrated seawater with distilled water or evaporation of filtrated seawater for trace elemental experiments. For isotopic experiments, culture water was diluted to several fixed conditions from 40‰ seawater which was concentrated by evaporation at 50°C. I used the filtrated water which collected at Hamana-Lake for *A. beccarii* experiments. The filtrated seawater which collected at Omaezaki were used for *R. bradyi* experimental runs. These waters of two systems showed clear relation between salinity and oxygen isotopic ratio (Figure 2b). Artificial seawater with constant oxygen isotopic composition was used to know the effect of salinity to foraminiferal $\delta^{18}O$. Artificial seawater was made from the artificial seawater salt SEALIFE (Marine Tec KK) which was diluted with distilled water. In this way, I can to prepare three conditions of artificial water with a constant $\delta^{18}O$ value (Figure 2b). Mg/Ca and Sr/Ca in the seawater were measured before and after each experimental run. Mg/Ca and Sr/Ca values were kept at 5.05 and 0.0084 (atomic ratios) respectively, and fluctuated <1% during experimental periods. The culture waters were exchanged every day to prevent changes in salinity and oxygen isotope ratio by evaporation. Temperatures were controlled during every experimental run by keeping petri dishes in incubators. Temperature fluctuated less than 1°C during experimental periods. The pH conditions of culture water were monitored with pH meter (Shindengen KK) both for *R. bradyi* and *A. beccarii*.

The petri dishes were kept under a white fluorescent light of 1500 lx on a 12 hour light-12 hour dark cycle. There are 10-20 specimens of foraminifera within each dish. Each culture experiment was conducted for about 60 days; then all specimens were rinsed with distilled water and oven-dried at 50°C. All specimens were kept in foraminiferal faunal slides until the measurements were made.

2.3 Natural populations

Foraminiferal samples for seasonal changes of Mg/Ca and Sr/Ca measurements were picked from coralline algae samples which were collected monthly from a specific tide pool at Omaezaki Cape (Figure 1 and Table 1) in 1987 and 1988 (Takahara, 1989MS). Foraminifera were picked once in two months. All samples were stained in 0.5% Rose Bengal-10% Formalin-seawater solution for 24 hours. Fixed samples were washed over a 250 mesh (ø=63 µm) sieve and dried at 50°C in an oven. The Mg, Ca and Sr contents of rose bengal



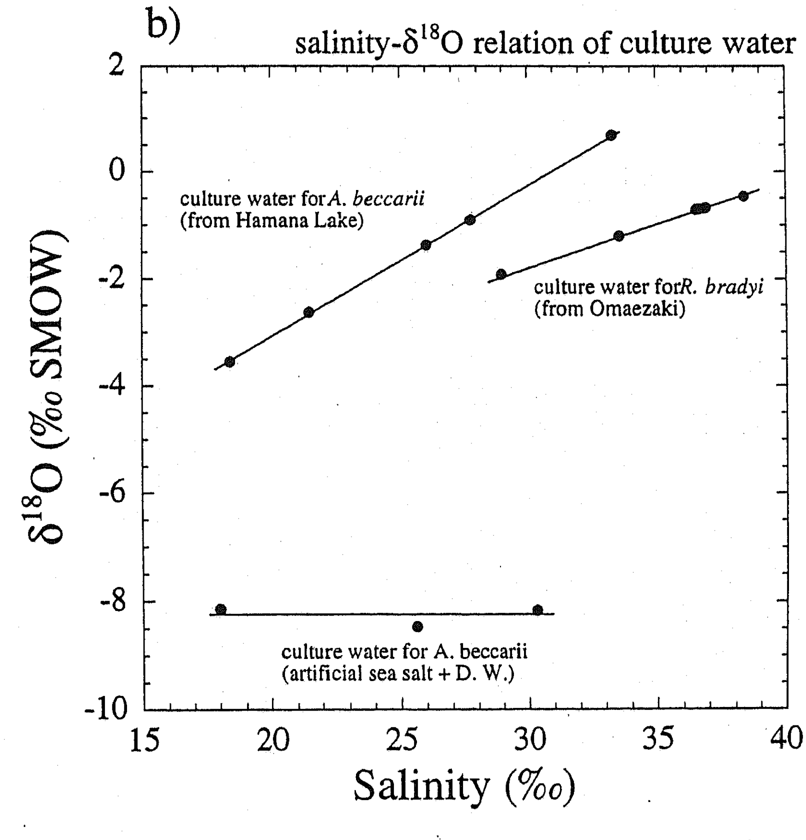


Figure 2: Oxygen isotopic composition and salinity of water for culture experiments and natural environments. a) Observed salinity and $\delta^{18}O$ of seawater which collected along the Japan Sea coast. Open circles indicate the $\delta^{18}O$ value of single measurement. Close circles indicate averaged $\delta^{18}O$. Solid lines indicate regression equations of averaged $\delta^{18}O$. b) Measured salinity and $\delta^{18}O$ of culture water. Close circles indicate single measurement of $\delta^{18}O$.

Table 1: Sampling localities and dates, temeperature, salinity and $\delta^{18}O$.

Locality	Date	Habitat	Average Temperature (°C)	Standard deviation	Salinity	Water $\delta^{18}O$ (‰SMOW)	Standard deviation
Sesonal samples (collected by Takahara 1989MS)							
Omaezaki	May 17, 1987	tide pool	17.2	1.4			
	July 12, 1987	tide pool	22.6	0.9			
	Sept. 20, 1987	tide pool	25.7	0.9			
	Nov. 23, 1987	tide pool	18.7	1.4			
	Jan. 21, 1988	tide pool	14.8	1.1			
	March 19,1988	tide pool	11.7	0.9			
	May 20, 1988	tide pool	17.2	1.4			
Geographical sample -1st time-							
Rumoi	Oct 16, 1995	rocky shore	17.1	1.8	32.88	-0.737	0.99
Otobe	Oct 17, 1995	rocky shore	19.0	1.6			
Matsumae	Oct 18, 1995	artificial concreat	18.7	1.5			
Oga	Oct 19, 1995	rocky shore	21.7	1.3	33.19	-0.723	0.06
Tsuruoka	Oct 20, 1995	rocky shore	21.5	1.1			
Wajima	Oct 21, 1995	artificial concreat	20.6	1.5			
Mikuni	Oct 22, 1995	tide pool	21.6	0.9	32.26	-0.843	0.02
Taisya	Oct 23, 1995	rocky shore	22.2	1.0			
Tsuyazaki	Oct 24, 1995	rocky shore	22.3	0.6	33.32	-0.743	0.08
Hirado	Oct 25, 1995	rocky shore	22.2	0.3	33.77	-0.580	0.12
Kushikino	Oct 26, 1995	tide pool	23.9	0.4	33.95	-0.517	0.06
Geographical sample -2nd time-							
Rumoi	June 27, 1997	rocky shore	14.2	2.2			
Tsuruoka	June 29, 1997	rocky shore	15.8	2.2			
Echizen-Matsushima	July 17, 1997	tide pool	20.9	1.0			
Taisha	July 18, 1997	rocky shore	22.6	0.8			
Kushikino	July 21, 1997	tide pool	25.1	2.3			

($C_{20}H_2C_{14}I_4Na_2O_5$) solution were measured with ICP-AES. Rose bengal solution didn't contain these elements above the detection limits. Rose bengal stained foraminifera were picked under the binocular microscope.

Seawater temperature records at Omaezaki Port, about 2 km north of the sample locality, were used for comparing between Mg/Ca or Sr/Ca and temperature. These measurements were made daily at 1 m below the average sea surface by the Omaezaki Meteorological Observatory Station of the Meteorological Agency of Japan.

Samples for geographical variation were collected along the coast of the Sea of Japan at five localities between 34°40'N and 48°50'N (Figure 1 and Table 1). These samples were collected in two intervals between Oct. 14 and Oct 28, 1995 and between June 27 and July 21, 1996. All sampling localities were selected to be close to a meteorological or a tidal gauge station, because temperature data are available from the Geographical Survey Institute of Japan or from the Meteorological Agency of Japan. The collected samples were fixed in a Rose bengal-10% Formalin-seawater solution directly after collection and treated at our laboratory with the same methods as the seasonal samples. The average temperature, salinity, water oxygen isotopic composition and habitation are shown in Table 1.

2.4 Measurements of Mg/Ca and Sr/Ca with ICP-AES, ICP-MS and AAS

The fundamental cleaning methods of foraminiferal tests for measuring trace elements were developed by Boyle (1981). Boyle and Keigwin (1985) sophisticated this cleaning method. All samples were cleaned following the cleaning method of Boyle and Keigwin (1985) with some modifications to measure for Mg, Ca and Sr contents of foraminiferal shell. The reductive cleaning steps of Boyle and Keigwin (1985) were skipped because Brown and Elderfield (1996) pointed out the step is not critical for Mg, Ca and Sr contents. I gently crushed specimens to open the whole chamber spaces, placed them in a solution of alkaline peroxide ($2x10^{-5}$N H_2O_2 in 0.1N NaOH) at 90°C for 10 min, then rinsed them with 0.001N HNO_3 for 1 min. Between each step, specimens were rinsed with double-distilled water at 3 times. The specimens were dissolved in 3 to 10 ml 0.3N HNO_3 for ICP-AES and ICP-MS. For AAS, the specimens were dissolved in 0.5 ml 0.1N HNO_3 to measure Mg and Sr. 0.1 ml solutions were divided from 0.5 ml and diluted up to 1ml with same nitric acid to detect Ca.

Analysis of Mg, Ca and Sr was performed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or inductively coupled plasma-mass spectroscopy (ICP-MS), at the Geological Survey of Japan, or Atomic Absorption Spectrometry (AAS) at Department of Life and Earth Science, Shizuoka University. For all measurements, several concentrations of standard solutions and blank solution were used to get calibration curve of each element. The samples of *P. opercularis* from culture and the latitudinal samples were measured by ICP-MS (Hewlett-Packard HP4500). Dwell times were 180 ms at mass-to-charge (m/z) ratios of 24, 43, and 88 for an acquisition time of 6s/run, total 12s. Samples and standard were spiked with an internal standard of ^{89}Y to correct for short-term variability and long-term drift. The precision was better than 4% (1 s) for Mg and 2% (1 s) for Ca. The samples of *Q. yabei* and the latitudinal samples of *P. opercularis* and *R. bradyi,* were analyzed by ICP-AES on a Jobin Yvon Instruments JY38S analyzer, at an analytical precision of better than 1% (1σ) for Mg, Ca and Sr. The culture samples of *E. crispum* and *R. bradyi* were measured by ICP-AES on a Thermo Jarrell Ash IRIS Advantage analyzer. The precision was better than 1% (1σ) for Mg, Ca and Sr. The samples of *A. beccarii* were measured by GFAAS on a Hitachi Atomic Absorption Spectrometer. The precision was better than 5% (1σ).

2.5 Measurements of Mg/Ca with EPMA

Selected specimens were rinsed with distilled water and embedded in epoxy resin. Ground and polished, relief-free sections of foraminiferal tests were then prepared to reveal fresh calcite surfaces of chamber walls. The analyses were carried out on an electron probe micro analyzer (EPMA) JEOL JXA 733 mark-II, at the Department of Life and Earth Science, Shizuoka University and JEOL JXA 8900RL at the Japan Marine Science and Technology

Center. Analyses were carried out with an accelerating voltage of 15 kV and a beam current of 12 nA. A counting time of 15 sec per element peak and 15 sec for the background before and after the peak measurement was chosen. In this study, the electron beam was focused on a spot approximately 2-4 μm in diameter. Element concentrations in the ppm-range were detected quantitatively. Periclase and Wollastonite served as standards.

2.6 Measurements of foraminiferal oxygen isotopic compositions with IRMS

Oxygen and carbon isotopic analyses were conducted on foraminiferal tests. Whole tests of cultured foraminiferal specimens and collected samples from natural population were measured. For several specimens, I measured some fragments, divided from a whole foraminiferal test. 10-80μg specimens were used for each measurement.

Some of the shells were roasted to check the roasting effects on the isotopic compositions of foraminifera. The roasting experiments were conducted with *P. nipponica* which collected Omaezaki. The isotopic compositions of roasted specimens were compared with the "raw" specimens. The roasting operations were conducted under vacuum at 350°C after being washed in ethanol in an ultrasonic bath. Other specimens were measured after just only ultrasonic cleaning in ethanol.

Isotopic analyses were conducted using the Fisons Optima isotope ratio mass spectrometer (IRMS) at the Department of Marine Geology, Geological Survey of Japan. The carbonate was then reacted with conc-phosphoric acid at 90.0°C. Results are expressed conventional δ notation defined by the following relationship

$\delta=(R_{sample} - R_{standard})/R_{standard} \times 1000$

Where R refers to $^{18}O/^{16}O$ or $^{13}C/^{12}C$. Analytical precision of $\delta^{18}O$ analyses was ±0.05‰ relative to the Vienna Pee Dee belemnite (VPDB) standard by replicate analyses of NBS-19 standard.

2.7 Measurements of water oxygen isotopic compositions with IRMS

$\delta^{18}O$ values of culture water were measured via CO_2 equilibration. Water $\delta^{18}O$ were detected the Fisons Prism IRMS at Research Institute for Hazards in Snowy Areas, Niigata University. The precision of replicate was ±0.02 versus Vienna Standard Mean Ocean Water (VSMOW).

I expressed oxygen isotopic ratios of foraminifer as both $\delta^{18}O$ values and the isotopic fractionation between calcite and water ($\delta^{18}O_C$-$\delta^{18}O_W$ or δ_C-δ_W), where both values are expressed in the conventional δ notation relative to VPDB. $\delta^{18}O_W$ values were recalculated from VSMOW to VPDB scale. This correction is necessary to compare $\delta^{18}O$ values of CO_2 measured which were produced by the reaction of calcite with conc-phosphoric acid and CO_2 equilibrated with water. The $\delta^{18}O_W$ correction value of –0.27‰ (Hut, 1987) is used through this study.

3. Results

3.1 Results of culture experiments

Foraminiferal specimens were grown under well-controlled environments during experimental periods. Table 2 indicates the temperature and salinity of all experimental runs. For example, changes in temperature, salinity and pH of *A. beccarii* and *R. bradyi* are shown in Figure 3.

The maximum deviation of temperature (1.6°C) was observed at the temperature experiments for *Q. yabei* (Table 2). The variation in salinity was less than 1‰ during experiments. These factors are enough to compare the foraminiferal chemical and isotopic compositions.

On the other hand, pH values considerably fluctuated from about 8 to 9.5. This large fluctuation may be occurred by photosynthesis of micro algal organisms. In this study, living micro algae were fed to foraminifers. They consumed dissolved carbon dioxide during photosynthesis, then produced resulting of a pH rise. It is difficult to prevent these changes of pH with the culture method now in use. There is a possibility of pH variation affecting the foraminiferal chemical and isotopic composition (e.g. Bemis et al., 1998). Therefore, it is necessary to revise the culture method.

3.1.1 Mg/Ca of cultured specimens

The results of foraminiferal Mg/Ca ratio corresponding on temperature experiments for five species are shown in Figure 4 and Table 2.

Magnesium contents were significantly different among five species. *Ammonia beccarii* indicated similar range of Mg/Ca to *E. crispum,* while Mg/Ca of *R. bradyi* was five times larger than the two species. Higher Mg/Ca of over 100 mmol/mol were observed in *P. opercularis* and *Q. yabei.*

Table 2: Mg/Ca and Sr/Ca of cultured specimens

Temperature (°C)	S.D.	Salinity	Average Mg/Ca	S.D.	Average Sr/Ca	S.D.
Ammonia beccarii						
Temperature Experiments						
15.2	0.3	26.1	1.5	0.0	1.6	0.1
17.6	0.9	26.1	1.5	0.4	1.7	0.2
24.0	0.4	26.1	1.8	0.4	1.6	0.2
27.3	0.4	26.1	2.8	0.6	1.7	0.1
Salinity Experiments						
24.0	0.4	18.4	1.1	0.3	1.4	0.2
		21.5	1.7	0.9	1.5	0.2
		26.1	1.8	0.4	1.6	0.2
		27.8	1.3	0.4	1.5	0.2
		33.3	1.4	0.3	1.6	0.1
Elphidium crispum						
Temperature Experiments						
10.0	0.1	35.6	1.7		1.1	
15.3	0.3		2.0		1.1	
17.7	0.9		2.8		1.1	
21.8	0.7		2.9		1.1	
25.1	0.1		3.6		1.2	
Salinity Experimens						
21.8	0.7	30.1	2.9		1.1	
		33.0	3.0		1.1	
		35.6	2.9		1.1	
		38.4	3.0		1.1	
Rosalina bradyi						
Temperature Experiments						
15.2	0.3	34.6	4.3	0.1	1.7	0.0
17.6	0.9		6.3	0.3	1.8	0.1
24.0	0.2		9.3	1.0	1.8	0.2
27.3	0.1		15.9	0.6	2.0	0.1
Salinity Experiments						
24.0	0.2	29.0	11.9	0.9	1.8	0.0
		33.6	10.2	0.4	1.8	0.1
		36.7	9.3	1.0	1.8	0.2
		36.9	12.2	1.3	1.8	0.2
		38.4	11.4	3.1	1.5	0.4

S.D.=Standard Deviation

Mg/Ca and Sr/Ca indicated as mmol/mol

Table 2 continued

Temperature (°C)	S.D.	Salinity	Average Mg/Ca	S.D.	Average Sr/Ca	S.D.
Planoglabratella opercularis						
Temperature Experiments						
10.6	0.7	1.3	115.3	6.2	2.4	0.3
12.7	0.2	0.8	115.0	3.6	2.4	0.2
15.3	0.1	0.4	123.3	5.3	2.2	0.3
17.9	0.2	0.6	126.5	5.5	2.3	0.2
Salinity Experiments						
17.9	0.2	28.3	129.8	4.5	2.2	0.0
		30.6	123.0	7.5	2.1	0.1
		33.6	125.7	7.9	2.2	0.1
		35.0	127.3	3.7	2.3	0.2
23.1	0.2	30.6	144.8		2.2	
		33.6	143.2	7.5	2.2	0.0
		35.0	142.7	1.1	2.3	0.0
Quinquelocurina yabei						
Temperature Experiments						
9.7	0.7	36.0	92.9		0.9	
14.8	1.6		110.1		1.4	
17.9	0.2		113.3	2.0	1.8	0.0
20.2	1.0		125.5	0.3	1.7	0.0
24.5	1.5		135.8		1.8	
Salinity Experiments						
17.9	0.2	28.5	114.1	0.3	1.8	0.2
		31.8	112.8	1.6	1.7	0.0
		34.6	113.3	2.0	1.8	0.0
		38.5	115.7	4.8	2.0	0.0

S.D.=Standard Deviation

Mg/Ca and Sr/Ca indicated as mmol/mol

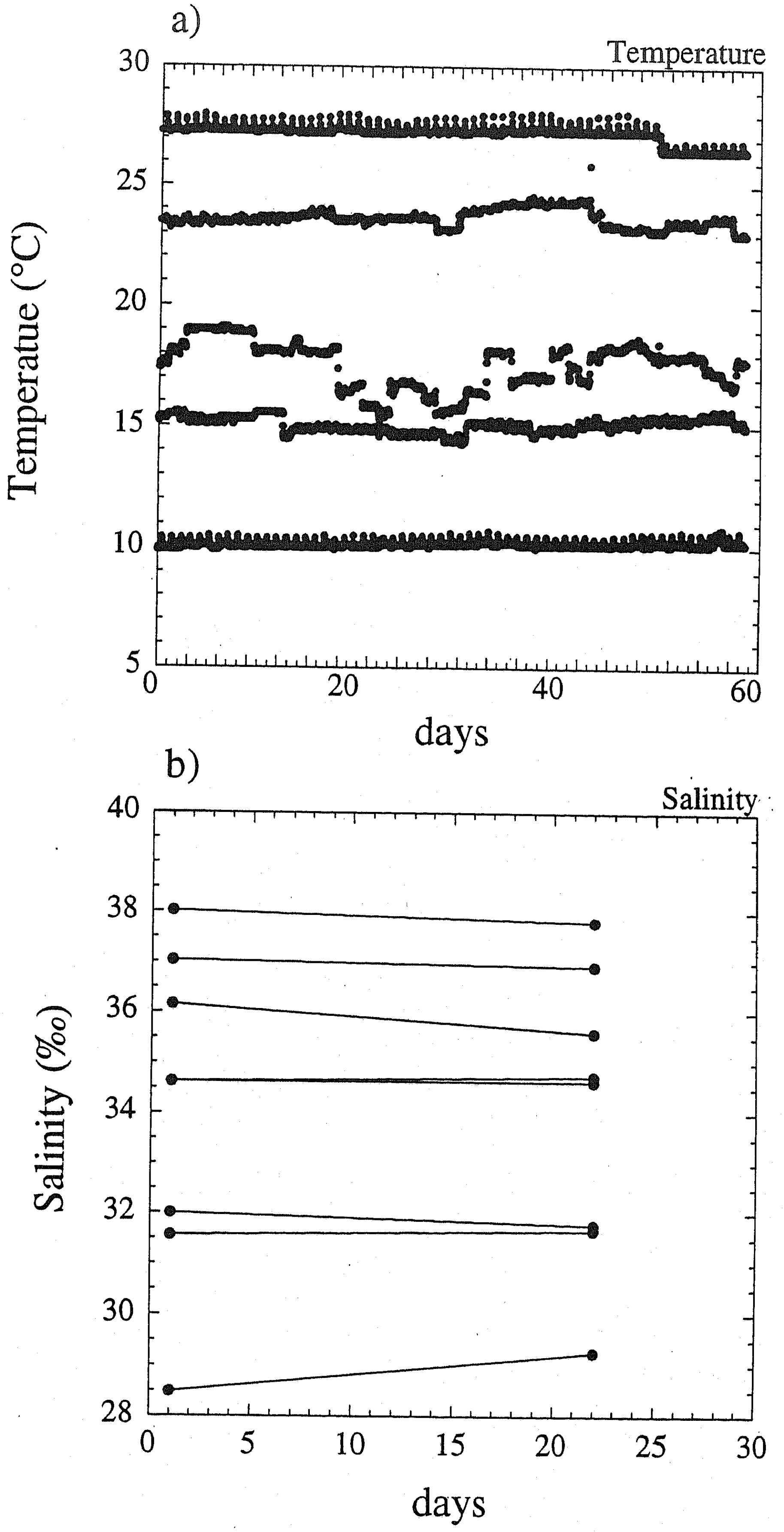
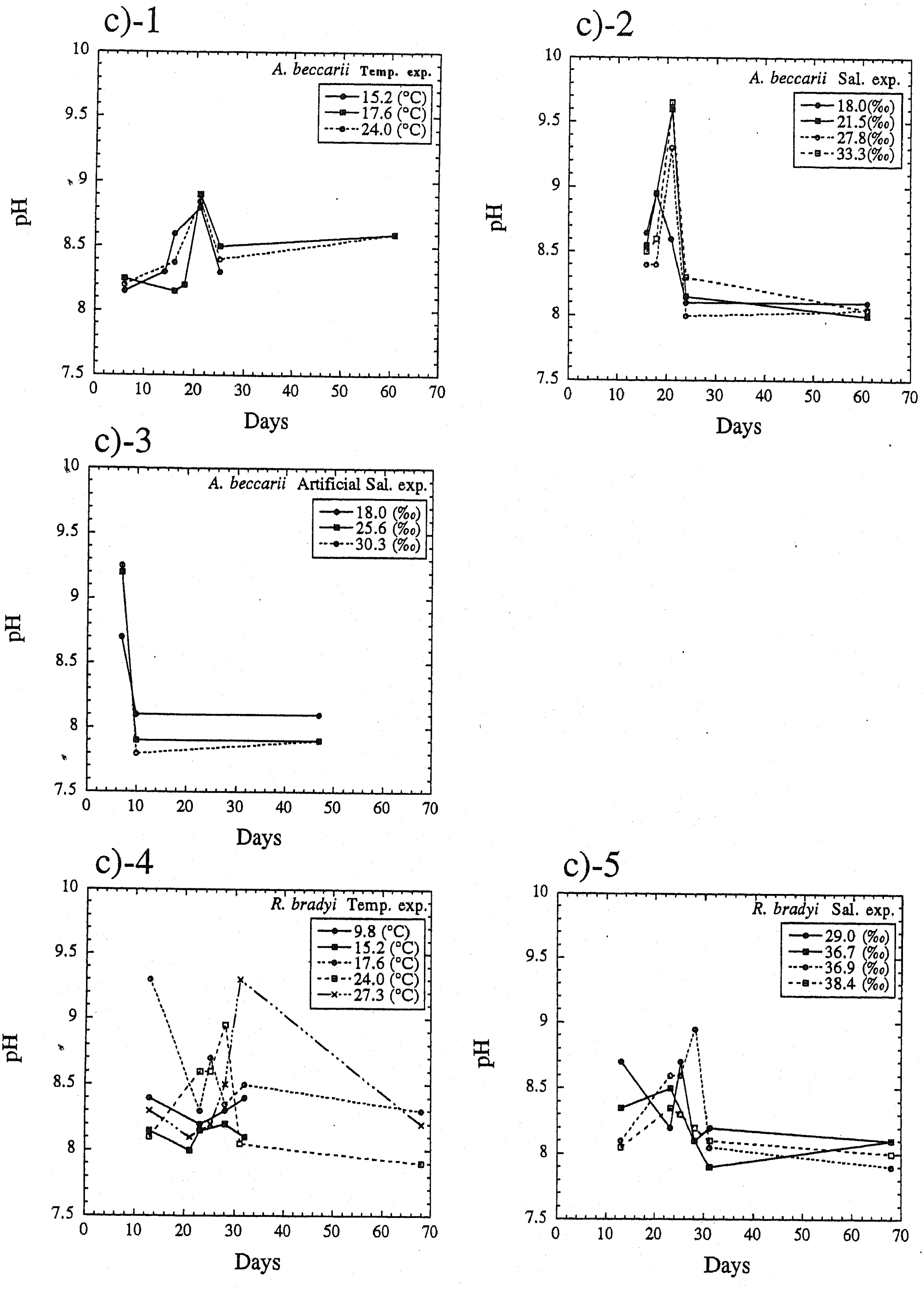


Figure 3:The monitored environmental factors of culture experiment: a)temperature, b) salinity c)pH. c)-1 temperature experiment of *A. beccarii* c)-2 salinity experiment of*A. beccarii* . c)-3 salinity experiment of *A. beccarii* with artificial sea water. c)-4 temperature experiment of *R. bradyi* . c)-5 salinity experiment of *R. bradvi.*



(Figure 3 continued)

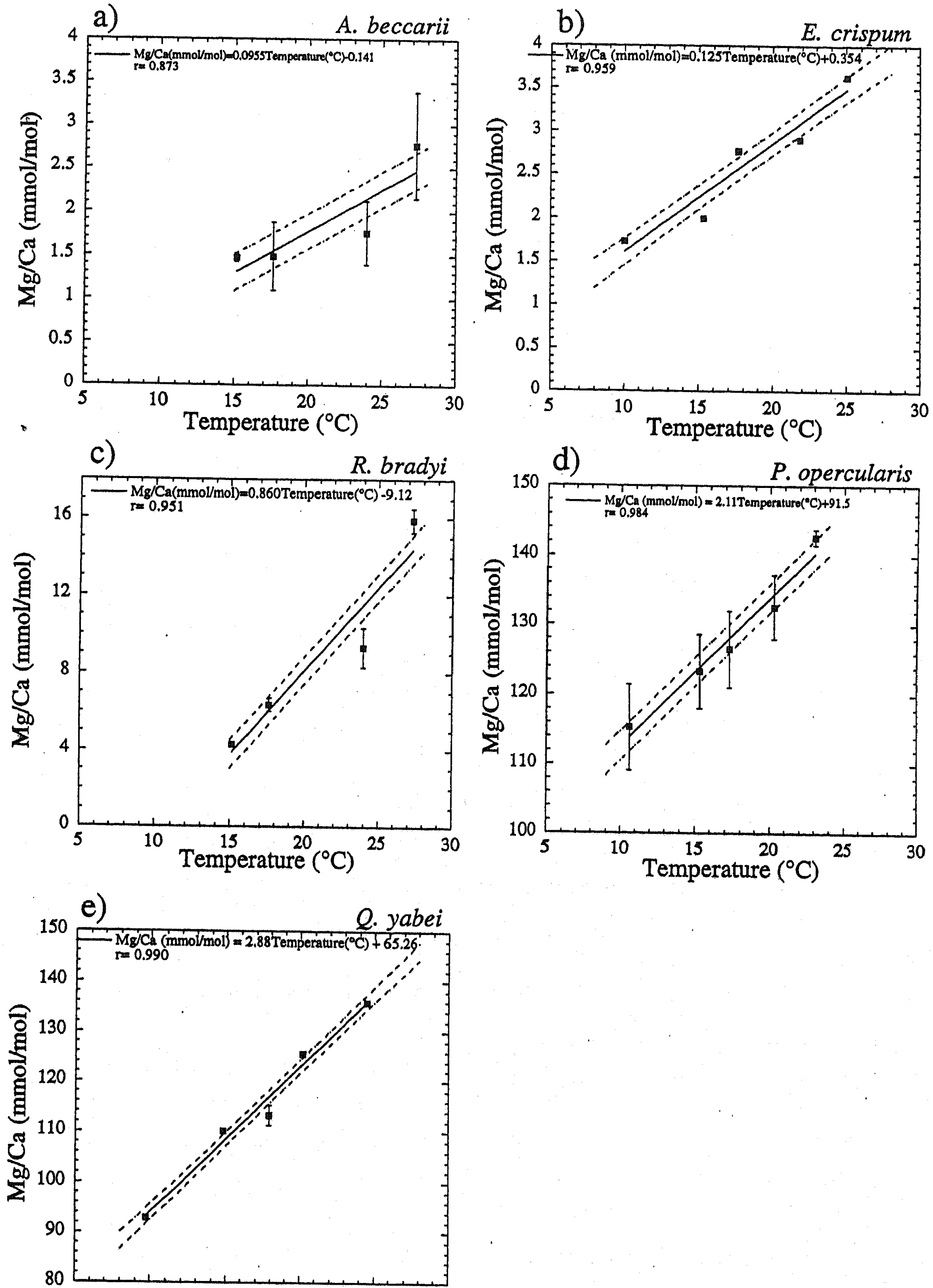


Figure 4: Mg/Ca of cultured specimens grown under various temperature conditions. Closed squares indicate average Mg/Ca of the same temperature condition. Each error bars indicate standard deviation. Solid lines indicate regression equations. Dashed lines show forecast interval at the 95% confidence level. a) *A. beccarii* b) *E. crispum* c) *R. bradyi* d) *P. opercularis* e) *Q. yabei.*

Mg/Ca of cultured specimens showed a strong dependence on temperature. The least square linear fitting are given as follows to the data is:

A. beccarii

Mg/Ca (mmol/mol)= 0.0955 temperature (°C) – 0.141 *r*=0.873 (1),

E. crispum

Mg/Ca (mmol/mol)= 0.125 temperature (°C) + 0.354 *r*=0.959 (2),

R. bradyi

Mg/Ca (mmol/mol)= 0.860 temperature (°C) – 9.12 *r*=0.951 (3),

P. opercularis

Mg/Ca (mmol/mol)= 2.11 temperature (°C) + 91.5 *r*=0.984 (4),

Q. yabei

Mg/Ca (mmol/mol)= 2.88 temperature (°C) + 65.3 *r*=0.990 (5),

where *r* is correlation coefficient. The linear regression equations are different among species. The slope of equation was very different for different species. The largest slope was observed with *Q. yabei*. The slope of *Q. yabei* is 29 times larger than *A. beccarii.*

The slopes of the equations seem to relate with Mg content. The slope of *Q. yabei* and *P. opercularis* indicate higher value than of *A. beccarii and E. crispum*. *R. bradyi* showed middle value of slope among these five species.

The results of foraminiferal Mg/Ca of salinity experiments are shown in Figure 5 and Table 2. Mg/Ca were almost constant at different salinity conditions. Figure 5d indicate that uptake of Mg/Ca ratios from different salinity of *P. opercularis* showed a constant value at the constant temperature. Mg/Ca of salinity may not affect foraminiferal Mg uptake at different temperature.

3.1.2 Sr/Ca of culture specimens

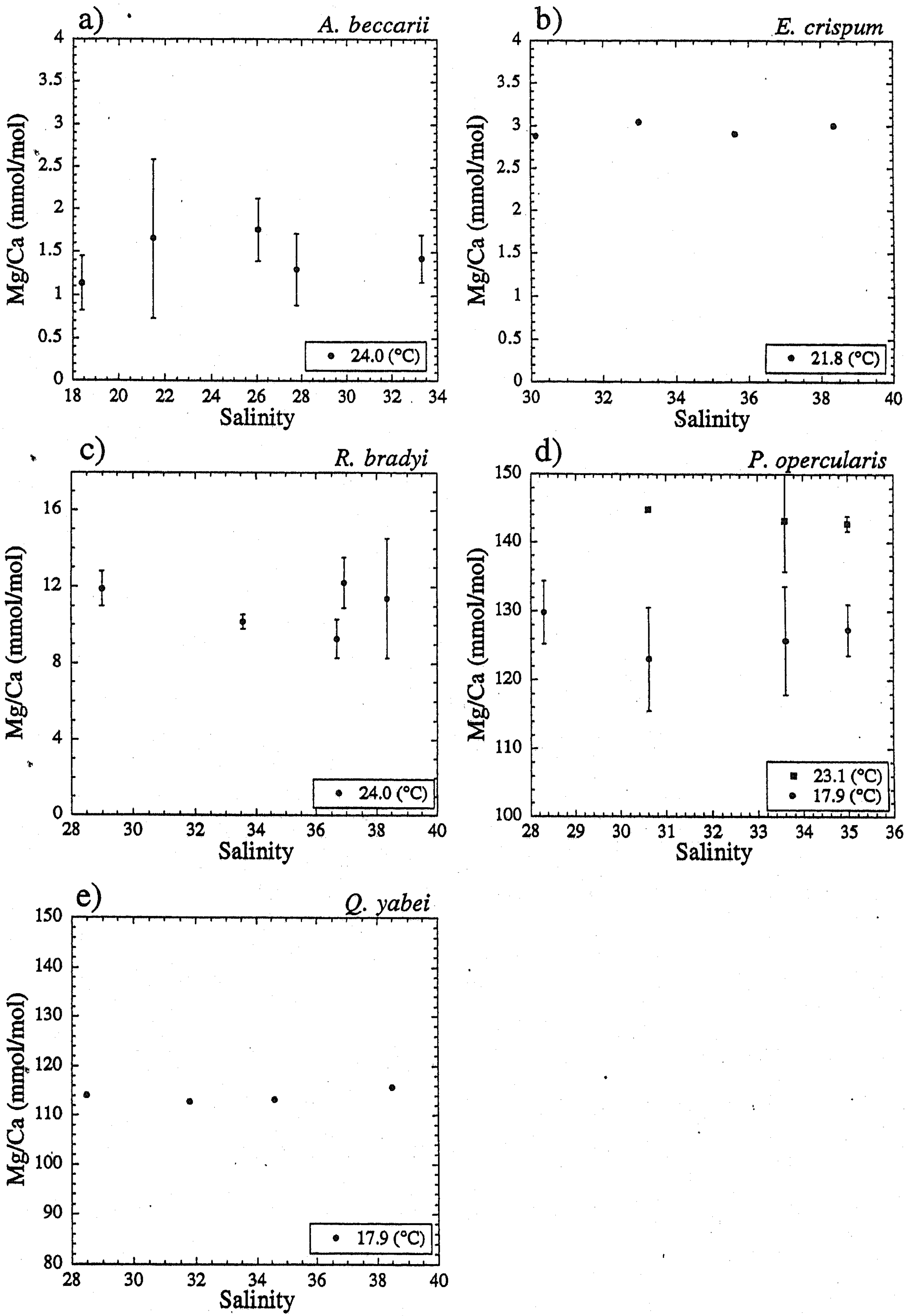


Figure 5: Mg/Ca of cultured specimens grown under various salinity conditions. Closed squares and circles indicate average Mg/Ca at same salinity condition. Closed circles show the results of 17.9°C and closed squares indicate the results of 23.1°C on plot d). Error bars indicate standard deviation. a) *A. beccarii* b*) E. crispum* c*) R. bradyi* d) *P. opercularis* e) *Q. yabei.*

Foraminiferal Sr/Ca of temperature experiments are presented in Figure 6 and Table 2. Different species showed different value of Sr/Ca ratio. Sr/Ca ratios were very similar among five species. The Sr/Ca range between the highest species of Sr/Ca and lowest species of Sr/Ca was about 1mmol/mol.

Sr/Ca of *R. bradyi* and *Q. yabei* seemed to increase with temperature. However, other species have no clear relationship between temperature and Sr/Ca. Temperature may possibly have some influence on foraminiferal Sr contents, but still unclear. These results suggest that Sr/Ca may be difficult to use as temperature proxy.

Foraminiferal Sr/Ca of salinity experiments indicated in Figure 7 and Table 2. Sr/Ca of each specimen indicate stable value through all salinity conditions. Salinity did not affect foraminiferal Sr uptake.

3.1.3 Measurement with electron probe micro analysis (EPMA)

a. Reproducibility of EPMA

Average, median and standard deviation of Mg/Ca ratios were measured within single chamber wall of *P. opercularis* using EPMA. The values became stable as measurement numbers increased (Figure 8). Mg/Ca ratios measured by EPMA deviated slightly one measurement after the other. This is due to the basic problem of EPMA which lies in the detection of trace elements with X-ray. The results should be affected by many factors such as surface conditions of samples, condition of carbon coating, density of material among others. Patchy distribution of Mg element in a test can also be an important reason for the observed relation. To avoid this problem, measurement was repeated within same chamber until Mg/Ca ratio attained stable values.

During first several measurements, all indicators showed very biased values. After 10 measurements, Mg/Ca gone stable values, even though Mg/Ca changed slightly after 20 times. Accordingly, measured 20 times or more in average on each chamber during this study.

Averaged values of Mg/Ca ratio were used instead of median of Mg/Ca to compare EPMA

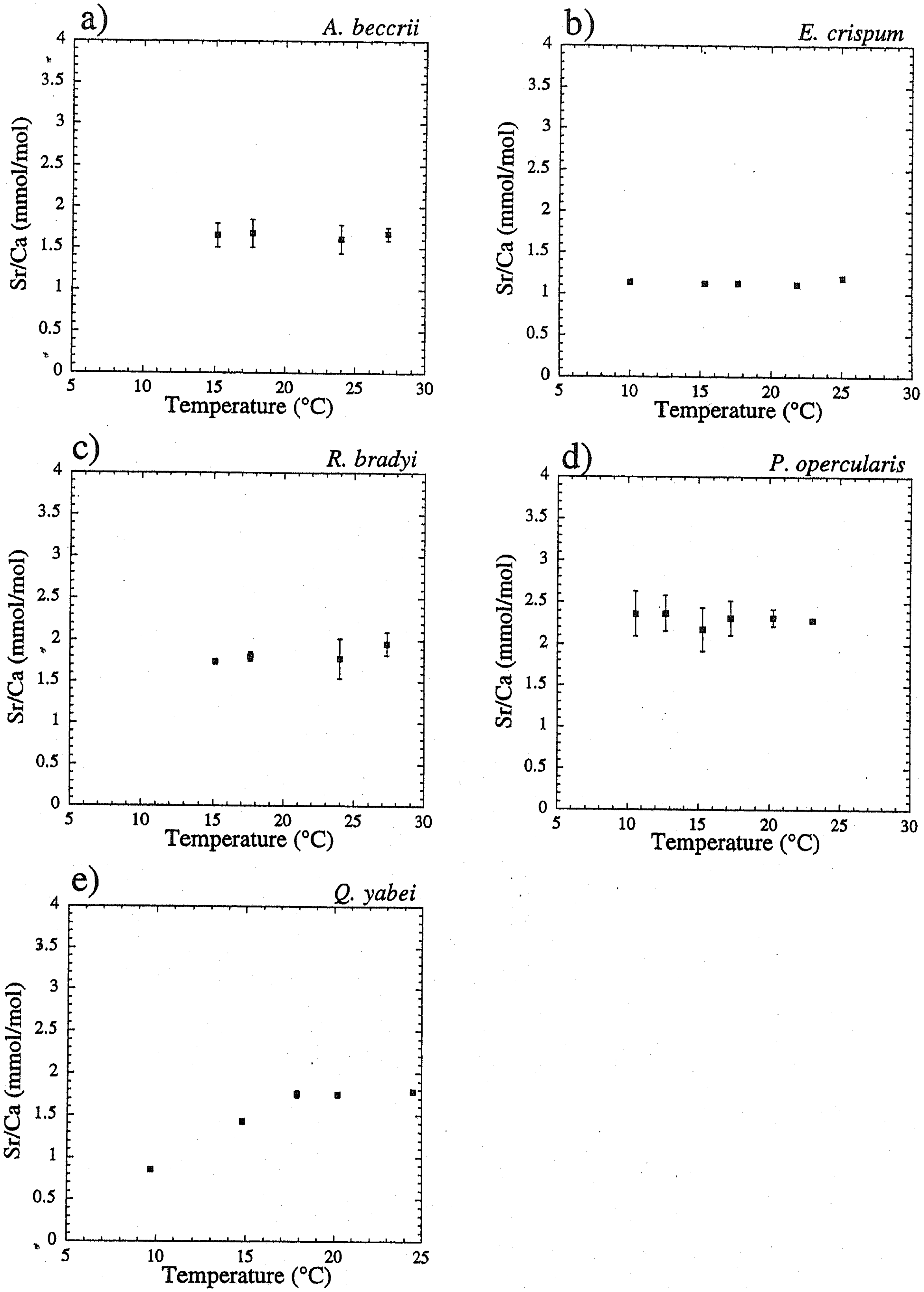


Figure 6: Sr/Ca of cultured specimens grown under various temperature conditions. Closed squares indicate average Sr/Ca at same temperature condition. Each error bars indicate standard deviation. a) *A. beccarii* b) *E. crispum* c) *R. bradyi* d) *P. opercularis* e) *Q. yabei.*

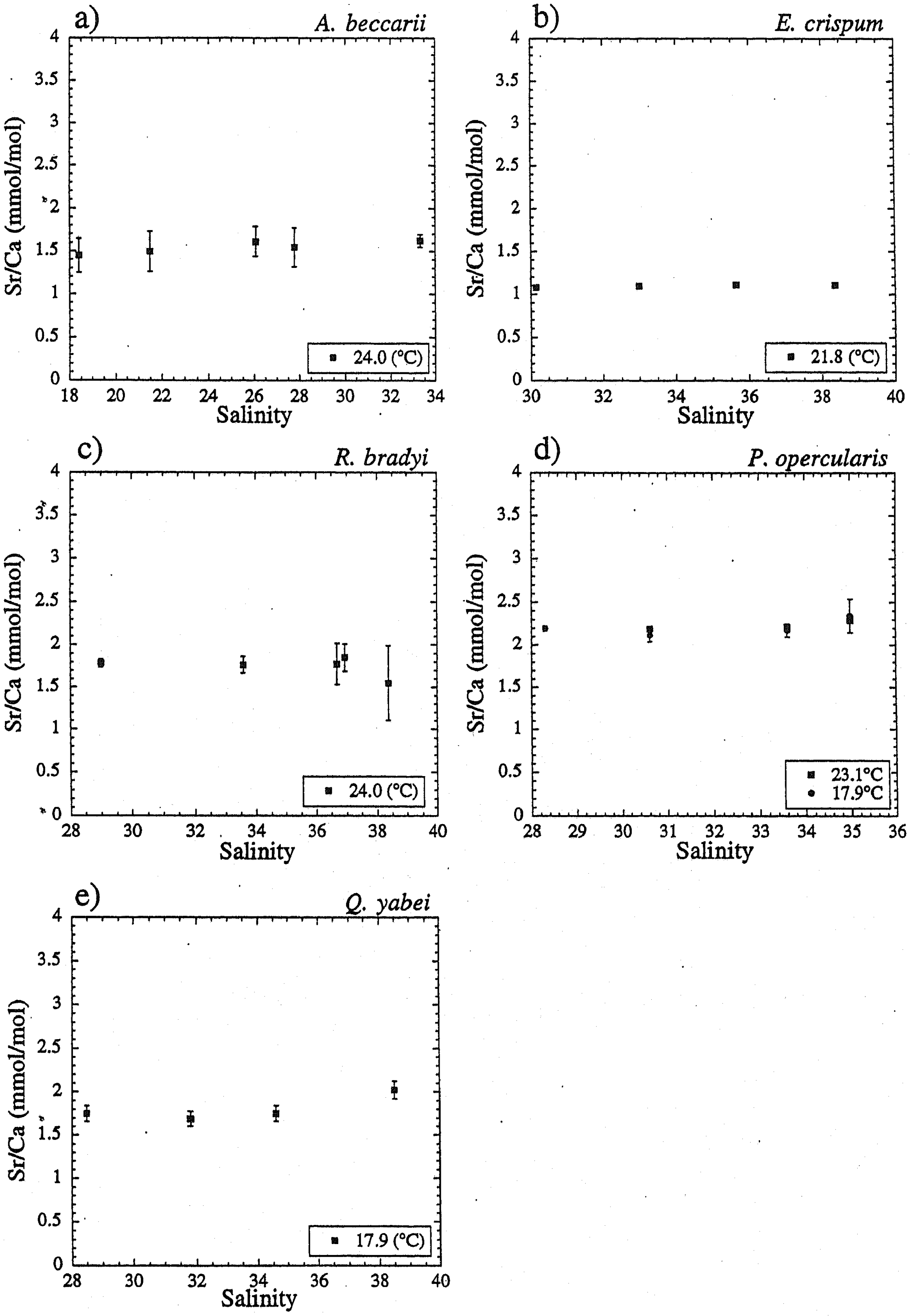


Figure 7: Sr/Ca of cultured specimens grown under various salinity conditions. Closed squares and circles indicate average Sr/Ca at same salinity condition. Closed circles show the results of 17.9°C and closed squares indicate the results of 23.1°C on plot d). Each error bars indicate standard deviation. a) *A. beccarii* b*) E. crispum* c*) R. bradyi* d) *P. opercularis* e) *Q. yabei.*

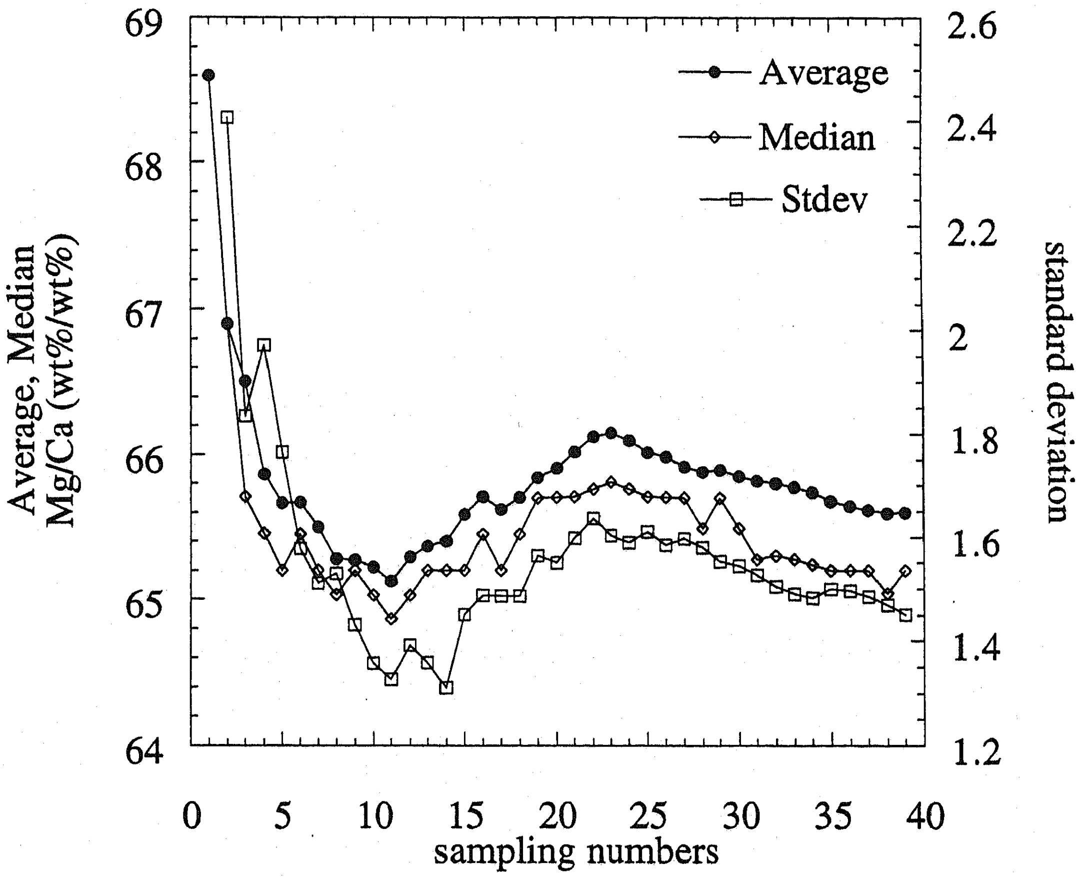


Figure 8: Repetition measurement of electron probe micro analysis. Closed circles indicate averaged Mg/Ca during repetition measurement numbers. Open diamonds indicate median of Mg/Ca. Open squares indicate standard deviation of Mg/Ca.

data to Mg/Ca ratio which measured by wet-chemical measurements (e.g. ICP-AES). Because, the dissolved solution of whole tests were used for wet-chemical method. The Mg content of solution probably will indicate close to the average Mg content of whole chamber rather than median value.

b. Calibration between temperature and average Mg/Ca measured using EPMA

The result of foraminiferal Mg/Ca of temperature experiments with *P. opercularis*, measured by EPMA is shown in Figure 9 and Table 3. Mg contents increase with temperature linearly with a regression of:

$$\mathrm{Mg/Ca_{EPMA}}\ (\mathrm{mmol/mol}) = 2.31\mathrm{Temperature}(^\circ\mathrm{C}) + 74.8 \qquad r=0.960 \qquad (6)$$

where r is correlation coefficient. The linear regression equation is different from the regression equation (4) of wet chemical measurement, because measurement method and standard material were different each other. Therefore, temperature must be calculated from EPMA Mg/Ca data by this equation (6).

Each measured Mg/Ca indicated large deviation, although the specimens were cultured under well-controlled temperature environments. This suggests that the Mg contents have heterogeneous distribution in foraminiferal test.

c. Mg distribution within single chamber wall

Partial measurements were made for the ultimate chamber of cultured *P. opercularis*, which calcified under stable temperature condition (Figure 10). Only 7-9 points were measured, as only a very narrow area is available to measure at the ultimate chamber. The results, therefore, should be semi quantitative.

Mg/Ca values deviated from 30mmol/mol to 140 mmol/mol within one chamber. Mg/Ca distributions were different from inner to outer part in a single chamber. Mg/Ca at outer part

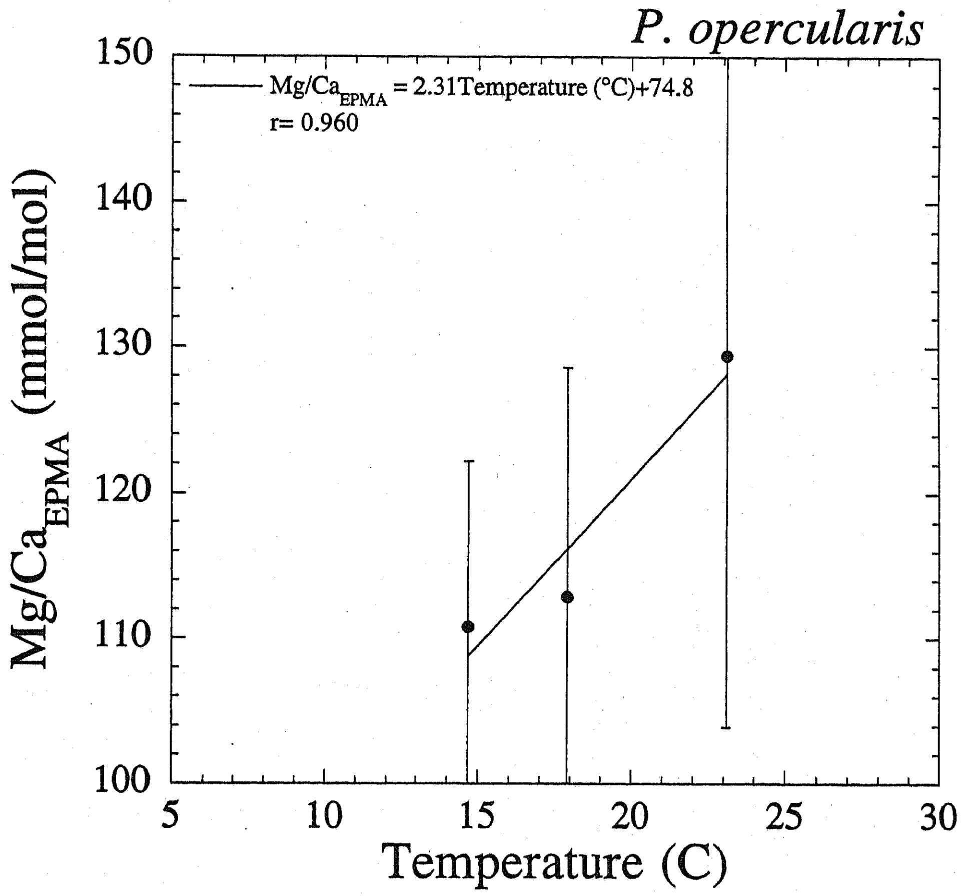


Figure 9: The calibration lines between temperature and Mg/Ca measured using electron probe. Closed circles indicate averaged Mg/Ca of each specimen which grown under well-controlled temperature. Solid line indicates regression equation. Each error bars indicate standard deviation.

Table 3: The calibration between temperature and Mg/Ca which measured by EPMA.

Temperature (°C)	Average of Mg/Ca (mmol/mol)	Standard Deviation
14.7	110.8	11.4
17.9	112.9	15.7
23.1	129.4	25.5

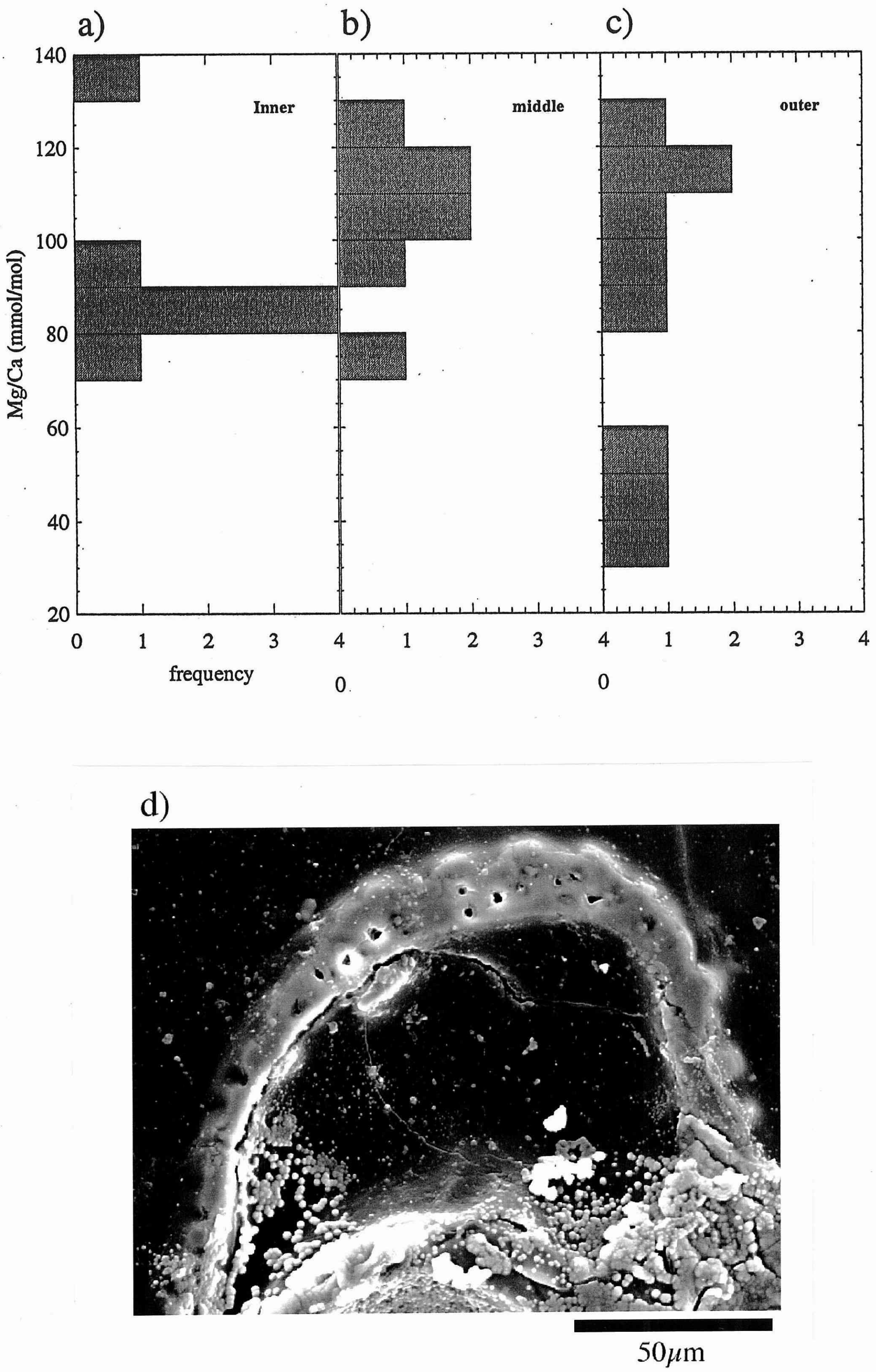


Figure 10: Heterogeneous distribution of Mg/Ca within ultimate chamber wall of cultured *P. opercularis*. Plots of a), b) and c) indicate the Mg/Ca distribution of inner, middle and outer part of the wall of single chamber respectively. SEM image of d) indicates measured chamber wall. Several halls can be observed which were volatilized by electron probe.

of a chamber showed lower value than those of middle or the inner part. Mg/Ca seemed to decrease from the inner part to the outer part. These results suggest that foraminiferal Mg contents have very irregular distribution within a single chamber, although the specimens were cultured under well-controlled temperature environments.

3.1.4 Isotopic composition of culture experiments

a. The check of roasting effect

At first, I checked measurement errors during preparation process. During sample preparation, roasting of calcite tests is a common procedure for removing organic matters (e.g. Bemis *et al.*, 1998). On the other hand, some papers measured foraminiferal isotopic composition without roasting step (e.g. Bijma *et al.*, 1998).

The roasted and raw foraminiferal $\delta^{18}O$ and $\delta^{13}C$ are shown in Figure 11. Three foraminiferal species of living *P. nipponica*, living *Q. yabei* and fossil *G. sacculifer* were used for checking roasting problem. Fossil materials may contain less organic matters than living tests.

The roasted *P. nipponica* indicated more scattered distribution than non-roasted specimens. The lighter isotopic composition of both $\delta^{18}O$ and $\delta^{13}C$ were obtained from roasted specimens. These data showed that $\delta^{18}O$ of roasted specimens were particularly different from non-roasted specimens. $\delta^{18}O$ of non-roasted specimens of *Q. yabei* indicated similar value. However, roasted specimens have large deviation on $\delta^{18}O$. $\delta^{13}C$ of *Q. yabei* indicated similar value between roasted and non-roasted tests. Both $\delta^{18}O$ and $\delta^{13}C$ of roasted specimens became lighter than non-roasted specimens for fossil *G. sacculifer.*

The changes in values between $\delta^{18}O$ and $\delta^{13}C$ were proportional with ratio of 2:1 for *P. nipponica* and *G. sacculifer*. The reason of proportional change of $\delta^{18}O$ and $\delta^{13}C$ might be due to the effect of water, generally. Water may be decomposed from organic matter by roasting process. Since *P. nipponica* were living samples, many organic matters still remained within tests. The deviation range of *G. sacculifer* is too smaller than that of *P. nipponica*. However,

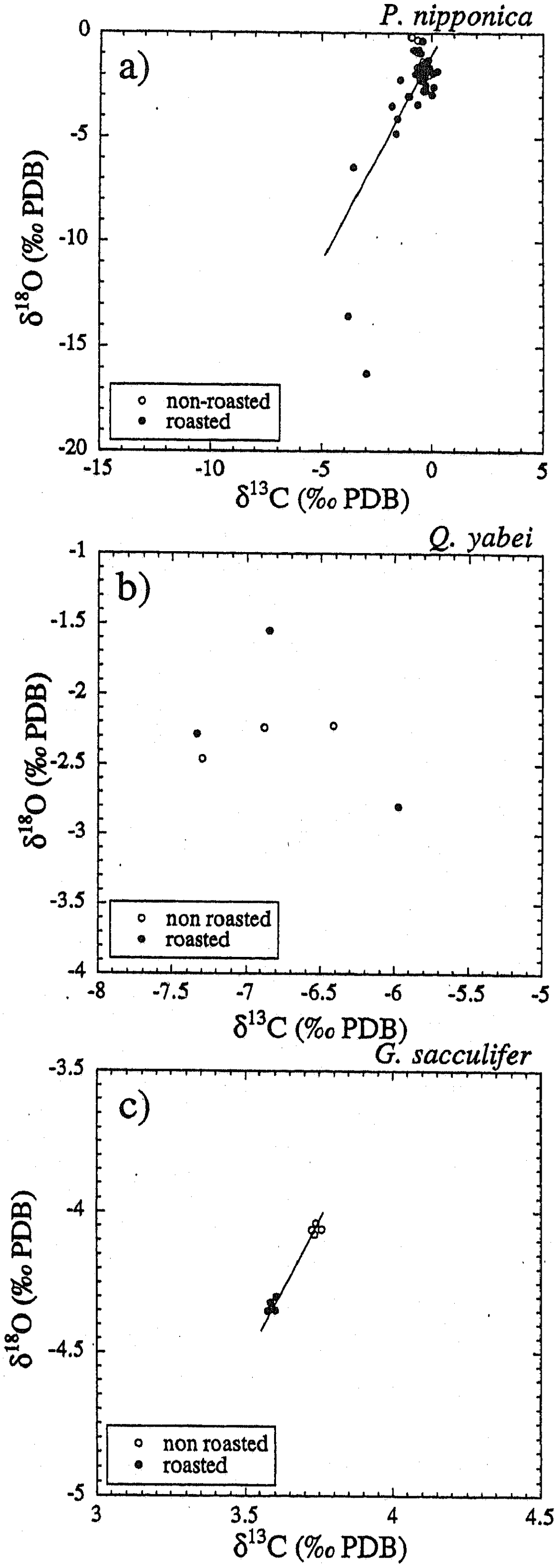


Figure 11: Roasting effect on foraminiferal oxygen isotopic composition. Open circles show non roasted specimens. Close circles indicate roasted specimens. Solid lines indicate 1:2 ratio of change between $\delta^{18}O$ and $\delta^{13}C$. a) *P. nipponica* b) *Q. yabei* c) *G. sacculifer.*

the deviations suggest that the fossil *G. sacculifer* have some organic material. Also these is a possibility of some inter crystalline organic material or intra crystalline organic material remaining.

The deviations of *Q. yabei* indicate a different trend with other species. The deviations of *Q. yabei* are not so systematic when compared with other two species. It means that water effect is not the most important source of deviation for *Q. yabei.* Many complex chemical reactions may occur during roasting operation under high temperature. Therefore, some chemical materials which have oxygen were made from organic material. These chemical materials, perhaps, affected oxygen isotope of original calcite of *Q. yabei.*

These results suggested that roasting procedure certainly caused a change original isotopic composition of the test. Therefore, all isotopic measurements were carried without roasting step during this study.

b. Oxygen isotopic composition of temperature controlled experiments

The results of the value of $\delta^{18}O_c$-$\delta^{18}O_w$ of temperature experiments for *A. beccarii* and *R. bradyi* are shown in Figure 12 and Table 4.

The value of $\delta^{18}O_c$-$\delta^{18}O_w$ became lighter, temperatures became higher for both species. The value of $\delta^{18}O_c$-$\delta^{18}O_w$ had very strong relationship with culture temperature. These isotopic data of $\delta^{18}O_c$-$\delta^{18}O_w$ are described by linear equations:

R. bradyi,

$(\delta_c-\delta_w)=-0.179$ Temperature (°C) $+3.16$ $\quad r=0.993 \quad$ (7)

A. beccarii,

$(\delta_c-\delta_w)=-0.168$ Temperature (°C) $+2.89$ $\quad r=0.999 \quad$ (8)

where *r* indicate regression coefficient. Both the slope and the intercept were similar for the two species. These results suggested that foraminiferal oxygen isotopic composition mainly depend on temperature. Species wise differences were not so obvious.

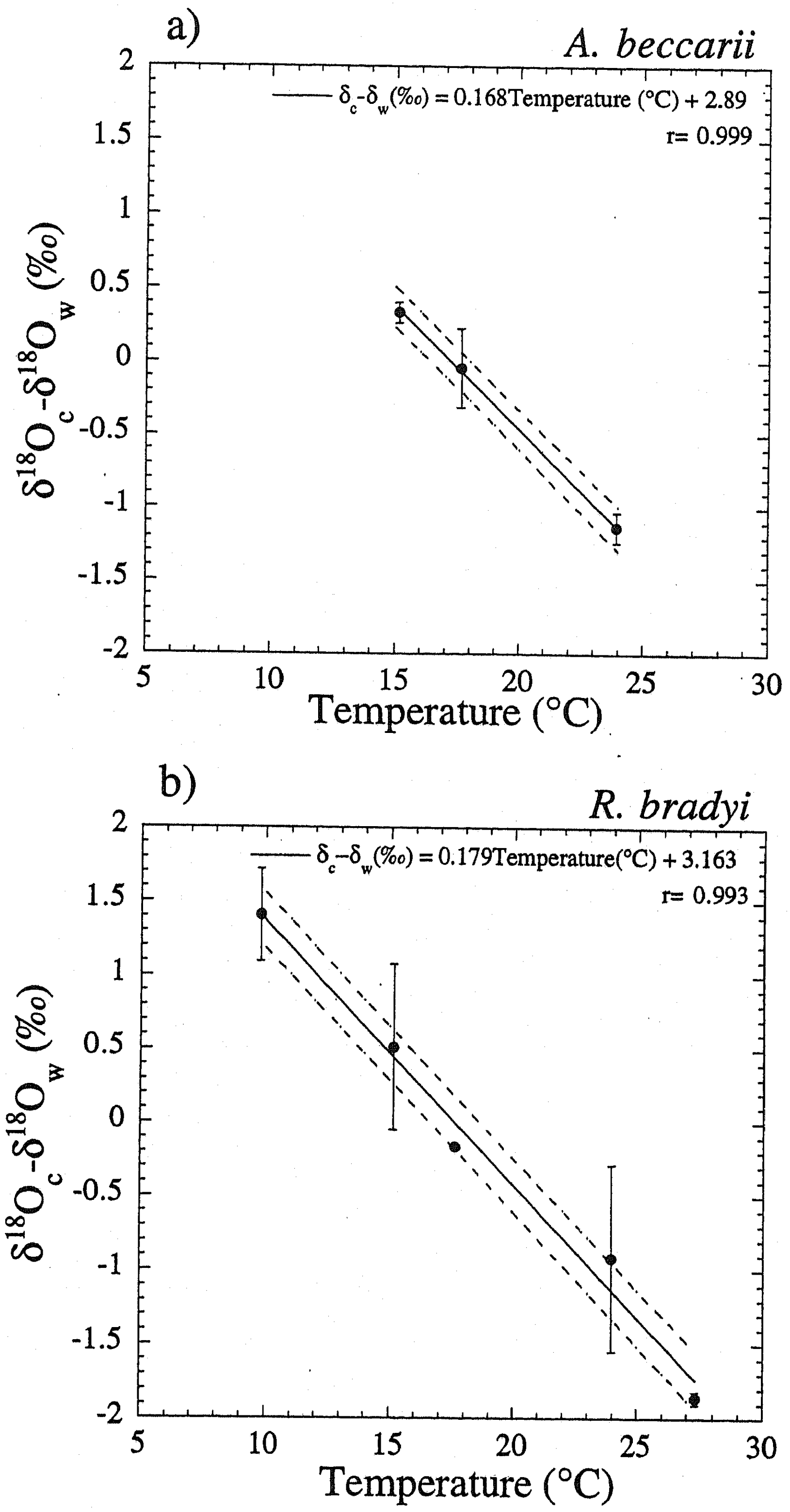


Figure 12: Oxygen isotopic composition of cultured specimens, grown under various temperature conditions. Closed squares indicate averaged δ_c- δ_w value of the same temperature condition. Each error bars indicate standard deviation. Solid lines indicate regression equations. Dashed lines show forecast interval at the 95% confidence level. a) *A. beccarii* b) *R. bradyi.*

Table 4: Isotopic composition of cultured specimens.

Temperature (°C)	S.D.	Salinity (‰)	water $\delta^{18}O$ (‰SMOW)	foram $\delta^{18}O$ (‰PDB)	S.D.	δ_c-δ_w	S.D
Ammonia beccarii							
Temperature experiments							
15.2	0.3	26.06	-1.37	-0.838	0.07	0.262	0.07
17.6	0.9			-1.218	0.27	-0.118	0.27
24.0	0.4			-2.306	0.10	-1.206	0.10
Salinity experiments							
24.0	0.4	18	-3.55	-4.254		-0.974	
		21.48	-2.63	-3.553		-1.193	
		26.06	-1.37	-2.306	0.10	-1.206	0.10
		27.78	-0.9	-1.549	0.22	-0.919	0.22
		33.32	0.68	0.168	0.14	-0.702	0.05
Salinity experiments with artificial seawater							
24.0	0.4	18	-8.14	-8.011	0.52	-0.141	0.52
		25.6	-8.47	-7.863	0.55	0.337	0.55
		30.3	-8.17	-7.506		0.394	
Rosalina bradyi							
Temperature experiments							
9.8	0.1	36.56	-0.72	0.887	0.31	1.337	0.31
15.2	0.3			-0.007	0.56	0.443	0.56
17.6	0.9			-0.683		-0.233	
24.0	0.2		-0.7	-1.416	0.63	-0.986	0.63
27.3	0.1		-0.72	-2.381	0.05	-1.931	0.05
Salinity experiments							
24.0	0.2	29	-1.92	-2.758		-1.108	
		36.68	-0.7	-1.416	0.63	-0.986	0.63
		36.93	-0.68	-1.861	0.25	-1.451	0.25
		38.36	-0.46	-0.862	0.27	-0.672	0.27

S.D.=Standard Deviation

c. Oxygen isotopic composition of salinity controlled experiments

The results of foraminiferal $\delta^{18}O$ and the values of $\delta^{18}O_c$-$\delta^{18}O_w$ of salinity experiments for *A. beccarii* and *R. bradyi* are shown in Figure 13 and Table 4.

The $\delta^{18}O$ values changed with salinity for both species (Figure 13a and 13c). The $\delta^{18}O$ of both species got heavier with the salinity becoming higher. The relationship between foraminiferal $\delta^{18}O$ and salinity is very clear. However, the values of $\delta^{18}O_c$-$\delta^{18}O_w$ indicated no systematic change through all salinity conditions (Figure 13b and 13d).

These results suggest that foraminiferal $\delta^{18}O$ were affected not by salinity but by oxygen isotopic composition of ambient water, because salinity of culture water related with $\delta^{18}O$ of culture water directly as shown in Figure 2b. The values of $\delta^{18}O_c$-$\delta^{18}O_w$ were cancelled the water $\delta^{18}O$ influence to foraminiferal $\delta^{18}O$. Therefore, the values of $\delta^{18}O_c$-$\delta^{18}O_w$ indicated similar values through all salinity conditions.

d. Oxygen isotopic composition of salinity controlled experiments with artificial seawater

The results of foraminiferal $\delta^{18}O$ and the values of $\delta^{18}O_c$-$\delta^{18}O_w$ of salinity experiments for *A. beccarii with* artificial seawater are shown in Figure 14 and Table 4.

Both foraminiferal $\delta^{18}O$ and the values of $\delta^{18}O_c$-$\delta^{18}O_w$ indicated similar values from 18‰ to 30‰.

Artificial culture water should take water $\delta^{18}O$ contents of distilled water even among different salinity conditions because artificial seawater made from complex salt crystals and distilled water with same oxygen isotopic composition. Therefore, oxygen isotopic values of artificial seawater indicate same value as distilled water. This is why foraminiferal $\delta^{18}O$ grown under different salinity of artificial water indicated similar value.

This result indicated that foraminiferal oxygen isotopic composition was not affected by quantity of ions but by water oxygen isotopic composition. This fact reinforced the result of salinity experiment.

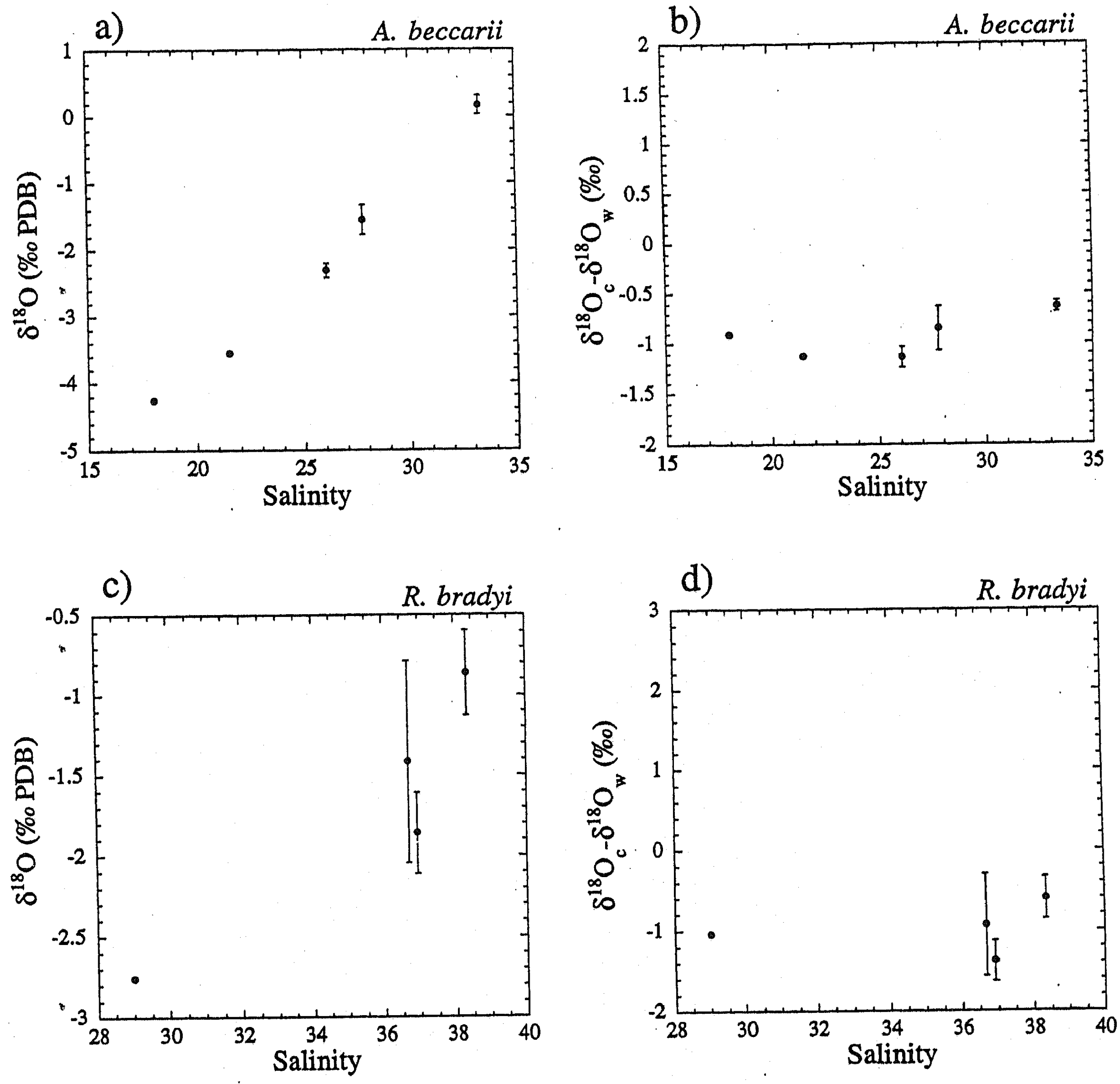


Figure 13: Oxygen isotopic composition of cultured specimens grown under various salinity conditions. Closed circles indicate average value of each condition. Each error bars indicate standard deviation. a) δ^{18}O value of *A. beccarii* b) δ_c- δ_w value of *A. beccarii* c) δ^{18}O value of *R. bradyi* d) δ_c- δ_w value of *R. bradyi.*

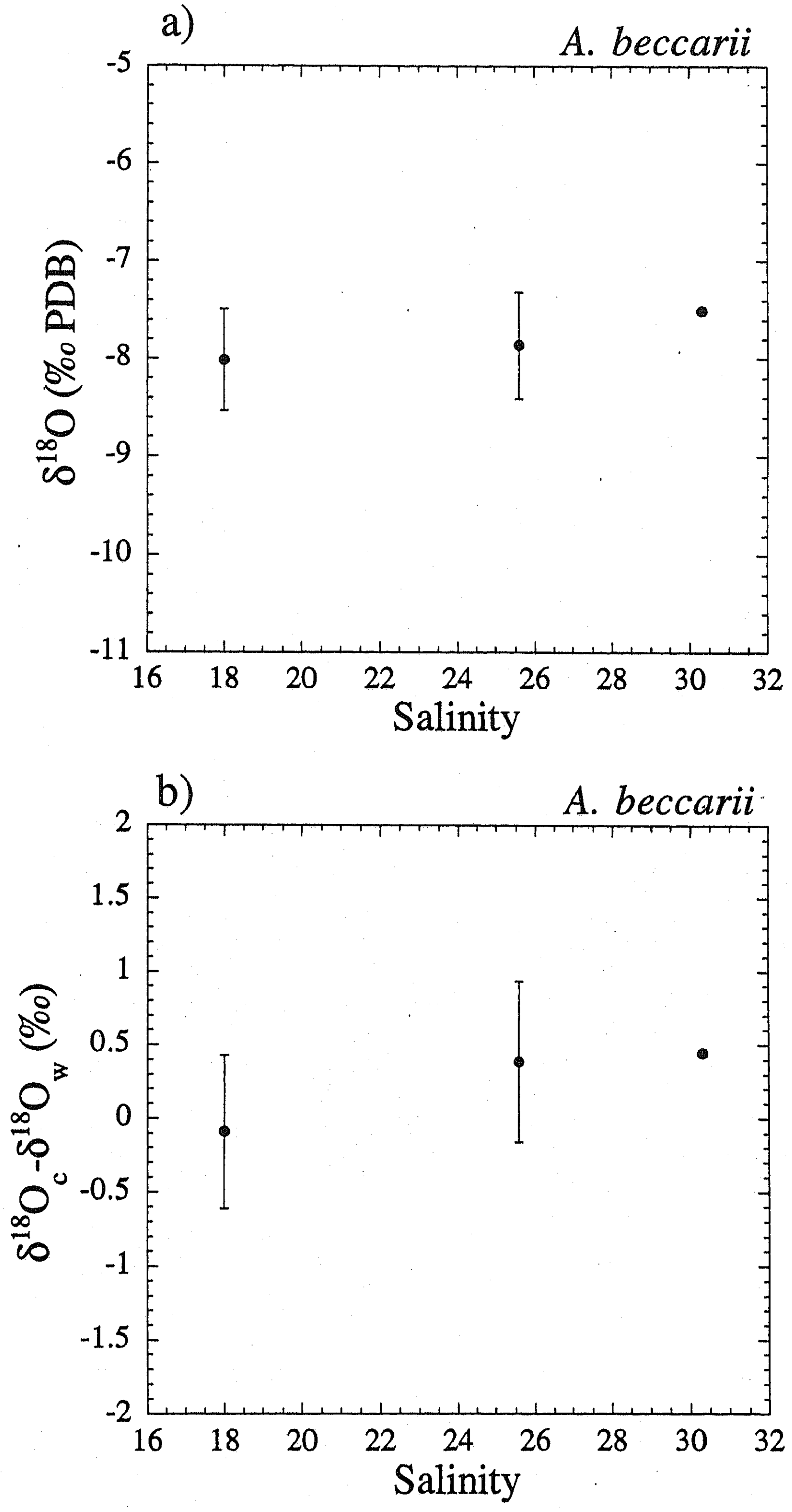


Figure 14: Oxygen isotopic composition of cultured specimens which grown under various salinity conditions with same water oxygen isotopic composition. Closed circles indicate averaged value of each condition. Each error bars indicate standard deviation. a) $\delta^{18}O$ value of *A. beccarii* b) δ_c- δ_w value of *A. beccarii*

3.2. Results of natural populations

3.2.1 Seasonal change of Mg/Ca

The seasonal variation of foraminiferal Mg/Ca ratios of *P. opercularis* and *Q. yabei* are shown with sea surface temperature (Figure 15 and Table 5).

The Mg/Ca ratios of both species varied similar to sea surface temperature through the year. From May to September, Mg/Ca of both species increased. From September to March, each Mg/Ca ratios decreased. And, from March to May, Mg/Ca increased, again.

In these figures, right vertical axes indicate foraminiferal Mg/Ca and are comparable to left vertical axes that indicate sea surface temperature corresponding to the equations of (4) and (5).

For *P. opercularis*, foraminiferal Mg/Ca indicate slightly low value from sea surface temperature through the year (Figure 15a). The annual range of the Mg/Ca values is similar to one of the sea surface temperature.

For *Q. yabei*, the annual range of foraminiferal Mg/Ca is smaller than one of the sea surface temperature.

These results suggest that the temperature variations were recorded in foraminiferal chamber wall as Mg/Ca ratios. However, the recorded temperature is different for each species. Foraminiferal temperature may carried species such ecological character as growth rate, life span and suitable environment to calcify their tests.

3.2.2 Mg/Ca variation within single specimens

Mg/Ca variation within single specimen of *P. opercularis* which grown at tide pools of Omaezaki cape is shown in Figure 16 and Table 6.

I gave the numbers to each chamber for comparing Mg/Ca ratios at each chamber. The number of the ultimate chamber is 1. The number of the penultimate chamber is 2. In this way, I gave the numbers from 1 to 7 for the specimen which was collected at 20, September,

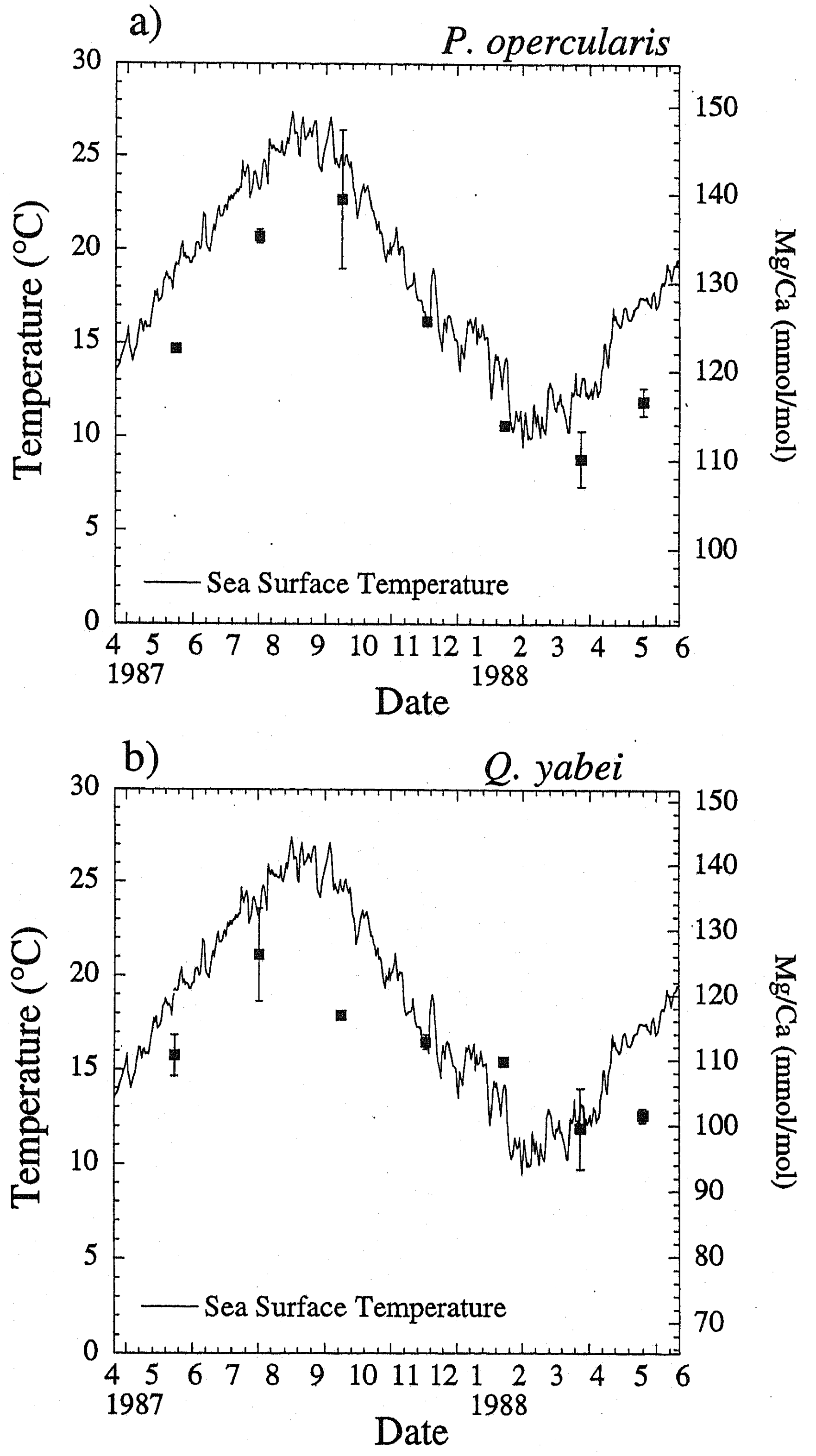


Figure 15: The seasonal change of Mg/Ca at Omaezaki Cape. Solid lines indicate sea surface temperature recorded at the nearest meteorological station. Closed squares indicate averaged Mg/Ca of each species collected on same day. Each error bars indicate standard deviation. The right axes of foraminiferal Mg/Ca is readable as temperature on each plot. The range of Mg/Ca axes were calculated from Mg/Ca thermometry of each species. a) *P. opercularis* b) *Q. yabei.*

Table 5: Seasonal change of Mg/Ca at Omaezaki and difference of temperature

Date	Average temperature(°C)	Mg/Ca (mmol/mol)	Average Mg/Ca (mmol/mol)	S.D.	Calculated temperature (°C)	difference from real tempaerature (°C)
P. opercularis						
17 May 1987	17.2	122.4	122.4		14.7	-2.5
20 Jul 1987	22.6	135.8	135.2	0.8	20.7	-1.9
20 Sep 1987	25.7	145	139.4	7.8	22.7	-3.0
23 Nov 1987	18.7	125.6	125.6		16.2	-2.5
21 Jan 1988	14.8	113.8	113.8		10.6	-4.2
19 Mar 1988	11.7	110.1	110.1	3.1	8.8	-2.9
4 May 1988	17.2	115.5	116.6	1.5	11.9	-5.3
Q. yabei						
17 May 1987	17.2	109.6	110.7	3.2	15.7	-1.5
20 Jul 1987	22.6	126.1	126.1	7.1	21.1	-1.5
20 Sep 1987	25.7	116.8	116.8		17.9	-7.8
23 Nov 1987	18.7	113.6	112.8	1.1	16.5	-2.2
21 Jan 1988	14.8	109.8	109.8		15.4	0.6
19 Mar 1988	11.7	103.9	99.5	6.1	11.9	0.2
4 May 1988	17.2	100.8	101.5	1	12.6	-4.6

S.D.=standard deviation

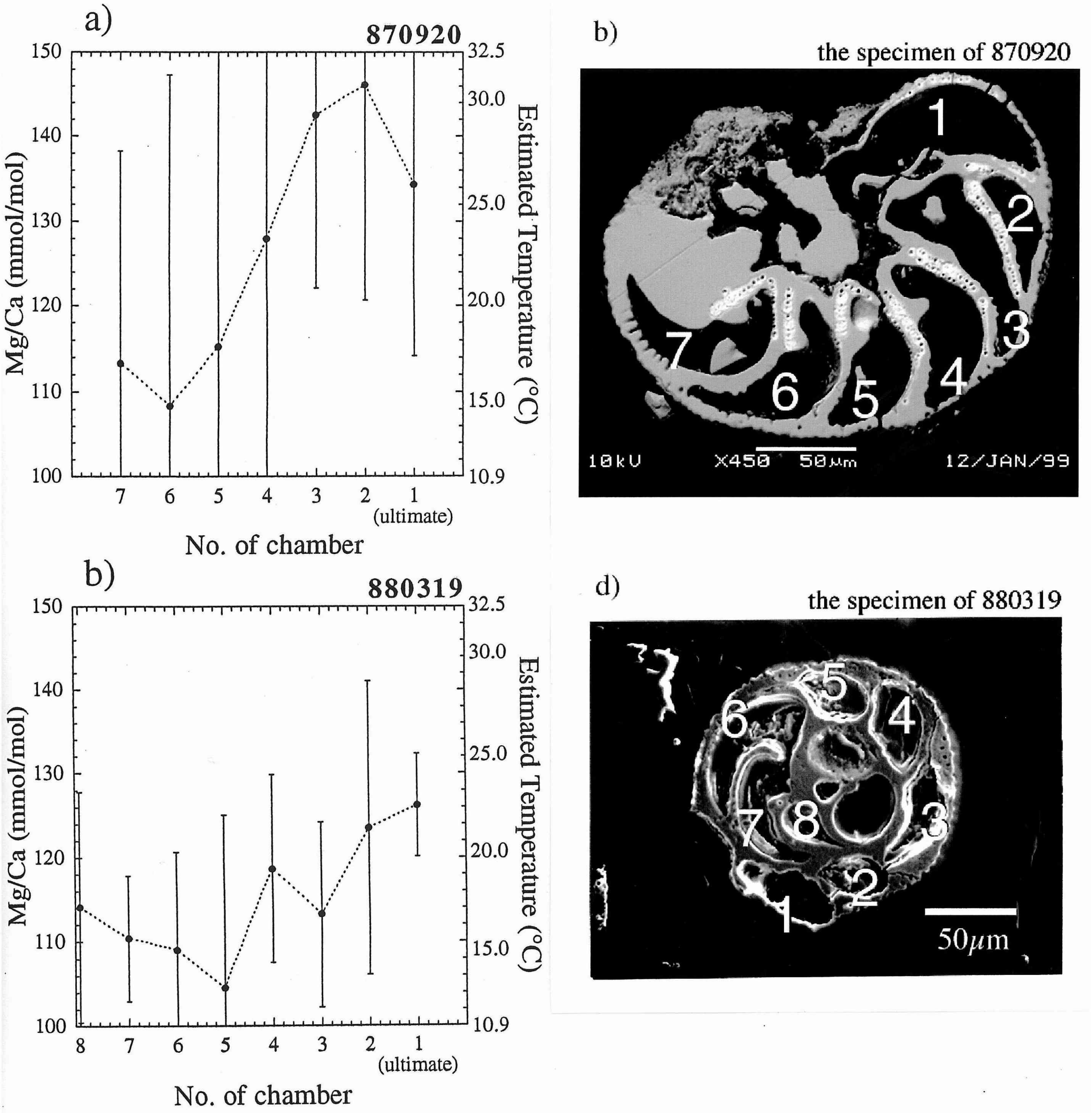


Figure 16: Chamber wise Mg/Ca variation within single specimen. Each closed circle indicates averaged Mg/Ca of each chamber. Error bars show the standard deviation of each chamber. Dashed lines connect averaged Mg/Ca between neighbored two chambers The number of chamber is given from 1 to 7 for the specimen which collected on 870920 and from 1 to 8 for the specimen which collected on 880319. These numbers are corresponding to the numbers which wrote on SEM images. a) *P. opercularis* which collected 870920 at Omaezaki cape. The specimen's SEM image is b). c) *P. opercularis* which collected 880319 at Omaezaki cape. The specimen's SEM image is d).

Table 6: The Mg/Ca of each chamber and calculated temperature.

No. of chamber	Averaged Mg/Ca (mmol/mol)	Standard deviation	Number of measurement	Calculated temperature (°C)
870920				
1 (ultimate)	134.4	20.2	31	25.8
2	146.2	25.5	46	30.9
3	142.6	20.4	42	29.4
4	128.0	33.4	46	23.0
5	115.3	47.5	45	17.5
6	108.4	39.0	39	14.6
7	113.3	24.9	33	16.7
880319				
1 (ultimate)	126.2	6.1	3	22.3
2	123.6	17.5	20	21.1
3	113.2	11.0	11	16.7
4	118.7	11.1	13	19.0
5	104.6	20.5	16	12.9
6	109.1	11.6	13	14.8
7	110.4	7.4	12	15.4
8	114.1	13.7	8	17.0

1987 (Figure 16a and 16b) and from 1 to 8 for the specimen which collected 19, March, 1988 (Figure 16c and 16d).

Foraminiferal Mg/Ca of chambers have different value. On the specimen which was collected on September, the Mg/Ca ratios increased from about 112 mmol/mol to about 146 mmol/mol from chamber No. 7 to No. 1 chamber. The Mg/Ca of the No. 1 chamber is lower than No. 2 chamber. The Mg/Ca value of No. 1 chamber is about 134 mmol/mol. The variation of Mg/Ca from older chamber to the newer chamber is similar to the temperature variation from early spring to fall. On the specimen which was collected on March, the Mg/Ca ratios decreased from No. 8 chamber to No. 5 chamber. The Mg/Ca ratios increased from chamber No. 5 to the No. 1 chamber. The lowest Mg/Ca value takes about 104 mmol/mol. The highest Mg/Ca is about 126 mmol/mol. This variation of foraminiferal Mg/Ca values from older chamber to new chamber is similar to the variation of the sea surface temperature from winter to spring.

These results suggested that Mg/Ca value of single chamber recorded the temperature when each chamber wall has calcified. Therefore, the Mg/Ca of whole chamber is integrated value of single chambers, if someone measures one specimen.

3.2.3 Mg/Ca and Sr/Ca of natural populations

The Mg/Ca of natural populations for four species, *R. bradyi*, *P. opercularis*, *Q. yabei*, *C. lobatulus*, are shown on Figure 17a, 17c, 17e and 17g. These foraminiferal Mg/Ca were compared with the average temperature for the 7, 10, 15, 30, 60, 120 and 180 days before sampling. Overall, the average temperature for the 30 days was the most comparable with Mg/Ca. On the average temperature of each period, the Sr/Ca ratios showed no clear relationship with average temperature. Therefore, both Mg/Ca and Sr/Ca of natural populations were compared with average temperature for the 30 days before sample collecting.

The Mg/Ca values indicated different range among four species. The lowest value distributions of Mg/Ca were indicated by *C. lobatulus*. *P. opercularis* and *Q. yabei* had the

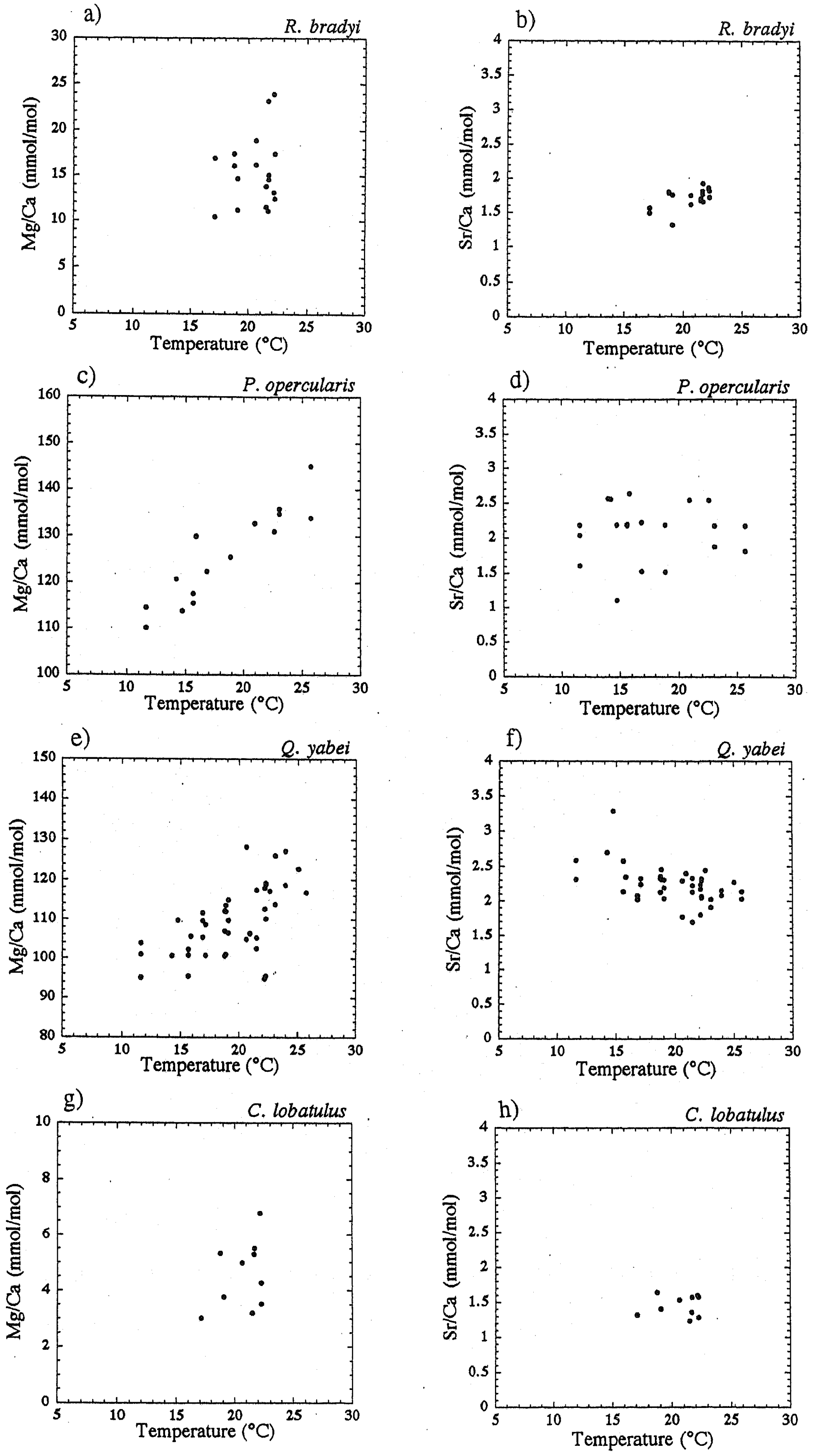


Figure 17: Mg/Ca of natural population. Closed circles indicate the result of each measurement. a), c), e) and g) indicate about Mg/Ca. b), d), f) and h) show Sr/Ca. a) and b) *R. bradyi*', c) and d) *P. opercularis*, e) and f) *Q. yabei*, g) and h) *C. lobatulus*.

highest distribution of Mg/Ca. *Rosalina bradyi* indicated slightly higher Mg/Ca than *C. lobatulus*.

The ranges of Mg/Ca for P. opercularis and Q. yabei were similar to the results of culture experiments (Figure 4d and 4e). The value distribution of Sr/Ca was higher than culture results for *R. bradyi* (Figure 4c).

Mg/Ca of all species appear to increase with temperature. For, *R. bradyi*, *P. opercularis* and *Q. yabei* Mg/Ca seemed to more scattered than culture results. Mg/Ca of *C. lobatulus* indicated positive relation with temperature. This relation was also not so clear as experimental results of other species.

These results indicate that the Mg/Ca of natural population were also derived by temperature. However, some complex factor may affect to foraminiferal Mg/Ca.

The Sr/Ca of natural populations for four species are shown on Figure 17b, 17d, 17f and 17h. These foraminiferal Sr/Ca were compared with the average temperature for the 30 days before sampling.

The Sr/Ca values were similar among four species. Almost Sr/Ca of all species plotted from 1mmol/mol to 3mmol/mol.

The range of Sr/Ca for *R. bradyi* and *P. opercularis* were likely to the results of culture experiments (Figure 6c and 6d). The value distribution of Mg/Ca was higher than culture results for *Q. yabei* (Figure 6e).

Sr/Ca of all species indicated no systematic change from low temperature to high temperature. Only Sr/Ca of *R. bradyi* have slightly positive relation. On the other hand, Sr/Ca of *Q. yabei* indicate slightly negative relationship to temperature. This is opposite to experimental result (Figure 6e).

These results suggest that foraminiferal Sr/Ca were not affected by temperature under natural environments. This is also the same tendency as that of culture experiments.

3.2.4 Oxygen isotopic composition of natural populations

The $\delta^{18}O$ values of *P. opercularis*, *Q. yabei*, *R. bradyi*, *E. crispum* and *C. lobatulus* of natural populations are compared with the average temperature for the 30 days before sampling (Figure 18).

The $\delta^{18}O$ indicated biased values at similar temperature (Figure 18a). The $\delta^{18}O$ distributed from –3.5 to 0 at 21°C. $\delta^{18}O$ values of the specimens lighter less than 20μg specimens show less variation than those of all size of specimens (Figure 18b). $\delta^{18}O$ of natural population show weak positive relation with average temperature.

The values of $\delta^{18}O$ of the different size of *C. lobatulus* which collected on fall of 1995 were compared with the average temperature of the 30 days before sampling for discussing size effect (Figure 19). Total values including small and large size took wide range of $\delta^{18}O$ values with temperature. The deviation of $\delta^{18}O$ reached 3.5‰ at 20°C. However, smaller sized specimens less than 20μg show more positive relations with temperature than larger specimens.

Oxygen isotopic compositions of the different part of the test were compared with the 30 days average temperature before sampling at autumn for *C. lobatulus* (Figure 20). The values of $\delta^{18}O$ of the part of ultimate and penultimate chambers indicate positive relationship with temperature. However, the value of $\delta^{18}O$ of the other chambers of tests did not indicate clear relations with temperature.

It is difficult to consider that the $\delta^{18}O$ of natural population were controlled only by temperature. Foraminiferal $\delta^{18}O$ will be affected not only by temperature but also by water $\delta^{18}O$ (Figure 12 and 13). The weak relationship between foraminiferal $\delta^{18}O$ and temperature may be caused by the effect of water $\delta^{18}O$ and others. These results suggest that foraminiferal $\delta^{18}O$ which grown under such biased environment as rocky shore are difficult to apply as temperature proxy alone, although the temperature relationship were clear (Figure 12).

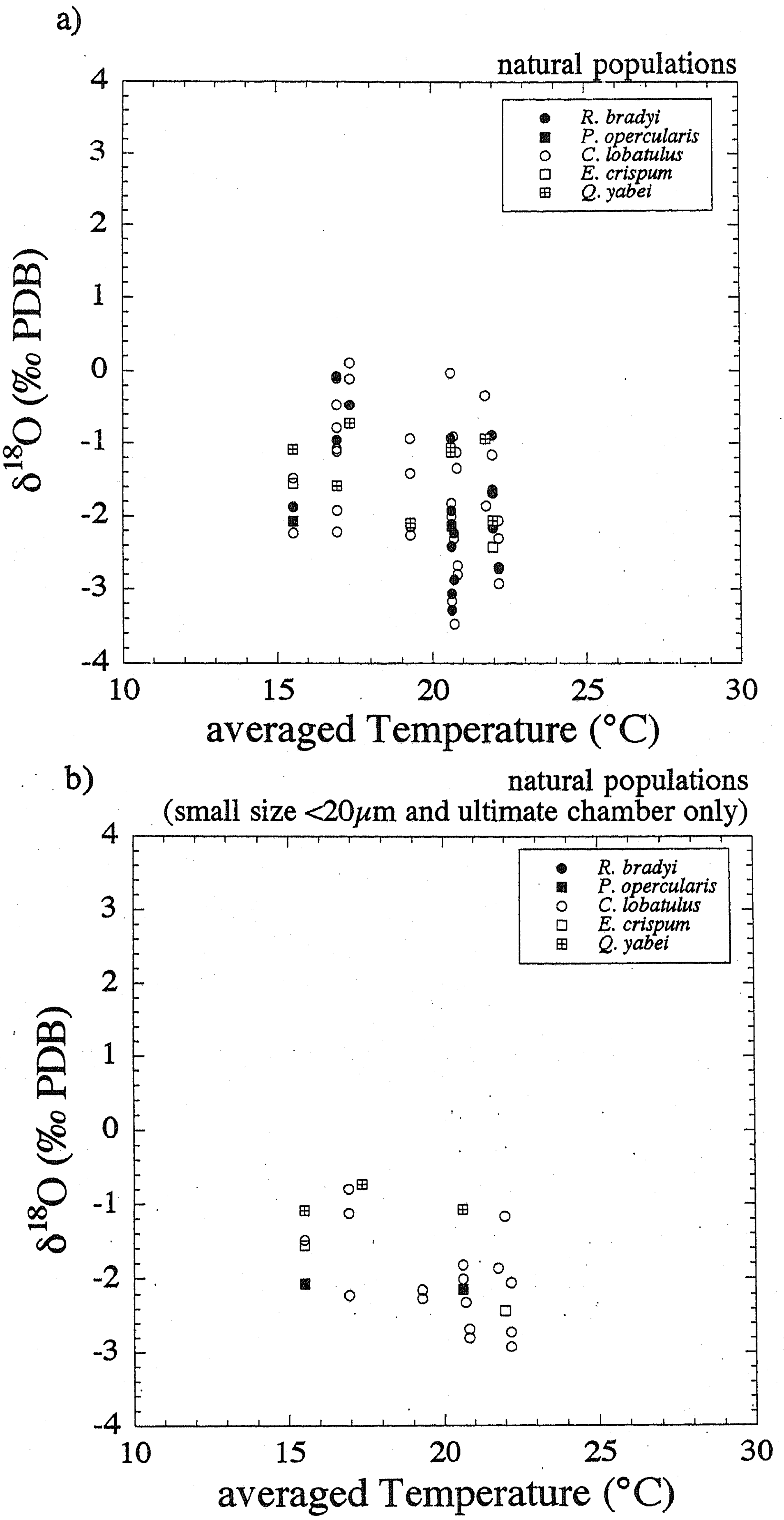


Figure 18: Oxygen isotopic composition of natural population. Each point indicate each measurement. a) all measured $\delta^{18}O$ value plotted. b) small weight specimens only plotted.

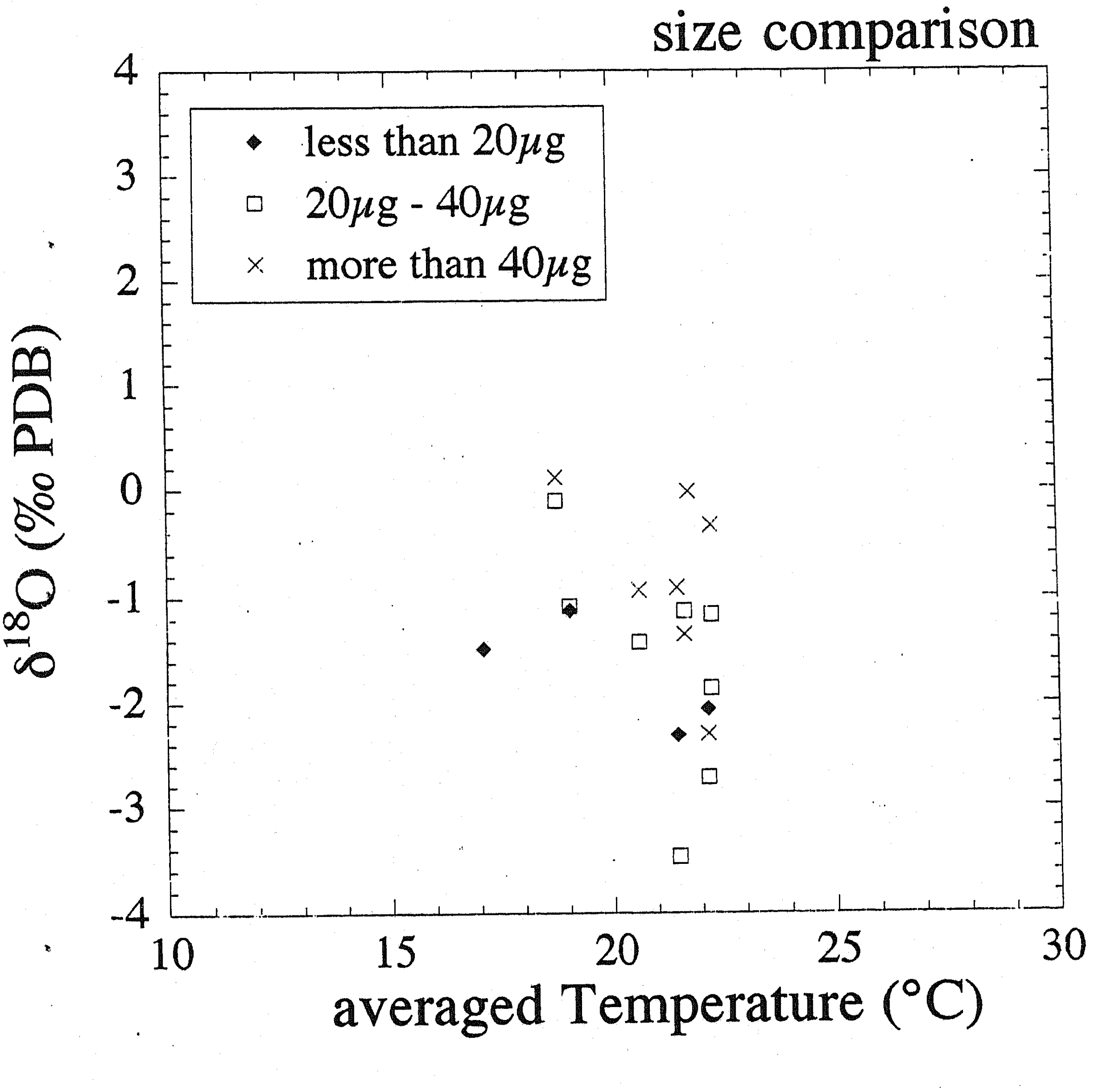


Figure 19: Size comparison of oxygen isotopic composition for natural population. Each point shows each measurement. Closed diamonds indicate the specimen which is less than 20μg. Open squares indicate the δ^{18}O value which weighs from 20μg to 40μg. Cross indicates the specimens which were heavier than 40μg.

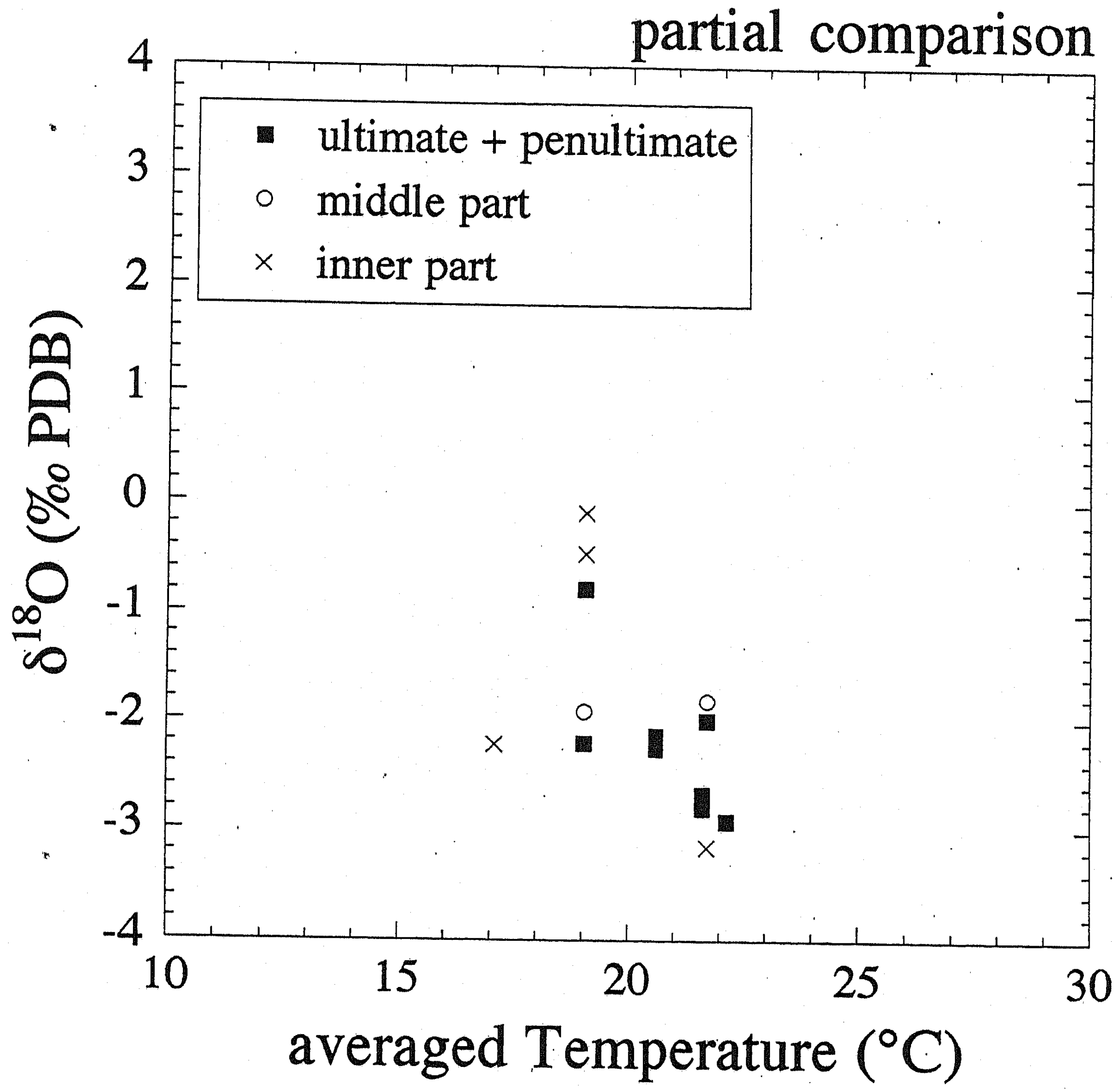


Figure 20: Partial difference of oxygen isotopic composition for natural population. A point shows the single measurement. Closed squares indicate δ^{18}O value of ultimate and penultimate chambers. Open circles indicate two chambers which added just before penultimate chamber added. Cross indicates inner part of the test.

4. Discussion

4.1 Evaluation of culture experiment

It is important that experimental results should reproduce natural environmental conditions. Physico-chemical conditions of culture water were mostly similar to those of natural environments except for substrates or daily fluctuation of environmental factors.

Substrate materials and shapes sometime have an impact on the shell shape of attached form foraminifers (e.g. *Rosalina bradyi*). However, water chemistry was same before and after experiments. Substrates will give no influence on water chemistry. Therefore, the uptake of magnesium and strontium will not be changed by substrates' effects. The oxygen isotopic composition of water indicated small fluctuation during experimental periods. However, this change may be due to the evaporation and condensation of water. Therefore, the differences in substrate have no influence on experimental results of Mg/Ca, Sr/Ca and oxygen isotopic composition.

Temperature, salinity and oxygen isotopic composition of water are the most important factors in this study. These will fluctuate every moment in natural environments. The sea surface temperature change daily and seasonally. Salinity and oxygen isotopic composition will be altered by rainfall and flood. The natural populations calcify their tests under such unstable environments. Therefore, the chemical compositions and isotopic compositions of natural populations will record very biased environmental information. On the other hand, experimental specimens experienced constant environment. Therefore, the recorded chemical and oxygen isotopic compositions of foraminifera were very different between the cultured specimens and natural populations. This difference of recorded information does not indicate the difference of calcification mechanisms but depend on the difference of experienced life history among specimens.

4.2 Mg/Ca thermometry

Mg/Ca thermometer for shallow water foraminifera has been established by Toyofuku *et al.* (2000) with culture experiments. The equations which were obtained from the equation of culture data from (1) to (5), are:

A. beccarii,

Temperature (°C) = 10.47 Mg/Ca (mmol/mol) + 1.476 (9)

The standard error is ±2.1°C

E. crispum,

Temperature (°C)= 8.00 Mg/Ca (mmol/mol) – 2.832 (10)

The standard error is ±1.4°C

R. bradyi,

Temperature (°C)=1.16 Mg/Ca (mmol/mol) + 10.60 (11)

The standard error is ±0.84°C

P. opercularis

Temperature (°C)=0.474 Mg/Ca (mmol/mol) + 43.36 (12)

The standard error is ±0.96°C

Q. yabei

Temperature (°C)=0.347 Mg/Ca (mmol/mol) + 2.267 (13)

The standard error is ±0.52°C

The resolution of equation is different for different species. For instance, on equation for *Q. yabei* (13) which show the lowest value of inclination, 1mmol/mol change of Mg/Ca correspond 0.35°C change of temperature. However, on equation of *A. beccarii* (9) which has the highest value of inclination, 1mmol/mol change of Mg/Ca indicate 10.5°C changes in temperature. Therefore, the Mg/Ca thermometer of high-Mg species will be more sensitive for paleotemperature reconstruction than those of low-Mg species. However, the dissolution of test carbonates change in relation to Mg contents of the test (Brown and Elderfield, 1996).

This means that high-Mg calcite is easy to dissolve. Therefore, it is important to know whether or not the material for measurements preserves original Mg content.

I tried to apply Mg/Ca thermometer to natural population. The Mg/Ca of *P. opercularis* and *Q. yabei* are available to adopt Mg/Ca thermometry in this study. The foraminiferal temperatures calculated by Mg/Ca thermometry (equation 12 and 13) show similar seasonal pattern of change to sea surface temperature both for *Q. yabei* and *P. opercularis* (Figure 15, Table 5). However, estimated temperature from Mg/Ca thermometry for each species show different values from recorded temperature at the nearest meteorological station. This study suggests that discrepancy exist between field sample and environments because foraminiferal tests grow chamber by chamber as shown in Figure 16. Different Mg/Ca were indicated among chambers of single specimen both in spring and autumn. The Mg/Ca of the whole test, thus, reflects the integrated temperature experienced during the whole life of an individual foraminifer, at least the part of its life when it was actively calcifying. The average temperature of fall specimen is 22.6 °C. This value is very close to 22.7 °C which is calculated from seasonal samples of September (Figure 15, Table 5). The calculated temperature by Mg/Ca thermometry using with bulk tests is 3.1°C lower than the averaged sea surface temperature. However, the average temperature of spring specimen is 17.4 °C. This value is 5.6°C higher than the average sea surface temperature. This fact is difficult to explain in this moment. Sea surface temperature reached at about 13°C in early part of March. The temperature of tide pool may be several degrees higher during daytime than sea surface temperature (Figure 21). However, this contradicts to the general trend of seasonal variation of *P. opercularis*. These results suggest that Mg/Ca of the specimen show the integrated life history of a specimen.

The seasonal variation of Mg/Ca of *P. opercularis* and *Q. yabei* is similar to the annual change of sea surface temperature (Figure 15). However, the annual range of *Q. yabei* is smaller than *P. opercularis*. Therefore, the different factors may affect to Mg/Ca of these species (Table 6).

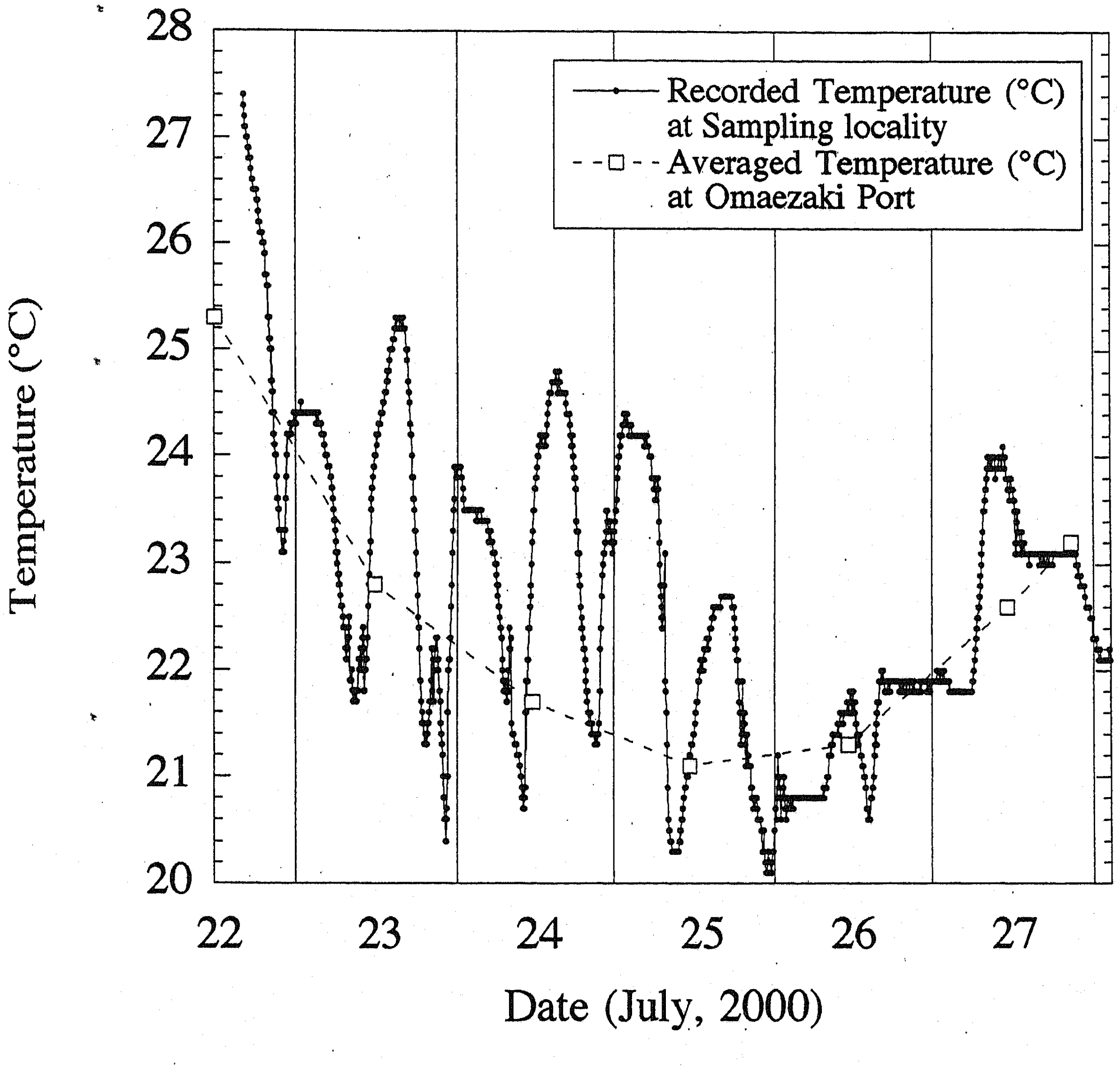


Figure 21: The diurnal variation of seawater temperature at tide pool and the nearest meteorological station. Small closed circles and the solid line indicate recorded temperature at tide pool. The temperature recorded every 30 min. Open squares and dashed line show the averaged temperature which observed at the closest meteorological station. The parallel lines that stand vertically to the horizontal axis indicate the border of each day.

For *P. opercularis*, the lowest and highest value of calculated temperatures are 8.8°C and 22.7°C respectively. The range of calculated temperature was 13.9°C. On the other hand, the lowest and highest temperature of recorded at observation station were 11.7°C and 25.7°C respectively. The range of temperature is 14.0°C. Therefore, the estimated annual range is very similar to recorded temperature at the nearest meteorological station. However, calculated temperature by Mg/Ca thermometry is lower than recorded temperature from 1.9°C to 5.3°C through a year. These samples were collected from tide pool where water temperature widely changes during day as shown in Figure 21. *P. opercularis* is supposed to add new chamber during the period of low temperature in a day. If such an assumption is correct, the estimated temperature from the foraminiferal Mg/Ca of *P. opercularis* should be lower value than the daily averaged temperature which measured at Omaezaki port.

For *Q. yabei,* the lowest and highest value of calculated temperatures are 11.9°C and 21.1°C respectively. The range of calculated temperature was 9.2°C. This annual range is less variable than recorded temperature and calculated temperature with *P. opercularis* (Figure 15 and Table 5). It is difficult to explain the reason why Mg/Ca values are low in comparison to measured value for *Q. yabei.* Because, the clear correlation was obtained between Mg/Ca and temperature through culture studies (Figure 4). It can be explained for the low variability of Mg/Ca in *Q. yabei,* if this species forms new chamber only within a limited range of temperatures. It is probable that *Q. yabei* can not calcify both the warmest season in summer and the coldest season in winter. It is needed to collect more seasonal data on the Mg/Ca values. It may also be required to find when and how the foraminiferal species add new chamber on their test.

The Mg/Ca of natural population are plotted with average temperature in Figure 22. Equation from culture experiments is also drawn. Both inclinations and ranges of Mg/Ca were similar between culture specimens and natural populations for *P. opercularis* and *Q. yabei.* The deviations of natural populations were larger than cultured specimens, because test of natural populations recorded biased temperature that was experienced during life

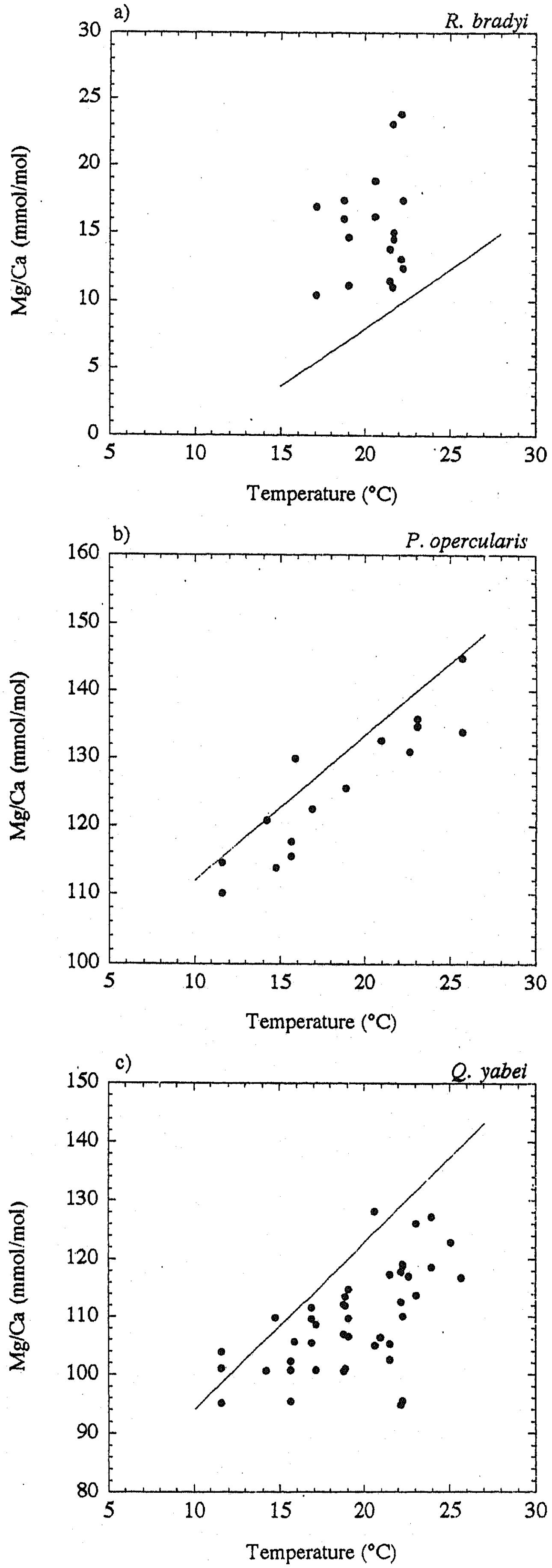


Figure 22: Mg/Ca comparison between cultured specimens and natural population. Closed circles indicate measured Mg/Ca of natural populations. Each point indicates each measurement. Solid lines show the regression line of experimental result of each species. a) *R. bradyi* b) *P. opercularis* c) *Q. yabei.*

history of each specimen. Mg/Ca of natural populations indicated lower values than measured temperature. Therefore, Mg/Ca of natural populations are distributed under the each regression line from culture experiments. It can be explained that sampling localities are tide pools and rocky shores where water temperature changed a lot in comparison to the tidal stations where annual water temperature were recorded (Figure 21). The daily temperature changes with the range from 20.2°C to 25.2 °C at 23rd, July, 2000. At the same day, average temperatures at meteorological station show 22.4°C. This shows that the temperature difference between daily fluctuation and recorded data was 2.8°C. If foraminifera only calcified during nighttime during summer, temperature recorded in a chamber should be lower than measured temperature at meteorological station. This may be one of the reasons why natural specimens show lower than recorded temperature.

Rosalina bradyi, however, show different trend between cultured specimens and natural populations. The Mg/Ca of natural populations for *R. bradyi* indicate higher value than cultured specimens (Figure 22a). Mg/Ca of natural populations were distributed above the regression line of culture experiment. If *R. bradyi* add new chambers only at the higher temperature hours during a day, the phenomena can be understood. Autoecology for each species, for instance growth curve, life cycle, microhabitat and others, are needed to evaluate Mg/Ca thermometry for natural populations.

4.3 What kinds of factors do control foraminiferal Mg/Ca and Sr/Ca?

4.3.1 The quantity of Mg

The range of Mg content varies widely among species (e.g. Figure 4). This means that the uptake amount of Mg differ from one species to the other (Figure 23). Mg contents of *A. beccarii* and *E. crispum* ranged from 0.1 to 0.4%. Mg contents of P. *opercularis* and *Q. yabei* reached to 10-15%. *Rosalina bradyi* have slightly lower Mg contents of about 0.5-1.5% than those of *Q. yabei* and *P. opercularis*. Mg contents are seemed to be discontinuous among species. Blackmon and Todd (1959) measured 131 genera, having calcareous tests, in 29

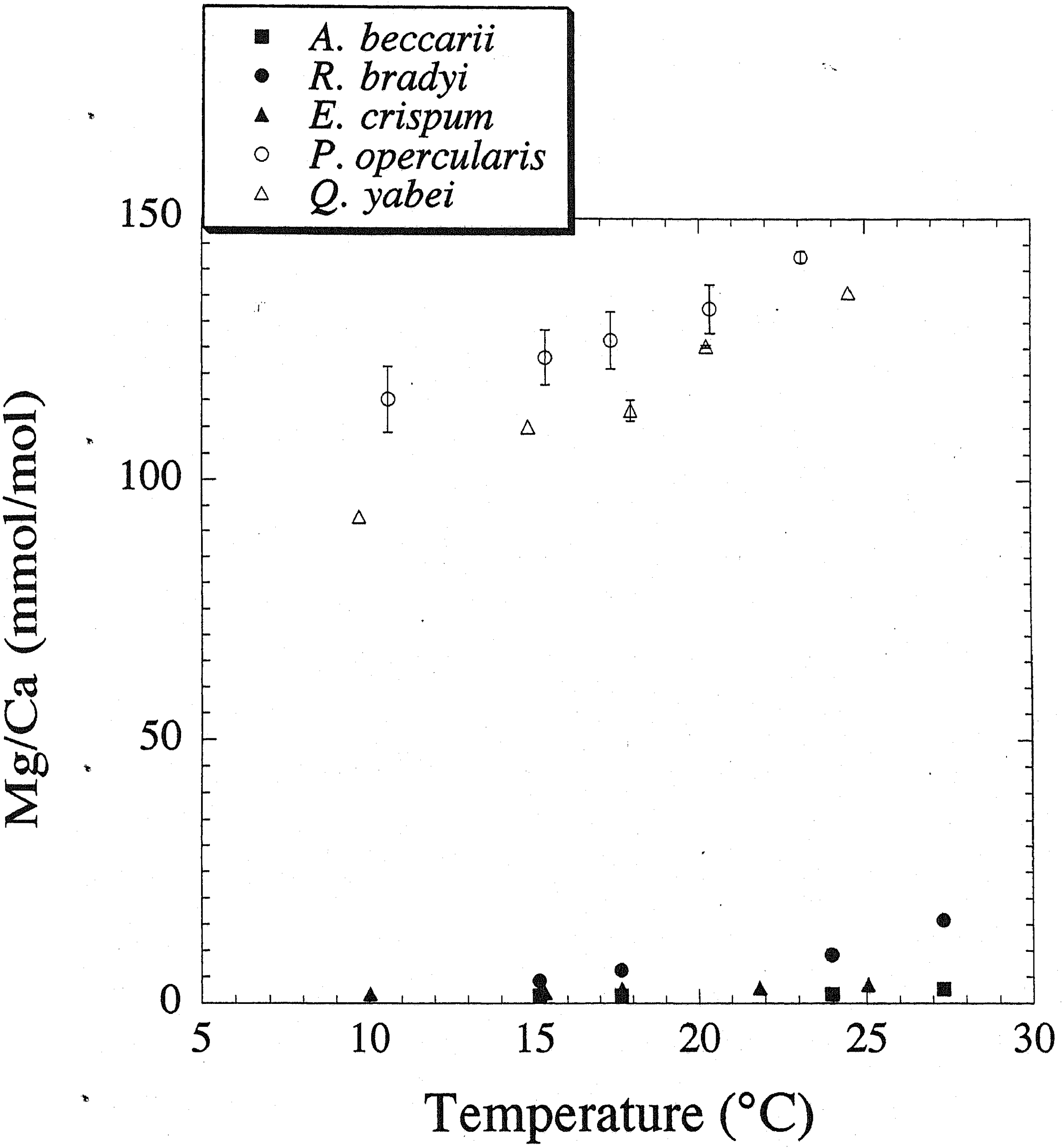


Figure 23: Cultured five species Mg/Ca in a single plot.

families with X-ray diffraction. They found 12 families have high- Mg content (over 100 mmol/mol), 10 families indicate low Mg content (less than 50 mmol/mol) and only 2 families indicate intermediate Mg content. They also found that differences in test formation well relate to Mg contents of the test. For instance, porcellaneous tests contain high Mg. Results from my research are basically concordant with Blackmon and Todd, except for *P. opercularis*. From the crystallographic point of view, *P. opercularis* belongs to calcareous hyaline foraminifera. This means Mg contents should be low. However, calcareous test of *P. opercularis* contains 10-15% of Mg contents.

4.3.2 Regression curve – linear regression or exponential regression -

Mg/Ca increase linearly with temperature for all species (Figure 4). It suggests that temperature is the most important factor to Mg uptake of foraminiferal tests. This observation is well matched with previous works which tried to calibrate the relationship between foraminiferal Mg and temperature (Nürnberg, 1995, Nürnberg *et al.*, 1996, Rosenthal *et al.*, 1997, Rathburn and DeDeckker 1997, Lea *et al.* 1999, Mashiotta *et al.*, 1999 and Lea et al., 2000). It may be probable that Mg contents of foraminiferal test are driven with temperature.

There are several problems whether regression between Mg/Ca and temperature is exponential curve or linear one. It is supposed that the fittest regression is one of the best ways to apply the paleoceanographic reconstruction by Hasting *et al.* (1998). They reconstructed the sea surface temperature of equatorial Atlantic and Caribbean Sea during 150 kyr with Mg/Ca thermometer of *G. sacculifer* which was fundamentally established by Nürnberg *et al.* (1996). Hasting *et al.* (1998) used linear regression equation, even though Nürnberg *et al.* (1996) established thermometer with exponential equation. The reason why Hasting *et al.* (1998) adopted the linear regression to their results is only because their values are fitter than exponential. However, this problem is strongly linked to consider what kind of mechanism Mg uptake to foraminiferal test.

In this study, every Mg/Ca was correlated with linear regression, even though many of previous papers fit with exponential (Nürnberg *et al.*, 1996, Rosenthal *et al.*, 1997, Mashiotta *et al.*, 1999, Lea *et al.*, 1999 and Lea *et al.*, 2000). They adopted exponential fit because Mg uptake should be controlled under thermodynamic theory. However, their Mg/Ca data were not enough to decide whether exponential regression is better than linear regression.

Mg show biased distribution within a chamber wall (Figure 10). It suggests that the mechanism of uptake of Mg may not occur under stable state. Foraminifera may take the initiative in uptake of Mg to their own test. Therefore, Mg contents show probably a complicated relationship with temperature.

The linear fitting also carry problems. Mg/Ca will take the minus value when temperature was very low on linear fitting. However, Mg content should not indicate minus value. If the temperature decrease too low, Mg contents also shall be close to zero. This is only because foraminifera can survive not so wide range of water temperatures (Bradshaw, 1961). The linear regression should extrapolate at the temperature range of out of data. Thus, every data from single specimen show biased distribution for temperature. Therefore, linear regression must be limited to apply only the range of temperature which foraminifera adapts.

4.3.3 Salinity effect to Mg/Ca

Mg/Ca show no systematic change with salinity. Nürnberg *et al.* (1996) showed Mg/Ca of *G. sacculifer* were affected by large change of salinity of about 10‰. The paper proposed an idea that Mg contents may be affected by foraminiferal vitality which may change with salinity. However, as discussed below, foraminiferal activities have no effect to Mg/Ca. The shallow water benthic foraminiferal species which were used for this study can survive very biased environments. Results from series of culture experiments indicated that growth rates of specimen for each species were affected by salinity (e.g. Tsuchiya, 2000MS, Kunimoto, 1995MS). However, Mg/Ca show no systematic change with salinity in my study. Therefore, growth rates are not so important to Mg/Ca of shallow water benthic species, too. These facts suggest that shallow water foraminiferal Mg/Ca is independent from water salinity and salinity related growth rate.

4.3.4 Sr/Ca of cultured foraminiferal specimen

It is difficult to find some relationship among foraminiferal Sr/Ca and environmental factors. *Elphidium crispum*, *R. bradyi* and *Q. yabei* showed some positive relationship between Sr/Ca and temperature. However, change in Sr/Ca between 10 and 30°C were in very similar range to salinity experiments with 28-40‰. These facts mean that it is difficult to use Sr/Ca for reconstructing past environment which did affect Sr/Ca temperature or salinity. Although, Mg/Ca is a better paleotemperature proxy than Sr/Ca.

4.3.5 The relationship between Mg/Ca and Sr/Ca

There is no clear relation between Mg/Ca and Sr/Ca intra-species comparison (Figure 24). All cultured foraminiferal Mg/Ca and Sr/Ca are given together on Figure 25. The range of Mg/Ca is about 100 times larger than Sr/Ca from low Mg species to high Mg species. The Sr contents of high Mg species may be larger than those of low Mg species. Sr contents of foraminiferal test may be affected by large variation of Mg contents.

Toyofuku (1997MS) observed that Mg ions actually constitute to foraminiferal calcite crystal with X-ray diffraction patterns for *C. lobatulus*, *P. opercularis* and *Q. yabei* (Figure 26). The solid solution were consisted with (Mg, Ca)CO_3. On the other hand, Sr is difficult to substitute the place of Ca in the calcite, because Sr ion is larger than Ca ion. Ichikuni (1994) tried to explain how to incorporate the larger ions to calcite. When Mn content increased in a crystal, the stability of crystal becomes unstable because the intervals of crystal lattice are narrower. Therefore the larger ions uptake to crystal lattice or inter lattice to cancel unstable factor. However, Ichikuni (1994) also pointed out this observation is not suitable for Mg and Sr contents of foraminifera. Because, Mg-ionic radius is too smaller than Mn-ionic one. However, Mg content of high-Mg calcite is more than 10% in this case. Therefore, the deformation of crystal lattice may occur. Perhaps, Sr ion can fill the deformed space of

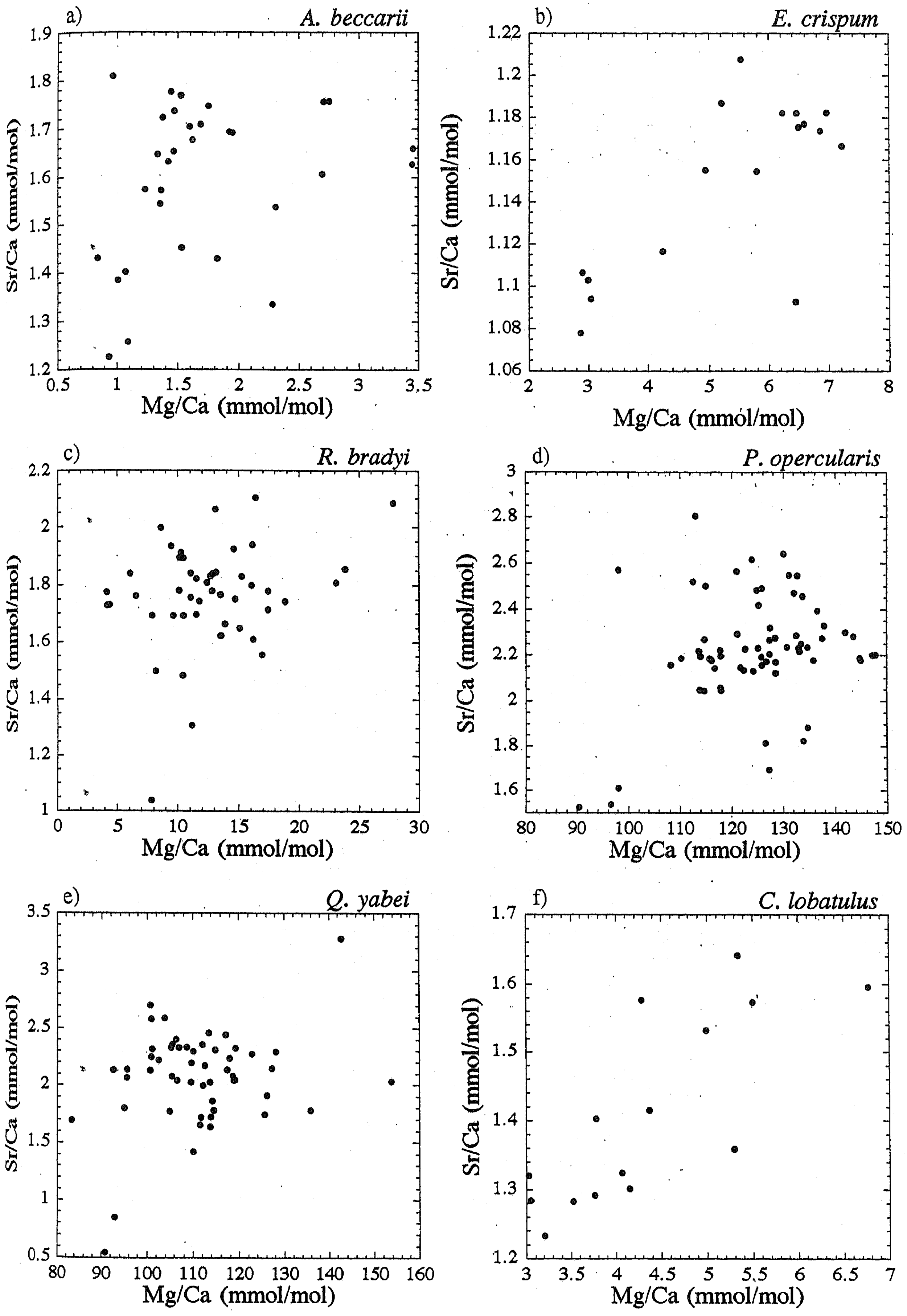


Figure 24: Intra specific comparison between Mg/Ca and Sr/Ca. The measurement results of culture specimens and natural populations are plotted. Each point indicates each measurement. a) *A. beccarii* b) *E. crispum* c) *R. bradyi* d) *P. oprcularis* e) *Q. yabei* f) *C. lobatulus*

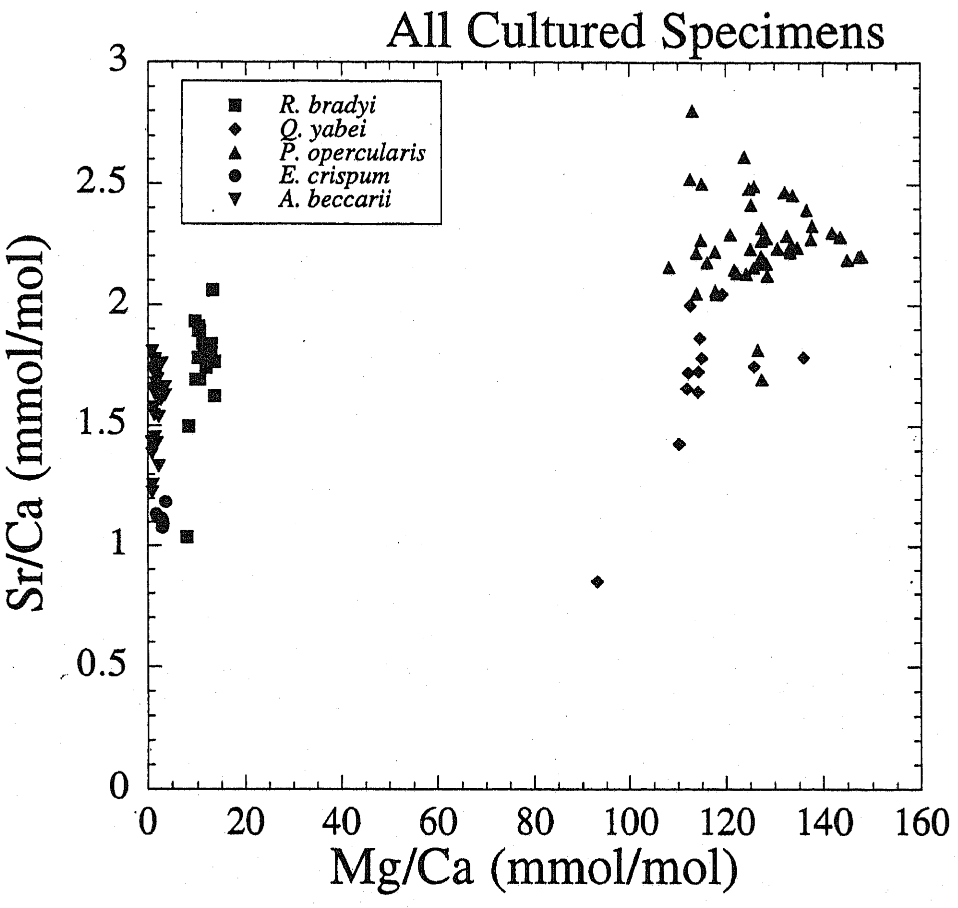


Figure 25: Species wise comparison between Mg/Ca and Sr/Ca.

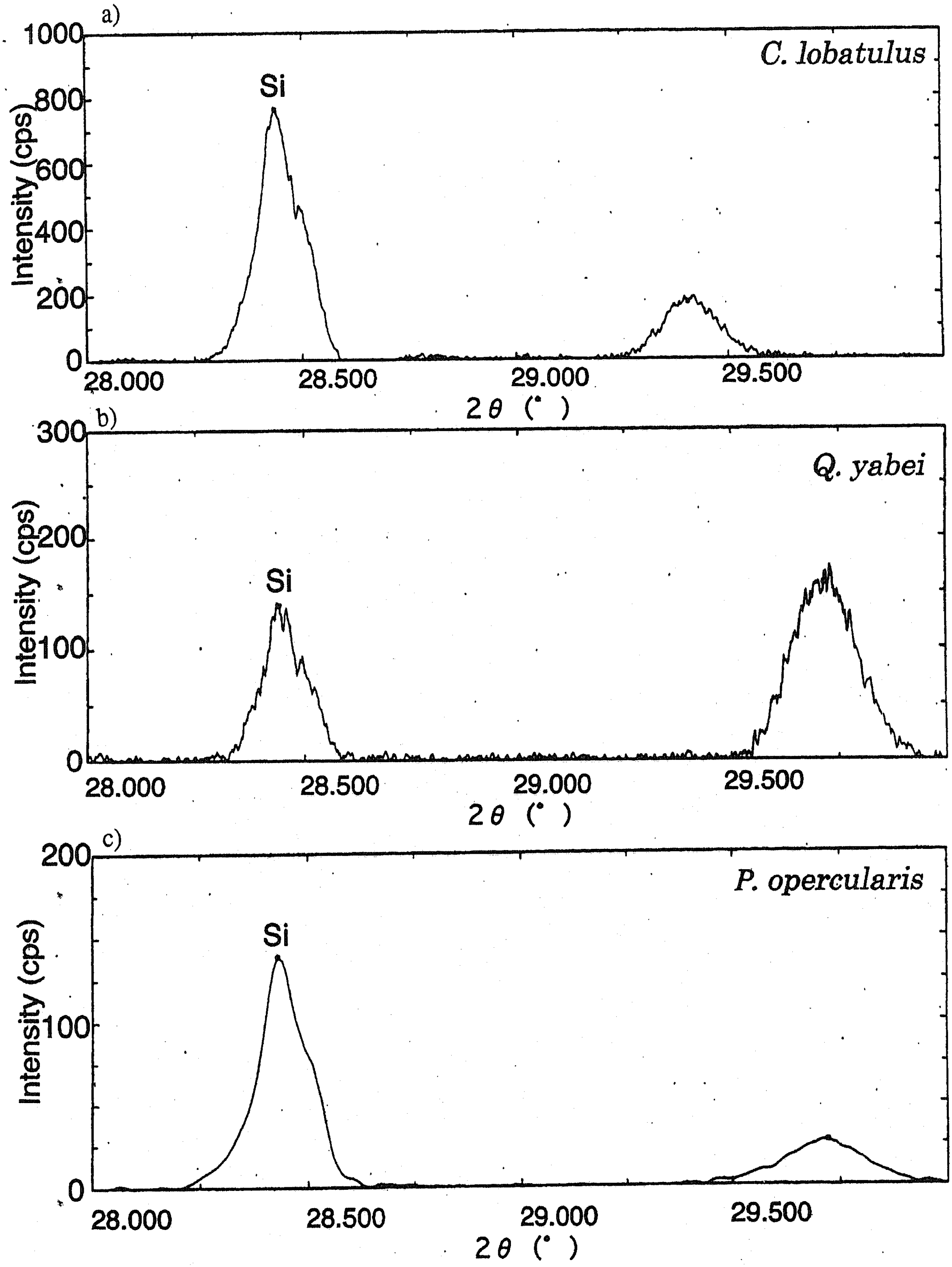


Figure 26: X-ray diffraction profiles of a)*C. lobatulus*, b)*P. opercularis* and c)*Q. yabei*.

crystals. An observation of crystal structure of foraminiferal tests directly is needed to confirm this hypothesis.

4.3.6 Growth rate effect to Mg/Ca and Sr/Ca

Previous works showed Mg and Sr contents of carbonates were influenced by the growth rate of carbonate crystal through inorganic precipitation experiments (Morse and Bender, 1990). In inorganic precipitation, with crystal growth rate being rapid, the uptake amount of magnesium increasing. In this study, there is no observation of growth rate of calcite crystal of foraminiferal test. However, there is some possibility that the difference of crystal growth rate during chamber formation due to the difference of Mg/Ca ratio among species. If crystal growth speed can be measured, direct comparison between Mg contents and growth speed shall be made more accurately.

4.3.7 pH effect to Mg/Ca and Sr/Ca

Culture water pH show fluctuation some time (Figure 3c). Culture water pH were monitored only during the experimental period for *A. beccarii* and *R. bradyi*. No pH data available for other experimental periods. These changes of pH may occur by photosynthesis of micro algae. Therefore, unsettled change of pH possibly occurred for other experimental periods.

Lea *et al.* (1999) reported that pH affected Mg/Ca of *G. bulloides* and *O. universa*. They showed the foraminiferal Mg/Ca decreases about 6% per 0.1 pH change and Sr/Ca increases about 0.5 to 1% per 0.1 pH change.

The Mg/Ca of *A. beccarii* show small deviation from regression line (Figure 4a). The Mg/Ca point of 24.0 °C is lower than whole trend of *A. beccarii*. However, pH of this experimental condition indicated similar trend with other conditions (Figure 3c-1). The Mg/Ca point of 24.0 °C of *R. bradyi* is also lower than general trend of other points. However, pH of this condition indicated not so higher value than other conditions. Therefore, pH change may not affect to foraminiferal Mg/Ca strongly.

In this study, pH may change by accident, because culture water replaced frequently. Therefore, foraminiferal Mg/Ca and Sr/Ca will be affected by sporadic pH change. This sporadic change of pH may be one of the reason the deviation of Mg/Ca and Sr/Ca.

4.4 Oxygen isotopic composition of culture specimens

$\delta^{18}O$ value became lighter, culture temperature became higher (Figure 12, Table 4). This is the same as general trend of many previous studies. The equations were similar between *A. beccarii* and *R. bradyi.* (equation 7 and 8). These equations were differ from many previous equations (e.g. Craig, 1965). Tarutani et al. (1969) reported that relative to calcite at 25°C, magnesian carbonates were enriched by 0.06‰/mol% Mg with synthetic carbonates. Kim and O'Neil (1997) pointed out that precipitation rates had little or no influence on the isotopic composition of synthetic carbonates. Therefore, the difference of the equation among species may be due to the difference of concentration of trace elements among species. This problem will be clearer to measure oxygen isotopic composition of cultured high-Mg foraminiferal test such as *P. opercularis* and *Q. yabei.*

Recently, laboratory experiments with planktonic foraminifera have demonstrated that the carbonate ion concentration ($[CO_3^{2-}]$) of seawater affect oxygen isotopic composition of foraminifera (Spero and Lea, 1993; Bemis *et al.* 1998). However, the mechanisms driving the effects of $[CO_3^{2-}]$ on the oxygen isotopic composition of foraminifera are not well understood. In this study, pH of culture water were small variation during experimental periods (Figure 3c). The variations of pH during experimental periods are different each other (Figure 3c-1 to 3c-5), although the intercept of equation was similar each other in this study (equation 7 and 8). The change of pH may occur like sporadic event. Therefore, the general trends of oxygen isotopic composition were not affected by pH. This sporadic change of pH may be one of the reason for the deviation of $\delta^{18}O$.

The difference of equation between this study and previous studies might be explained by species problem, so called vital effect. Therefore, specific equations of foraminiferal $\delta^{18}O$ and temperature and water $\delta^{18}O$ for each species or genera must be established to estimate past environments.

δ_c-δ_w values did not change with salinity for both *A. beccarii* and *R. bradyi* (Figure 13). This means that solved ions do not affect foraminiferal $\delta^{18}O$. Artificial salinity experiments confirmed this fact experimentally. Nobody has not gotten a proof that salinity only affect to foraminiferal $\delta^{18}O$ without changing water $\delta^{18}O$. Artificial seawater can be prepared with same $\delta^{18}O$ even at different salinity conditions. This is great advantage to test salinity effect. My results clearly show that salt (ion) quantity did not affect foraminiferal $\delta^{18}O$.

4.5 Establishment of both temperature and salinity double proxies by combining Mg/Ca thermometry and oxygen isotopic composition

In this study, both Mg/Ca thermometer and $\delta^{18}O$-water and temperature relationship was obtained for *A. beccarii* and *R. bradyi*. Paleotemperature and salinity can be predicted by combining two equations. Temperature value can obtain independently from Mg/Ca thermometry. If we substitute temperature value and $\delta^{18}O$ equation, We can obtain $\delta^{18}O$ of water.

for *A. beccarii*

Temperature (°C)= 10.47 Mg/Ca (mmol/mol) + 1.476

$\delta^{18}O_{water} = 0.168$ Temperature (°C) $-2.89+ \delta^{18}O_{foram} + 0.27$

The standard error is ±0.8°C

for *R. bradyi,*

Temperature (°C)= 1.16 Mg/Ca (mmol/mol) + 10.60

$\delta^{18}O_{water} = 0.179$ Temperature (°C) $-3.16+ \delta^{18}O_{foram} + 0.27$

The standard error is ±1.0°C

where the factor of 0.27 is used to convert from calcite on the PDB to water on the SMOW (Hut, 1987). Water oxygen isotopic composition can transform to salinity, if the relationship between $\delta^{18}O$ water and salinity is known. In this study, the relationship between salinity and $\delta^{18}O$ for The Sea of Japan is indicated by the following equation (Figure 2).

Salinity (‰) = $5.435\ \delta^{18}O_{water} + 36.91$.

The standard error is ±0.12‰

In these equations, overestimated temperature and foraminiferal $\delta^{18}O$ is the source of errors in water $\delta^{18}O$ and salinity. When we use temperature equation of *R. bradyi*, 1°C of difference led 0.18‰ deviation of water $\delta^{18}O$ and 0.97‰ difference of salinity. Usually, the standard errors of Mg/Ca thermometry are between 0.5 and 1 °C. The measurement error of $\delta^{18}O$ is about 0.05‰. The error of salinity will be about 1.25‰ caused by the error propagation.

I tried to evaluate these equations both from foraminiferal oxygen isotopic composition and foraminiferal Mg/Ca thermometry with *R. bradyi* (Table 7). The values of calculated salinity are shown in Table 7. The salinity was assumed to be about 33‰ for localities where no salinity data is available. This value is the intermediate value among localities which measured salinity. The values of calculated salinity ranged from 31.3±3.5‰ to 47.0±1.0‰. Even though calculated salinity indicated higher value than measured salinity, almost measured and assumed values of salinity were contained within the error limits of calculated salinity. These results indicate that the double proxies, established by this study will be able to apply to paleo-temperature and paleo-salinity reconstruction. However, the error of calculated salinity is too large for practical use in recent paleoceanographic study.

These double proxies need to measure not only foraminiferal Mg/Ca but also foraminiferal oxygen isotopic composition. These values were measured with respective specimen. These specimens were collected from very shallow water. In shallow water, seawater temperature will change more than 5°C (e.g. Figure 21). Seasonal change of seawater temperature is also

Table 7: Oxygen isotopic composition and calculated salinity with *R. bradyi* .

Sample locality	Average Mg/Ca (mmol/mol)	Calculated temperature (°C) from Mg/Ca	Average forainiferal $\delta^{18}O$ (‰ PDB)	Calculated foraminiferal salinity (‰)	Measured salinity(‰)
Rumoi	13.7	26.0±4.7	-1.873	36.3±4.6	32.88
Otobe	12.9	25.2±2.5	-0.517±0.631	42.9±5.9	
Matsumae	16.7	29.1±1.0	-0.466	47.0±1.0	
Oga	14.8	27.1±0.4	-2.288±0.853	35.1±5.0	33.19
Tsuruoka	12.7	24.9±1.7	-2.601±0.332	31.3±3.5	
Tsuyazaki	14.9	27.2±3.6	-1.605±0.432	39.0±5.8	33.32

large (e.g. Figure 15). Specimens add their chambers under this very biased environmental condition. The recorded information may differ from specimen to specimen. Therefore, measured Mg/Ca were different each other. Each oxygen isotopic composition differed among specimens. The calcification temperature is different between the specimens which measured Mg/Ca and the specimens which measured oxygen isotopic compositions. All these discrepancies will get on the double proxies. Therefore, the calculated salinity have large error in this study.

These facts indicate that paleosalinometer using foraminiferal oxygen isotopic composition will give the best result when combined with foraminiferal Mg/Ca thermometry, since foraminiferal Mg contents and $\delta^{18}O$ were fixed at same time. Therefore this method can always provide the accurate value of integrated temperature and $\delta^{18}O$ of water of whole foraminiferal test. However, Mg/Ca ratios and $\delta^{18}O$ are not measurable with single foraminiferal test at this moment. Therefore, we must measure Mg/Ca and $\delta^{18}O$ values each other. In order to evaluate that the two groups of foraminiferal specimens have similar life history, we have to measure each once Mg/Ca and $\delta^{18}O$ value.

It is ideal to measure both Mg/Ca and $\delta^{18}O$ for same foraminiferal specimen, because life history is the same. However, the detection limits prevent this idea. At this moment, it is impossible to measure both Mg/Ca and $\delta^{18}O$ for single specimens of foraminifera. Ecological information such as life span and growth rate is also important to evaluate the obtained results. In future, the paleoceanographic knowledge should certainly increase if micro sampling technique and micro-detection technique of both Mg/Ca and $\delta^{18}O$ are developed to measure single specimens using nano-technology.

5. Summary and Conclusions

The purpose of this study is to directly compare among foraminiferal Mg/Ca, Sr/Ca and $\delta^{18}O$ with temperature, salinity and water $\delta^{18}O$ through culture experiments. Five species of shallow water benthic foraminifers were cultured under well-controlled conditions.

I obtained the following results.

1. Mg contents of calcitic tests are very different among foraminiferal species. Mg/Ca increase linearly with temperature for all species. However, the regression equation of Mg/Ca differed very much for each species. Salinity does not affect the Mg/Ca for each species. Therefore, foraminiferal Mg/Ca can apply to paleo-temperature reconstruction as Mg thermometry.
2. It is difficult to find some relationship between foraminiferal Sr/Ca and experimental environments. Therefore, Sr/Ca may be difficult to use as temperature proxy.
3. Experimental results showed clear relationship between foraminiferal $\delta^{18}O$ and temperature. Foraminiferal $\delta^{18}O$ value was also affected directly by water $\delta^{18}O$. Salinity (the quantity of ions) has no systematic influence on foraminiferal $\delta^{18}O$. Foraminiferal $\delta^{18}O$ are difficult to apply as temperature proxy, although the temperature relationship were clear at experimental results, because foraminiferal $\delta^{18}O$ will be affected not only by temperature but also by water $\delta^{18}O$ value.

4. Theoretically, both temperature and salinity can be calculated by a combination of both Mg/Ca thermometry and $\delta^{18}O$ measurements. I tried to introduce two equations, Mg/Ca and $\delta^{18}O$, for *A. beccarii* and *R. bradyi* through culture experiments. They are,

for *A. beccarii*

Temperature (°C)= 10.47 Mg/Ca (mmol/mol) + 1.476

$\delta^{18}O_{\text{water}}$ = 0.168 Temperature (°C) -2.89+ $\delta^{18}O_{\text{foram}}$ + 0.27

for *R. bradyi,*

Temperature (°C)= 1.16 Mg/Ca (mmol/mol) + 10.60

$\delta^{18}O_{water} = 0.179$ Temperature (°C) $- 3.16 + \delta^{18}O_{foram} + 0.27$

Latter equations of both species provide water $\delta^{18}O$ value from temperature and foraminiferal $\delta^{18}O$. Using foraminiferal oxygen isotopic composition will give the best result to combine with foraminiferal Mg/Ca thermometry, since foraminiferal Mg contents and $\delta^{18}O$ were fixed at the same time. This method will be able to provide always the accurate value of integrated temperature and $\delta^{18}O$ of water of whole foraminiferal test experienced. Therefore, we have to evaluate whether or not two groups of foraminiferal specimens have similar life history, using each one Mg/Ca and $\delta^{18}O$ values.

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References

Bemis, E. B., Spero, H. J., Bijima, J. and Lea, D. W., 1998, Reevaluation of oxygen isotopic composition of planktonic foraminifera: Experimental results and revised paleotemperature equations. *Paleoceanography*, 13, 150-160.

Berthold, W. U, 1976, Ultrastructure and function of wall perforations in *Patellina corrugata* Williamson, Foraminiferidae. *Journal of Foraminiferal Research*, 6, 22-29.

Bijma, J., Hemleben, Ch., Huber, B. T., Erlenkeuser, H. and Kroon, D., 1998, Experimental determination of the ontogenic stable isotope variability in two morphotypes of *Globigerinella siphonifera* (d'Orbigny). *Marine Micropaleontology,* 35, 141-160.

Blackmon, P. D. and Todd, R., 1959, Mineralogy of some foraminifera as related to their classification and ecology. *Journal of Paleontology*, 33, 1-15.

Bouvier-Soumagnac, Y. and Duplessy, J. C., 1985, Carbon and oxygen isotopic composition of planktonic foraminifera from laboratory culture, plankton tows and recent sediment : Implications for the reconstruction of paleoclimatic conditions and of the global carbon cycle. *Journal of Foraminiferal Research*, 15, 302-320.

Boyle, E. A., 1981, Cadmium, zinc, copper, and barium in foraminiferal tests. *Earth Planetary Science Letters*, 53, 11-35.

Boyle, E. A., 1988, Cadmium: Chemical tracer of deepwater paleoceanography. *Paleoceanograhy*, 3, 471-489,.

Boyle, E. A. and Keigwin, L. D., 1985, Comparison of Atlantic and Pacific paleochemical records for the last 215,000 years: Changes in deep ocean circulation and chemical inventories. *Earth Planetary Science Letters*, 76, 135-150.

Bradshaw, J. S., 1957, Laboratory studies on the rate of growth of the foraminifer, "*Streblus beccarii* (Linné) var. *tepida* (Cushman)". *Journal of Paleontology*, 31, 1138-1147.

Bradshaw, J. S., 1961, Laboratory experiments on the ecology of foraminifera: *Cushman Found. Foram. Reserch Contribution.*, 12, 87-106,.

Brassel, S. C., Eglinton, G.,Marlowe, I. T., Pflaumann, U. and Sarnthein, M., 1986, Molecular stratigraphy: A new tool for climatic assessment. *Nature*, 320, 129-133.

Broecker, W. S. and Peng, T. H., 1982, *Trasers* in the Sea. 690 pp., Lamont Doherty Earth Obs., Palisades, N. Y.

Brown, S. J. and Elderfield, H. 1996, Variations in Mg/Ca and Sr/Ca ratios of planktonic foraminifera caused by postdepositional dissolution: Evidence of shallow Mg-dependent dissolution. *Paleoceanography,* 11, 543-551.

Chave, K. E., 1954, Aspects of the biochemistry of magnesium: 1. Calcareous marine organisms. *Journal of Geology*, 62, 266-283.

Cronblad, H. G. and Malmgren, B. A., 1981, Climatically controlled variation of Sr and Mg in Quaternary planktonic foraminifera. *Nature*, 291, 61-64.

De Deckker, P. and Corregé, T., 1992, A new paleothermometer: The magnesium to calcium ratio in benthic ostracod valves, papers presented at Forth International Conference on paleoceanography. GEOMAR, Kiel, Germany, Sept. 21-25.

Dodd, J. R., 1965, Environmental control of strontium and magnesium in *Mytilus*. *Geochimica Cosmochimica Acta*, 29, 85-89.

Elderfield, H. E., Bertram, C. J. and Erez, J., 1996, A biomineralization model for the incorporation of trace elements into foraminiferal calcium carbonate. *Earth Planetary Science Letters*, 142, 409-423.

Elderfield, H. E., Ganssen, G., 2000, Past temperature and $\delta^{18}O$ of surface ocean waters inferred from foraminiferal Mg/Ca ratios. *Nature*, 405, 442-445.

Emiliani, C., 1955, Mineralogy and chemical composition of the tests of certain pelagic foraminifera. *Micropaleontlogy*, 1, 377-380.

Emiliani, C. and Edwards, G, 1953, Tertiary Ocean Bottom Temperatures. *Nature*, 171, 887-888.

Epstein, S., Buchsbaum, R., Lowenstam, H.and Urey, H.C., 1951, Carbonate-Water isotopic temperature scale, *Geological Society America Bulletin*, 62, 417-426.

Epstein, S., Buchsbaum, R., Lowenstam, H. A. and Urey, H. C., 1953, Revised carbonate-water isotopic temperature scale. *Geological Society America Bulletin*, 64, 1315-1325.

Erez, J. and Luz, B., 1983, Experimental paleotemperature equation for planktonic foraminifera. *Geochimica Cosmochimica Acta*, 47, 1025-1031.

Hasting, D. W., Russell, A. D. and Emerson, S. R., 1998, Foraminifera magnesium in *Globigerinoides sacculifer* as a paleotemperature proxy. *paleoceanography*, 13, 161-169.

Horibe,Y. and Oba, T., 1972, Temperature scales of aragonite-water and calcite-water systems. *Paleontological Society of Japan.*, 23-24, 69-79.

Hut, G., 1987, Consultants group meeting on stable isotope reference samples for geochemical and hydrological investigations. *Rep. to Dir. Gen., Int. At. Energy Agency, Vienna*, 42.

Ichikuni, M., 1994, Trace elements of carbonate (in Japanese), *Gekkan Chikyu,* 16, 372-380.

Imbrie, J. and Kipp, N. G., 1971, A new micropaleontological method for quantitative paleoclimatology: application to a late Pleistocene Caribbean core, in: *The late Cenozoic Glacial ages.* (K. K. Turekiand ed.), Yale University Press.

Izuka, S. K., 1998, Relationship of magnesium and other minor elements in test of *Cassidulina subglobgosa* and *corriangulata* to physical oceanic properties, *Journal of Foraminiferal Research*, 18, 151-157.

Kitazato, H., 1994, Foraminiferal microhabitats in four marine environments around Japan. *Marine Micropaleontlogy*, 24, 29-41.

Kitazato, H., 1998, Experimental Paleontology: An effective approach for screening and establishing biological proxies of paleoceanography –Review and perspective. *Journal of Geography*, 107, 258-273.

Kim, S. T., and O'Neil, J. R., 1997, Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochimica Cosmochimica Acta*, 61, 3461-3475.

Klein, R. T., Lohmann, K. C. and Kennedy, G. L., 1997, Elemental and isotopic proxies of paleotemperature and paleosalinity: Climate reconstruction of the marginal northeast Pacific ca. 80 ka. *Geology*, 25, 363-366.

Koshio, M., 1992MS, Life history and test morphology of *Ammonia beccarii* (Linné) (foraminifer) in Hamana Lake, central Japan, master thesis, Institute of Geosciences, Shizuoka University, 65pp, Feb., 1992.

Kunimoto, A., 1995MS, Analysis of growth rate and morphological variation of the benthic foraminifer *Ammonia beccarii* (Linné) (in Japanese with English abstract), graduate thesis, Institute of Geosciences, Shizuoka University, 39pp, Feb., 1995.

Lea, D. W., Mashiotta, T. A. and Spero, H. J., 1999, Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing. *Geochimica Cosmochimica Acta*, 63, 2369-2379.

Mashiotta, T. A., Lea, D. W. and Spero, H. J., 1999, Glacial-interglacial changes in Subantarctic sea surface temperature and δ^{18}O-water using foraminiferal Mg. *Earth Planetary Science Letters*, 170, 417-432.

McCrea, J. M., On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.*, 18, 849-857, 1950.

Mitsuguchi, T., Matsumoto, E., Abe, O., Uchida, T. and Isdare, P. J., 1996, Mg/Ca thermometry in coral skeletons. *Science,* 274, 961-963.

Morse, J. W., and Bender, M. L, 1990, Partition coefficients in calcite: Examination of factors influencing the validity of experimental results and their application to natural systems. *Chemical Geology*, 82, 265-277.

Nürnberg, D., 1995, Magnesium in tests of *Neogloboquadorina pachyderma* sinistral from high northern and southern latitude. *Journal of Foraminiferal Research*, 25, 350-368.

Nürnberg, D., Bijma, J. and Hemleben, Ch., 1996, Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures. *Geochimica. Cosmochimica Acta,* 60, 803-814, 1996.

Nürnberg, D., Müller, A. and Schneider, R. R., 2000, Paleo-sea surface temperature calculations in the equatorial east Atlantic from Mg/Ca ratios in planktic foraminifera: A comparison to sea surface temperature estimates from $U^{k'}_{37}$, oxygen isotopes, and foraminiferal transfer function. *Paleoceanography,* 15, 124-134.

O'Neil, J. R., Clayton, R. N. and Mayeda, T. K., 1969, Oxygen isotope fractionation in divalent mental carbonates. *J. Chemical Physics.*, 51, 5547-5558.

Palmar, M. R. and Edmond, J. M., 1989, The strontium isotope budget of the modern ocean. *Earth Planetary Science Letters,* 92, 11-26.

Rathburn, A. E. and DeDeckker, P., 1997, Magnesium and strontium compositions of Resent benthic foraminifera from the Coral Sea, Australia and Prydz Bay, Antarctica. *Marine Micropaleontoleontology*, 32, 231-248.

Rosenthal, Y., Boyle, E. A. and Slowey, N., 1997, Temperature control on the incorporation of magnesium, strontium, fluorine, and calcium into benthic foraminiferal shells from Little Bahama Bank: Prospects for thermocline Paleoceanography,. *Geochimica Cosmochimica Acta*, 61, 3633-3643.

Savin,S. M. and Douglas, R. G., 1973, Stable isotope and magnesium geochemistry of recent planktonic foraminifera from the South Pacific. *Geological Society of America Bulletin*, 84, 2327-2342.

Shackleton, N. J., 1974, Attainment of isotopic equilibrium between ocean water and the benthoonic foraminifera genus *Uvigerina*: Isotopic changes in the ocean during the last glacial. *Cent. Nat. Rech., Sci. Colloq. Int.*, 219, 203-209.

Smith, H. S., Delafontaine, M. and Flemming, B. W., 1988, Intertidal barnacles – Assessment of their use as paleo-environment indicators using Mg, Sr, $^{18}O/^{16}O$ and $^{13}C/^{12}C$ variations. *Chemical Geology*, 73, 211-220.

Spero, H. J., and Lea, D.W., 1993, Intraspecific stable isotope variability in the planktic foraminifera *Globigerinoides sacculifer*: Results from laboratory experiments, *Marine Micropaleontology*, 22, 221-234.

Takahara, K., 1989, Morphological analysis by plastogamy experiments on the benthic foraminifera *Glabratella* (in Japanese with English abstract), undergraduate thesis, Inst. of Geosci., Shizuoka Univ., 61pp, Feb. 1989.

Tarutani, T., Clayton, R. N., and Mayeda, T. K., 1969, The effect of polymorphism and magnesium substitution on oxygen isotopic fractionation between calcium carbonate and water. *Geochimica Cosmochimica Acta*, 46, 1183-1191.

Toyofuku, T, 1997, Experimental evaluation of the use of Mg/Ca and Sr/Ca ratios of benthic foraminiferal tests as sea water temperature proxies, master thesis, Inst. of Geosci., Shizuoka Univ., 48pp, Feb. 1997.

Toyofuku, T., Kitazato, H., Kawahata, H., Tsuchiya, M. and Nohara, M., 2000, Evaluation of Mg/Ca thermometry in foraminifera: Comparison of experimental results and measurements in nature. *Paleoceanography*, 15, 456-464.

Tsuchiya, M., Phylogenetic relationships among species of Glabratellidae (foraminifera): Comparisons of molecular with morphological and ecological perspective. Doctoral Dissertation, Graduate school of the Science and Technology, Shizuoka Univ., Feb. 2000.

Urey,H. C., 1947, The thermodynamic properties of isotopic substances. *J. Chem. Soc.,* 1947, 562-581.

Plate 1

1. *Ammonia beccarii* (Linné) forma 1
2. *Elphidium crispum* (Linné)
3. *Rosalina bradyi* (Cushman)

a. dorsal view, b. side view, c. ventral view.

Scale bar indicates 100 μm

Plate 1

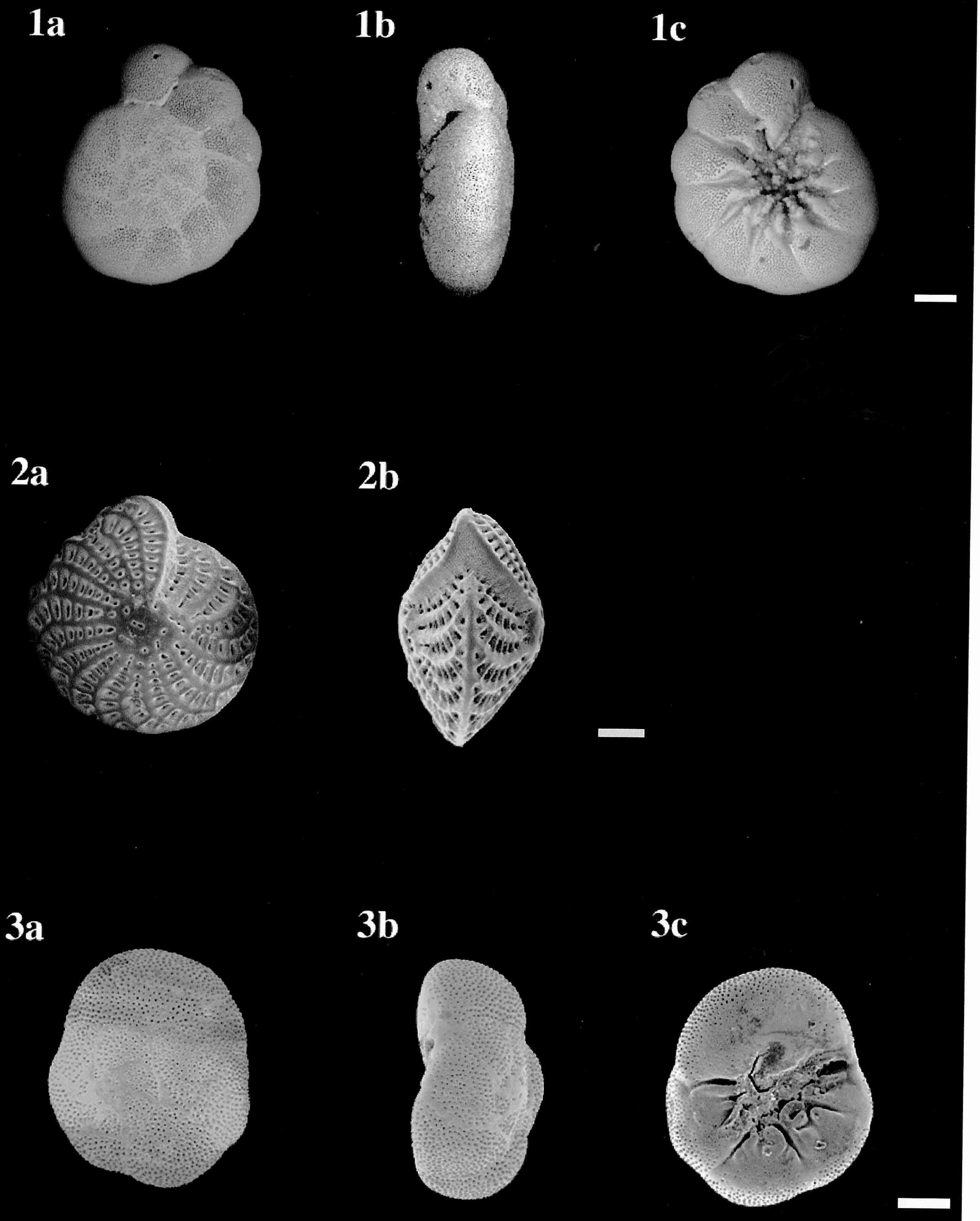

Plate 2

1. *Planoglabratella opercularis* (d'Orbigny)
2. *Cibicides lobatulus* (Walker and Jacob)
3. *Quinqueloculina yabei* Asano

a. dorsal view, b. side view, c. ventral view.

Scale bar indicates 100 μm

Plate 2