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Sodium, magnesium and strontium in the tests of planktonic foraminifera
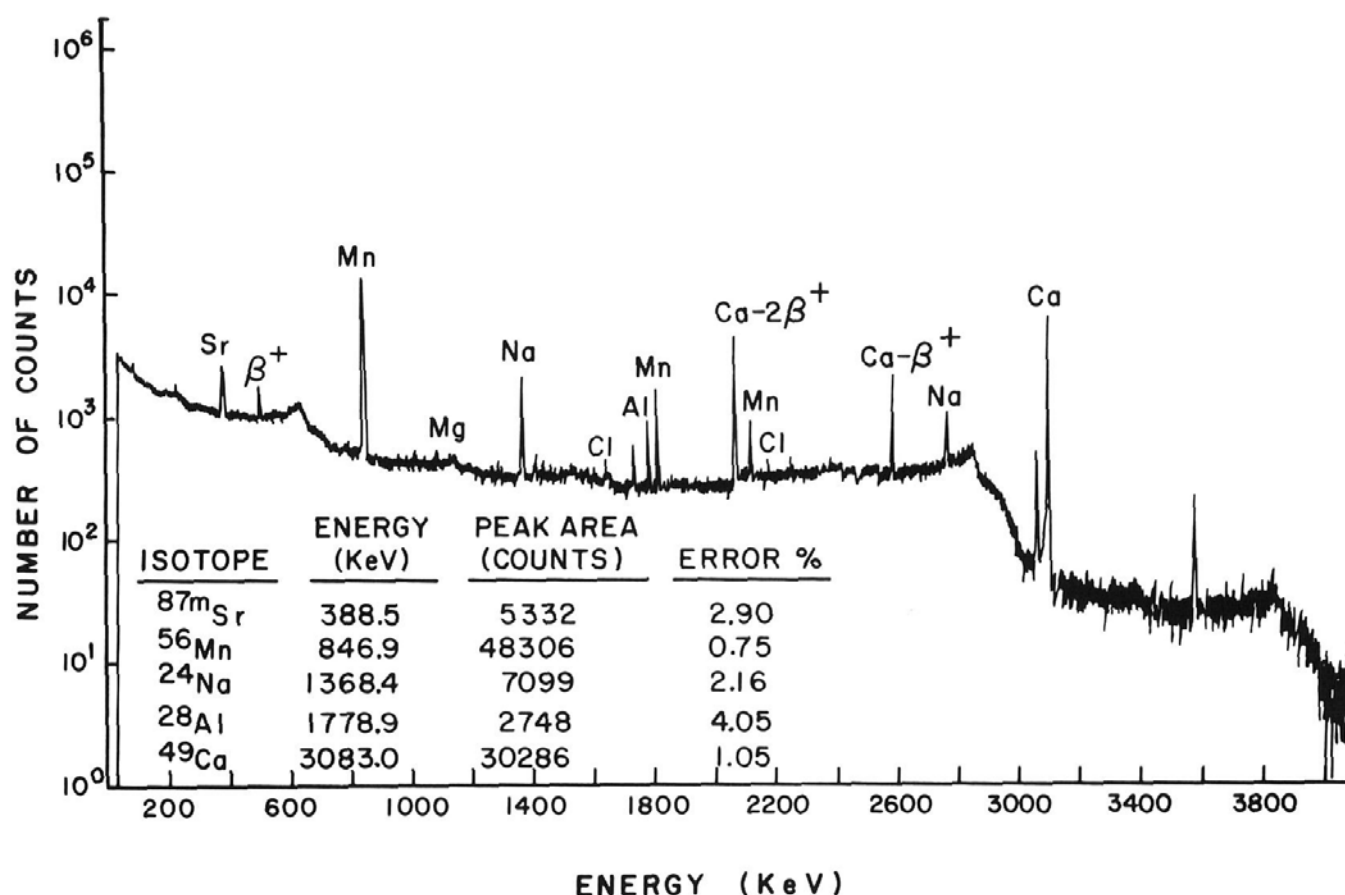
ABSTRACT

We have determined Na/Ca, Mg/Ca, Sr/Ca, Al/Ca and Cl/Na atom ratios in about sixty samples of individual species of planktonic foraminifera. Na/Ca and Sr/Ca ratios are constant in different tests of one species, but Mg/Ca ratios show considerable variability. Data indicate that Na and Sr are distributed homogeneously throughout the tests, while Mg is distributed heterogeneously.

Na/Ca, Mg/Ca and Sr/Ca ratios of different species from an Upper Pleistocene assemblage from the Tasman Sea covary, with shallow-living species having the highest ratios. Atom ratios of Recent North Atlantic *Globigerinoides sacculifer* (Brady) and *G. ruber* (d'Orbigny) samples do not show any clear-cut temperature dependence. It appears that at one location atom ratios increase with temperature or a temperature-related factor, and that over a broad geographical area variables other than temperature affect trace element abundance.

INTRODUCTION

The study of the distribution of "sea salt major cations" (herein defined as Na, K, Mg, Ca and Sr) in foraminiferal calcite is of interest for a number of reasons. First, the distribution of these elements may provide an insight into biochemical processes occurring during calcification. Second, if investigations of Recent skeletal chemistry reveal that trace element abundances vary in a quantifiable way with environmental parameters, we can use skeletal chemistry as an ecological and paleoecological index. Third, the study of fossil skeletal chemistry is our prime hope for deducing past variations in the chemistry of sea water.

Our interest in these problems has prompted us to undertake a comprehensive study of foraminiferal calcite chemistry; the purpose of this paper is to summarize our results to date. Our effort builds on results of a number of earlier workers. Blackmon and Todd (1959) found that benthic foraminifera had skeletons composed dominantly of high magnesian calcite, but planktonic foraminifera were composed of calcite containing less than 2 mole percent $MgCO_3$. Emiliani (1955), Switzer and Boucot (1955), and Mayer (1932) also found that the skeletons of planktonic foraminifera were composed of calcite. Emiliani (1955) determined the TiO_2, Al_2O_3, SiO_2, Fe_2O_3, MnO, MgO, and SrO contents of eight samples composed of single species of planktonic foraminifera. He found that the SrO content was fairly constant at a level of 0.13%, but that all other concentration values varied sympathetically in a way that could be ascribed to the presence of contaminating detritus. Krinsley (1960) analyzed ten samples for MnO, TiO_2, Al_2O_3, MgO, CuO, and NiO, and concluded (contrary to the belief of Emiliani) that the shells contained on the order of 0.15% by weight MgO that could not be ascribed to detrital contamination. Lipps and Ribbe (1967) reinforced this conclusion with their electron microprobe work, showing that those parts of the foraminiferal tests free of detritus contained about 0.2% by weight MgO. Savin and Douglas (1973) determined the $MgCO_3$ contents and δO_{18} of foraminifera and found that the tests contained between 0.1 and 0.4% by weight MgO. With the exception of *Globorotalia truncatulinoides* (d'Orbigny) MgO content of foraminiferal calcite increased as isotopic temperature increased. The most extensive data in the literature on planktonic foraminiferal chemistry are the analyses of Kilbourne and Sen Gupta (1973). They found that the Mg content increased linearly with habitat temperature and that solution-susceptible species had higher Mg contents than more resistant species. Results of Savin and Douglas (1973) also agreed with this latter conclusion, leading those authors to suggest that the Mg content controlled solution susceptibility.

ISOTOPE	ENERGY (KeV)	PEAK AREA (COUNTS)	ERROR %
^{87m}Sr	388.5	5332	2.90
^{56}Mn	846.9	48306	0.75
^{24}Na	1368.4	7099	2.16
^{28}Al	1778.9	2748	4.05
^{49}Ca	3083.0	30286	1.05

TEXT-FIGURE 1
Gamma spectrum of a *G. sacculifer* sample counted for 1000 sec. starting twenty-five minutes after the beginning of a fifteen-minute irradiation.

In this paper we report on our investigation along the lines begun by these workers. We have done partial dissolution experiments to check for selective leaching of any of the sea salt major cations, and have analyzed individual tests of the same foraminiferal species separately to check for intraspecies variability. We have analyzed the composition of various size fractions of two foraminiferal species to check for chemical changes during ontogeny. Finally, we have analyzed samples of tests of *Globigerinoides ruber* (d'Orbigny) and *G. sacculifer* (Brady) separated from selected North Atlantic core tops to check for environment-dependent geographical variations.

EXPERIMENTAL PROCEDURES AND RESULTS
Preparation and cleaning of samples
Raw sediment samples are washed in a hot calgon solution and sieved through a 63-micron screen. The dried residue is then sieved through the appropriate size screen depending on which species are to be analysed. Fifteen to twenty individual specimens of particularly large species (> 250 microns) and anywhere from 30–100 specimens of smaller species are separated from the entire sample. Specimens of each individual species are placed in polyethylene vials and ultrasonically cleaned in deionized water. Small foraminiferal fragments, clay minerals, and coccoliths are removed from suspension with an eye-dropper. This procedure is repeated at least twice; then 2–3 more deionized water washings are performed. A balance must be reached between the cleaning ability of the ultrasonic vibrations and pulverization of the foraminiferal tests. The specimens are dried and 0.5–1 mg. of material is transferred to 1–cc. polyethylene irradiation vials. A last visual inspection of the specimens under a binocular microscope enables the removal of unclean specimens and a final verification of the identifications.

Neutron activation analyses
Polyvials to be irradiated are positioned in an irradiation rabbit and irradiated for 15 minutes with a thermal neutron flux of 4×10^{12} thermal neutrons cm.$^{-2}$ sec.$^{-1}$ in the reactor of the Rhode Island Nuclear Science Center. After irradiation the samples are transferred to new vials

for counting, which commences 25.0 minutes after the start of the irradiation and continues for 1000 seconds (clock time). Samples are counted on a Ge(Li) detector coupled to a 4096–channel pulse height analyzer; at the completion of a count the data are read onto magnetic tape and integrated using the Gamanal program. A typical spectrum is shown in text-figure 1.

Standards for Na, Sr, and Ca are prepared by pipetting 100 μl. of a solution containing 36.7, 45.9, and 917 ppm Na, Sr, and Ca, respectively onto a Delbag filter. The drop of standard solution is allowed to evaporate in a "clean bench", after which it is sandwiched between another section of the filter and punched out to form a small disk 1 cm. in diameter. The standard is then sealed in a small polyethylene bag and is ready for irradiation. Standards and samples are irradiated using the same protocol. After irradiation the filter disc is removed from its polyethylene wrap and pressed to the bottom of another vial with Al foil. This insures that the standard disc is very close to the detector so that sample and standard counting geometries are identical.

Al, Ca standards are prepared in a manner analogous to the Na, Sr, Ca standards (each filter disc contains 4.72 and 94.3 μg. of Al and Ca respectively). A high Cl blank in the filter necessitated the preparation and irradiation of a NaCl standard solution (100 μl aliquots were counted after irradiating a 124 ppm NaCl solution).

In a typical spectrum (text-figure 1), photopeaks occur from ^{24}Na, ^{27}Mg, ^{87m}Sr, ^{49}Ca, ^{28}Al, ^{38}Cl, and ^{56}Mn gamma ray emissions (table 1). Since irradiation and counting time intervals are kept constant, decay corrections need not be computed when calculating sample composition from sample and standard data. Elemental ratios are computed by comparing ratios of peak areas in samples with those of standards. Calculation of elemental ratios instead of absolute element concentrations obviates the need to weigh the sample and monitor the neutron flux during an irradiation; the Ca in the sample is a measure of the amount of sample present and the ^{49}Ca activity serves as an internal neutron flux monitor. In this and many other studies of carbonate chemistry the ratio of the cation to Ca is more relevant to problems being studied than are actual elemental concentrations.

Results of a number of replicate analyses are shown in tables 2 and 3. Samples are in two groups — composite samples containing about 10 foraminifera tests and weighing about 1 mg., and samples consisting of individual tests randomly picked from the composite sample. For composite samples, the precision (standard deviation of replicate analyses from the mean) of Na/Ca and Sr/Ca ratios is $\pm2\%$; for individual samples the precision is $\pm3\%$ for Na/Ca and $\pm8\%$ for Sr/Ca. Mg generally is not determined by this method since its concentration

TABLE 1
Isotope decay information*

Isotope	Half life	Decay mode	Decay energy (KeV)	Relative peak Intensity
^{24}Na	15.0 h.	β—, γ	1368.4	100.0
		β—, γ	2754.1	100.0
		β—, γ	3850.0	0.1
^{27}Mg	9.46 min.	β—, γ	170.8	1.2
		β—, γ	843.8	100.0
		β—, γ	1014.5	37.5
^{28}Al	2.32 min.	β—, γ	1778.7	100.0
^{38}Cl	37.3 min.	β—, γ	1642.7	74.5
		β—, γ	2167.6	100.0
^{49}Ca	8.80 min.	β—, γ	3084.4	100.0
		β—, γ	4071.9	8.0
^{52}V	3.75 min.	β—, γ	1434.3	100.0
^{56}Mn	155 min.	β—, γ	846.7	100.0
		β—, γ	1811.2	29.4
		β—, γ	2112.6	16.0
		β—, γ	2523.6	1.6
^{66}Cu	5.10 min.	β—, γ	1039.2	100.0
^{87m}Sr	170 min.	I.T.	388.5	100.0
^{139}Ba	82.9 min.	β—, γ	165.8	100.0

*Taken from: Filby, R. H., Davis, A. I., Shah, K. R., Wainscott, G. G., Haller, W. A., and Cassatt, W. A., *Gamma ray energy tables for neutron activation analysis*, Washington State University, 1970.

is too low to obtain good counting statistics from the 1014 KeV gamma of ^{27}Mg; the stronger 844 KeV gamma is obscured due to the high count rate of ^{56}Mn (at 847 KeV).

Elements present in amounts near the detection limit using this procedure could in some cases be detected with greater precision by altering irradiation and counting conditions. ^{28}Al, for example, has a half life of 2.3 minutes, so that most of it has decayed before counting has commenced. By decreasing the time before a sample is counted, Al precisions could be improved. An increase in counting time would improve Cl precisions, while conditions as outlined above are optimal for a simultaneous Mg, Sr, Na, and Ca determination. In carbonates where Mg concentrations are greater than 1%, its ratio to Ca can be determined to a precision of less than 5% by this method. In samples with lower Mg levels, precision can be improved only by using a Ge(Li) detector with a higher efficiency or by using large samples with a Compton suppression system.

The technique described above has a number of attractive features: 1) It allows the simultaneous determination of most of the important elements being considered in studies of biogenic carbonate chemistry and carbonate diagenesis. Na and Sr are routinely measured; Mg is measured accurately at levels greater than 1%; Cl provides an index of sea salt contamination (Land and Hoops, 1973); and Al indicates the extent of detrital contamination. Other metals (such as Mn, V, Cu and Ba) which are of interest in Ca carbonates and other carbonate systems can be determined by this method with significant precision if their concentrations are high enough. 2) Small samples can be accurately analyzed. Counting statistics for a 700 μg. sample are better than 5% for Na, Sr, and Ca. Counting statistics for samples as

TABLE 2
Chemical composition of composite and individual Upper Pleistocene foraminifera samples from Site 208, D.S.D.P. Leg 21. All results are given in units of atom ratios in the whole sample. n.d. = not detectable. * = Mg analyses not performed.

Species	Size fraction (μ)	Irradiation number	Na/Ca x 10³	Mg/Ca x 10³	Sr/Ca x 10³	Cl/Na x 10²	Al/Ca x 10³	Nature of sample
Globigerinoides conglobatus	>417	361	6.3	3.1	1.46	2	n.d.	composite
Globigerinoides ruber	>417	527	6.4	*	1.44	2	3.2	composite
" "	351–417	528	6.6	*	1.45	3	6.3	composite
" "	295–351	529	6.5	*	1.51	n.d.	6.7	composite
" "	250–295	530	6.6	*	1.49	4	3.0	composite
" "	124–250	531	6.5	*	1.42	3	1.7	composite
Globigerinoides sacculifer	>417	359	6.5	4.6	1.53	n.d.	2.5	composite
" "	351–417	521	6.1	3.9	1.34	4	0.7	composite
" "	295–351	522	6.2	4.3	1.42	4	2.6	composite
" "	250–295	523	6.1	4.1	1.38	3	1.8	composite
" "	124–250	524	6.3	4.7	1.42	n.d.	5.4	composite
Neogloboquadrina dutertrei	>417	515	6.1	3.9	1.49	n.d.	8.0	composite
Globorotalia truncatulinoides	>417	518	5.7	2.3	1.42	n.d.	n.d.	fragments of tests
" "	>417	362	5.9	*	1.44	3	n.d.	composite
" "	>417	457	6.4	*	1.56	10	n.d.	individual test
" "	>417	458	7.3	3.7	1.56	n.d.	n.d.	individual test
" "	>417	459	6.2	2.7	1.49	5	n.d.	individual test
" "	>417	460	6.3	1.90	1.61	8	n.d.	individual test
" "	>417	461	6.1	1.58	1.42	n.d.	n.d.	individual test
" "	>417	462	6.3	1.60	1.43	n.d.	n.d.	individual test
Globorotalia crassaformis	>417	382	5.2	*	1.32	3	3.6	composite
repeat		481	5.2	2.6	1.25	4	4.1	
Globorotalia crassaformis	>417	516	5.3	2.9	1.40	n.d.	n.d.	composite
Globorotalia menardii	>417	381	5.1	*	1.39	2	0.8	composite
repeat		480	4.8	2.8	1.31	n.d.	0.6	
Globorotalia menardii	>417	519	4.9	2.4	1.34	4	1.2	fragments of tests
Globorotalia tumida	451	357	4.4	2.1	1.34	n.d.	n.d.	composite
" "	417	354	4.8	2.1	1.33	n.d.	n.d.	fragments of tests
Globigerinella siphonifera	417	363	6.0	4.0	1.24	n.d.	n.d.	composite
Orbulina universa	417	364	5.3	*	1.54	n.d.	n.d.	composite
" "	417	503	6.4	*	1.62	n.d.	2.4	individual test
" "	417		5.1	*	1.45	n.d.	n.d.	individual test
Pulleniatina obliquiloculata	417	353	5.3	2.5	1.41	5	1.4	composite
" "	417	520	5.6	2.7	1.44	4	2.9	fragments of tests
Sphaeroidinella dehiscens	417	517	5.3	3.1	1.36	2	1.9	fragments of tests
" "	417	365	5.1	2.6	1.31	2	n.d.	composite
" "	417	383	4.9	*	1.29	n.d.	n.d.	individual test
repeat		482	5.3	1.60	1.53	n.d.	n.d.	
Sphaeroidinella dehiscens	417	384	5.4	*	1.28	7	n.d.	individual test
repeat		483	5.2	2.6	1.53	n.d.	n.d.	
Sphaeroidinella dehiscens	417	385	5.4	*	1.04	n.d.	0	individual test
repeat		484	5.8	3.1	1.18	16	2.4	
Sphaeroidinella dehiscens	417	434	5.7	2.7	1.47	3	n.d.	individual test
" "	417	435	5.4	2.6	1.39	n.d.	n.d.	individual test
" "	417	436	5.8	3.4	1.34	n.d.	n.d.	individual test

low as 100 μg. are: Ca, 4%; Na, 7%; Sr, 12%. 3) The method is non-destructive, thus allowing subsequent chemical, isotopic and microscopic analysis of the same sample. 4) The method is rapid and simple; up to twenty-two samples can be analyzed during an eight-hour period.

Atomic absorption analyses

Since Mg could not be determined in these samples due to its low concentration and due to the presence of Mn, Mg/Ca ratios were determined using a Perkin-Elmer 503 flame atomic absorption spectrophotometer. Splits of the activated samples were dissolved in 5 ml. of 1N HNO_3 with La added to make the solution 1,000 ppm in La; the Mg concentration of this solution was then determined. A 1/10 dilution of the first solution was then made in order to determine Ca. La was added to the second solution so that its concentration in this solution was also 1,000 ppm. A set of standards was prepared in 1N HNO_3 so that the Mg/Ca ratios in the standards was

TABLE 3
Chemical composition of composite *G. sacculifer* and *G. ruber* samples from the 250 μ size fraction of North Atlantic core tops. n.d. = not detectable. * = Mg analyses not performed.

Core	Latitude & longitude	Average August temperature (°C)	Average August salinity (°/oo)	Species	Irradiation number	Na/Ca x 10³	Mg/Ca x 10³	Sr/Ca x 10³	Cl/Na x 10²	Al/Ca x 10³
V4-32	35°03' N. 11°37' W.	21.1	36.7	G. sacculifer	612	6.8	*	1.46	7	1.6
				repeat	815	7.4	3.6	1.45	41	3
V23-96	29°48.2' N. 15°05.5' W.	22.0	36.8	G. ruber	594	7.2	3.7	1.50	9	n.d.
				G. sacculifer	613	7.7	6.3	1.42	n.d.	26
V29-170	22°28' N. 20°04' W.	23.2	36.6	G. ruber	595	7.0	3.6	1.38	6	3.8
				G. sacculifer	614	6.3	3.9	1.31	n.d.	3.7
V23-101	19°53' N. 25°32' W.	24.3	36.6	G. ruber	596	6.9	2.9	1.42	n.d.	2.1
				G. sacculifer	615	6.7	*	1.35	2	22
				repeat	816	6.4	6.3	1.30	14	19
V23-112	17°16' N. 46°45' W.	24.9	36.8	G. ruber	597	7.8	7.1	1.53	n.d.	1.8
				G. sacculifer	616	6.1	4.2	1.30	n.d.	7.8
V23-105	17°12' N. 35°50' W.	25.6	36.5	G. ruber	598	7.1	*	1.32	n.d.	n.d.
				G. sacculifer	617	5.7	4.3	1.29	n.d.	5.6
V23-107	17°29' N. 40°40' W.	26.0	36.5	G. sacculifer	618	5.8	*	1.36	4	1.5
				repeat	817	5.8	3.3	1.41	4	0.9
V16-20	17°56' N. 50°21' W.	27.1	36.5	G. sacculifer	619	6.8	14.0	1.40	n.d.	47
A179-13	23°30' N. 76°00' W.	28.6	36.5	G. sacculifer	620	6.1	5.1	1.27	5	2.8
V3-128	23°45.5' N. 92°28.5' W.	29.0	36.5	G. sacculifer	621	7.6	*	1.26	6	40
				repeat	818	7.4	7.8	1.44	27	40
A181-07	19°10' N. 59°45' W.	28.1	34.2	G. sacculifer	823	7.5	*	1.41	18	42
V9-31	08°14' N. 37°52' W.	27.4	35.0	G. sacculifer	824	6.8	*	1.42	13	14
V25-46	09°19' N. 42°59.6' W.	27.8	35.7	G. sacculifer	825	6.9	*	1.20	49	5.7

similar to that of the samples. A 1/10 dilution of the Mg standard thereby allowed the determination of Ca, as in the sample analysis.

Dissolution experiment

A batch of *G. sacculifer* tests was picked from Upper Pleistocene Deep-Sea Drilling Project (D.S.D.P.) sample 21-208-2cc (sample notation follows the order of D.S.D.P. leg-site-core-section, depth in section, cc denotes core catcher); the site is located in the Tasman Sea at latitude 26°06.61' S., longitude 161°13.27' E., in waters 1545 m. deep. Core 2, from which our sample was taken, represents an interval 1564–1573 m. below the drill floor and 9–18 m. below the sea floor. Groups of the *G. sacculifer* tests were dissolved in 1-ml. portions of dilute HNO_3. The normality of the acid added to each group of tests was suitable to dissolve a given percentage of $CaCO_3$. The tests were allowed to sit in the acid for 48 hours; they were next washed several times with distilled water and dried in an oven. Atom ratios in the tests were then determined by neutron activation analysis. The amount of sample available was insufficient for Mg determination. Results are summarized in table 4 and text-figure 2.

RESULTS AND DISCUSSION

Results of determinations of Na/Ca, Mg/Ca, Sr/Ca, Cl/Na and Al/Ca atom ratios in foraminifera from the above-mentioned Upper Pleistocene D.S.D.P. sample are presented in table 2. Analytical data for two species from North Atlantic surface sediments are given in table 3.
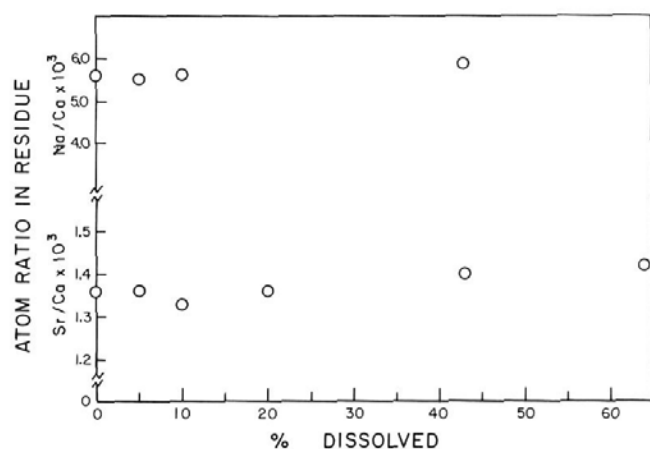
Distribution of Sr, Na and Mg in the foraminiferal tests

All previous workers have argued that strontium in foraminiferal tests is substituted for calcium in the calcite

lattice; our results are consistent with this. There is no covariation between Sr and Al, or Sr and Cl, indicating that contaminating aluminosilicate and chloride salts do not bear significant amounts of strontium in the samples examined thus far. Sr/Ca ratios remain constant during dissolution of successive portions of a foraminifera sample, indicating that Sr is homogeneously distributed throughout the calcite test (text-figure 2).

Sodium distribution is more complex. Aluminosilicate contamination may account for a significant amount of sodium in the foraminifera. In text-figure 3, Na/Ca ratios are plotted *versus* Al/Ca ratios. Foraminifera with no detectable aluminum have Na/Ca atom ratios ranging from 4×10^{-3} to 8×10^{-3}, showing without doubt that aluminosilicate contamination is not the sole source of Na in forams. Na/Ca ratios generally increase with increasing Al/Ca ratios, although there is a great deal of scatter due to interspecific differences in Na/Ca ratios. From these results, we estimate that the Na/Al ratio in the contaminating aluminosilicate is somewhere between 0.10 and 0.05. In the discussion, we arbitrarily omit from consideration all samples having Na/Ca ratios less than Al/Ca ratios. The maximum extent of detrital Na contamination in any included sample is therefore less than 10%.

Another potential source of contamination is sea salt. The Cl/Na ratios of the composite and fragmented samples average about 0.03, indicating that as much as 3% of the sodium may be due to contamination by a chloride salt. A few samples gave very high but irreproducible chlorine values (see table 3) while Na values for those samples are reproducible and constant; this
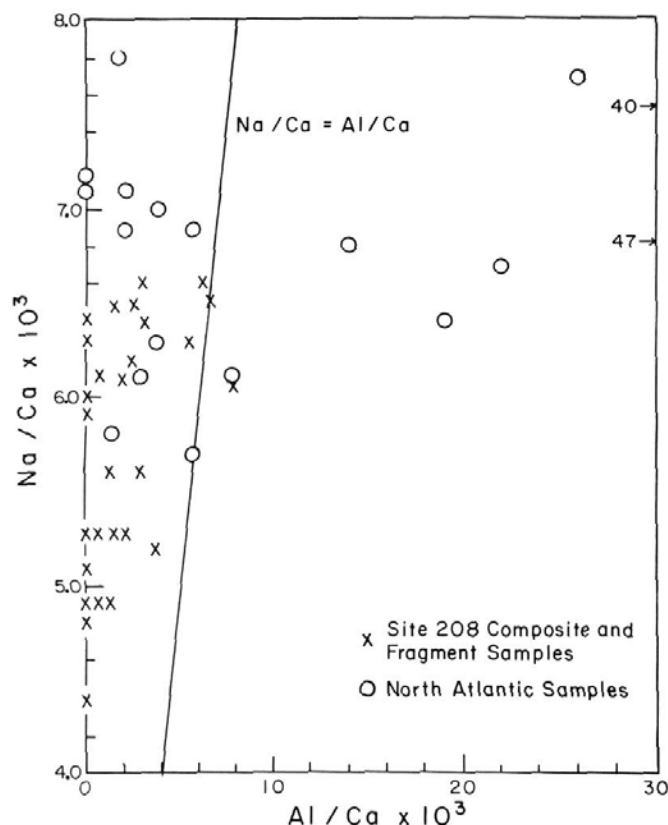
TEXT-FIGURE 2
Sr/Ca and Na/Ca atom ratios in residual calcite of *G. sacculifer* from D.S.D.P. sample 21-208-2cc after dissolution of varying amounts of the sample.

TEXT-FIGURE 3
Na/Ca *versus* Al/Ca atom ratios in all samples except those in which individual tests were analyzed. Numbers next to arrows indicate Al/Ca ratios of those samples.

observation, coupled with the fact that individual tests had higher Cl/Na ratios than composite samples, led us to believe that the presence of chlorine is due to laboratory contamination. As this would require addition of only a few hundred nannograms of Cl, contamination does not seem unlikely. We have assumed that no Na is associated with Cl in the analyzed samples, and make no correction for a chloride-bearing sodium phase.

Na/Ca ratios of foraminiferal calcite remaining after various fractions had been dissolved are shown in text-figure 2. There is no systematic change in the Na/Ca ratios of the residue, an observation consistent with the notion that sodium is homogeneously distributed throughout the lattice. This data thus gives some indication that sodium is dominantly associated with $CaCO_3$ and is not present as a labile surficial or ion-exchangeable component. The state of sodium is unclear. Since charge balance must be maintained, sodium cannot substitute directly for calcium in a $CaCO_3$ lattice without compensation (Amiel, Friedman, and Miller, 1973; Land and Hoops, 1973). It is clearly not balanced by chloride (as can be seen from our results) or by a trivalent or tetravalent cation such as Al^{+3}, Fe^{+3}, or Mn^{+4} (see results of Emiliani, 1955; Krinsley, 1960; Kilbourne and Sen Gupta, 1973; and this paper). There is no indication of whether or not Na is present as $NaHCO_3$; this is certainly a possibility. Amiel *et al.* (1973) suggested that Na in coralline aragonite is present as Na_2CO_3, and this may well be the case in foraminifera.

Mg abundances may include aluminosilicate contributions as is revealed in text-figure 4: Samples with high Al/Ca ratios clearly have high Mg/Ca ratios. We estimate that the contaminating aluminosilicate has a Mg/Al ratio of about 0.10. All samples with Al/Ca ratios greater than Mg/Ca ratios are omitted from further consider-
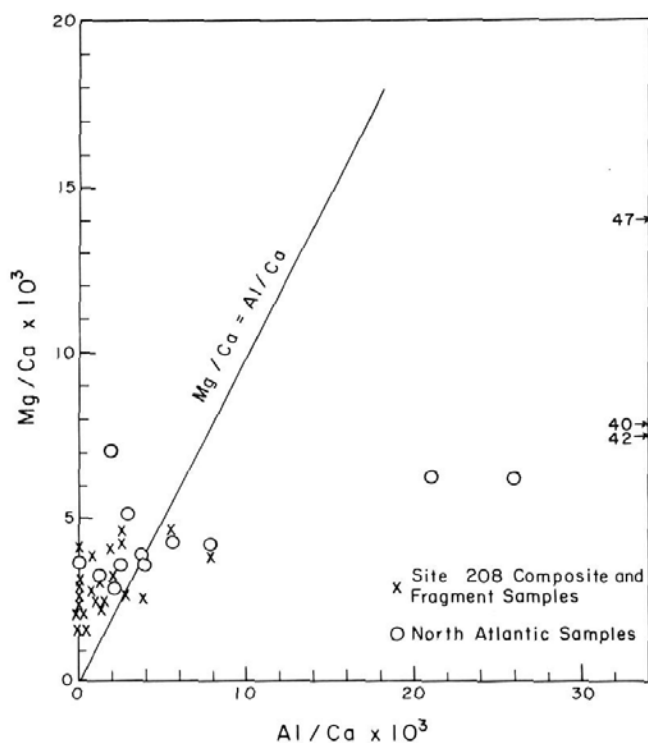
ation; those samples passing this criterion may have up to 10% of their Mg borne by contaminating aluminosilicate.

It is unclear from the data whether or not any Mg is associated with chloride. If the chloride is present as sea salt, it would not bear a significant amount of magnesium since the Mg/Cl atom ratio in sea water is 0.1. However, if the chloride is a laboratory contaminant, the Mg/Cl ratio in the chloride-bearing phase is completely unknown. We shall assume that there is no magnesium associated with chloride.

Magnesium is distributed in foraminifera far more heterogeneously than either Na or Sr, as is indicated by the fact that individual tests of planktonic foraminifera have Mg/Ca ratios far more variable than Na/Ca or Sr/Ca ratios (table 4). This has also been revealed by electron microprobe studies of Lipps and Ribbe (1967) and of our group (unpublished). Some of the Mg presumably substitutes for Ca in the calcite lattice. There may be other sites of Mg deposition; for example Mg may be present in ion-exchangeable and/or other labile positions as outlined by Amiel *et al.* (1973) for corals. In further discussion we will assume that all Mg is present

TEXT-FIGURE 4
Mg/Ca *versus* Al/Ca atom ratios in all samples except those in which individual tests were analyzed.

TABLE 4
Atom ratios in residues of *G. sacculifer* tests dissolved to various extents. * = none detected.

	Atom ratio in residue (10³)		
% dissolved	Na/Ca	Sr/Ca	Al/Ca
0	5.6	1.36	4.2
5	5.5	1.36	*
10	5.6	1.33	4.4
20	5.5	1.36	8.9
43	5.9	1.40	*
64	6.1	1.42	11.1

in the calcite, but we recognize the tenuous nature of this assumption and realize that it must be tested by future work.

Factors controlling Na/Ca, Mg/Ca and Sr/Ca ratios in foraminiferal calcite

Composite and fragmented foraminiferal samples not contaminated by aluminosilicate have Na/Ca atom ratios between 4.4×10^{-3} and 7.1×10^{-3}, Mg/Ca ratios between 1.6×10^{-3} and 4.6×10^{-3}, and Sr/Ca ratios from 1.20×10^{-3} to 1.54×10^{-3}. These results are in good agreement with the data of Emiliani (1955), Krinsley (1960), Kilbourne and Sen Gupta (1973), and Savin and Douglas (1973).

The Na/Ca and Sr/Ca atom ratios of calcite precipitated in thermodynamic equilibrium with sea water at 25°C are about 8×10^{-4} and 5×10^{-4} respectively according to the distribution coefficient data of White (1974) for sodium and Katz, Sass, Starinsky and Holland (1972) for strontium. Thus the Na/Ca and Sr/Ca ratios of foraminiferal calcite are much higher than the values predicted from distribution coefficient data. This is a real discrepancy which cannot be eliminated by consideration of ion pairing, pH of the parent solutions, minor enrichments and depletions of cations in parent solutions, or growth temperature of the organisms. Laboratory experiments have revealed two ways of enriching trace elements in calcite. First, rapid precipitation of calcite may produce
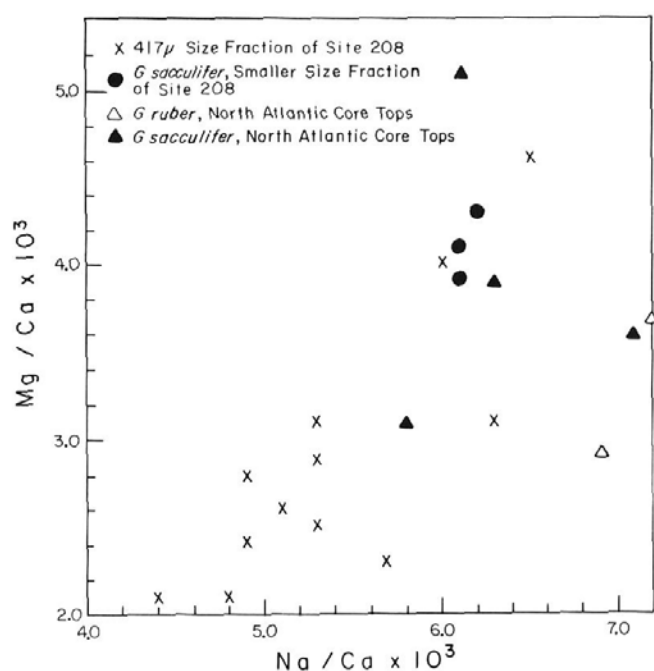
a solid with trace element contents higher than the values predicted from thermodynamic data (see, for example, the discussion of Katz et al., 1972). Second, the presence of an organic complexing agent which may be adsorbed on calcite surfaces has been shown to enrich calcite in sodium (White, MS). It may well be that one of these two factors is responsible for the high Na/Ca and Sr/Ca ratios.

Berner (1975) finds that in sea water solutions the most thermodynamically stable Mg-calcite contains from two to seven mole percent Mg. Foraminiferal calcite contains approximately an order of magnitude less Mg than the sea water thermodynamic optimum.

Why low Mg-calcite should form is unclear. One obvious explanation is that the composition of the crystallizing fluid is radically different from that of sea water. Where sea water has a Mg/Ca ratio of 5.2, the Mg/Ca ratio of a fluid precipitating such a low Mg-calcite as observed in these foraminifera would have to be less than 5×10^{-2}, according to the distribution coefficient of Katz (1973). Since Mg and Ca ions are physiologically important and the ability of a variety of organisms to regulate their intracellular ion composition has been demonstrated (Prosser, 1973), it may not be unreasonable to postulate that the foraminifera can regulate the ion composition of the fluid from which mineralization of the test occurs.
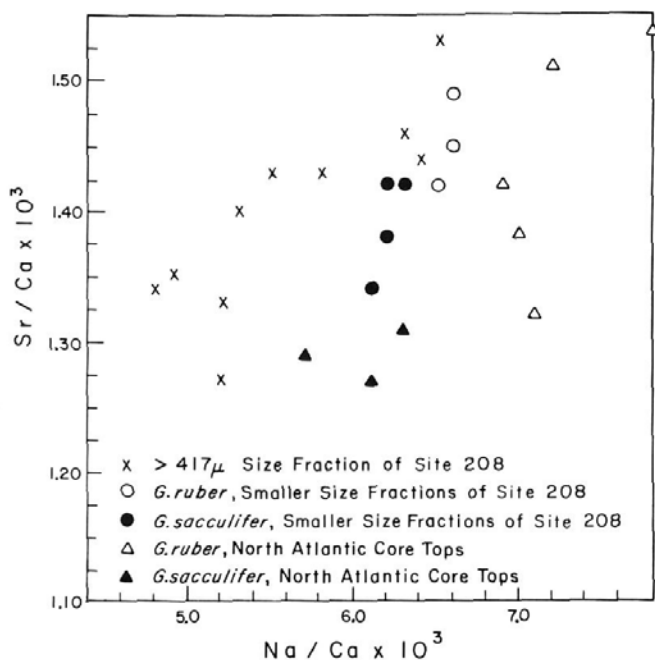
Angell (1967a, 1967b) has shown that for the calcitic benthic foraminifera *Rosalina floridana*, the addition of new test chambers results from secretions by pseudopodia which cover the newly forming chamber. The *Rosalina* test which is a result of this secretory activity is a high Mg-calcite (10–15 mole %). Whether the planktonic species secrete their tests by a similar process, and whether they extensively regulate the ion composition of the crystallizing fluid is unknown.

Alternate mechanisms can be proposed which could induce low Mg/Ca ratios in biogenically formed calcite. Organic complexing agents produced by the foraminifera could selectively complex Mg, thereby reducing its solution activity and hence allowing low Mg-calcite crystallization. However, there is no evidence in the literature either supporting or contradicting this hypothesis that suggests such an extensive differential complexation of Mg. Alternatively, *since an organic matrix is intimately*

TEXT-FIGURE 5
Mg/Ca *versus* Na/Ca for various samples. Only samples with Mg/Ca > Al/Ca and Na/Ca > Al/Ca are plotted.

TEXT-FIGURE 6
Sr/Ca *versus* Na/Ca for various samples. Only samples with Na/Ca > Al/Ca are plotted.

associated with biogenic carbonates (King and Hare, 1972; Travis, 1970), this organic matrix may "direct" crystal growth so that Mg is excluded. Meenashki *et al.* (1975) have reported a correlation between the amino acid composition of the organic matrix of a regenerating portion of *Nautilus* shell and the crystal polymorph of the shell, aragonite *versus* calcite. Whether such suggested control of crystal polymorph can be extended to include control of crystal ion composition is again unknown.

Variations of Na/Ca, Mg/Ca and Sr/Ca ratios

The variability in Na/Ca and Sr/Ca ratios among different tests of the same species is small (table 2); therefore the atom ratios obtained by analyzing samples of ten to twenty tests must be representative of the values for the species and size fraction studied. Consequently, the variations in atom ratios must be regarded as being true interspecific differences within the size fraction studied. The variations in atom ratios are similar to results obtained by other workers. Mg/Ca ratios are generally equal to or somewhat lower than those of Savin and Douglas (1973). Our lower values may be due to the fact that we measured Al and omitted clay-contaminated samples from consideration, whereas they did not. The most important difference between our values and those of Savin and Douglas is that our *G. truncatulinoides* samples had an average Mg/Ca ratio lower than that for any other species except *tumida*, whereas their *trun-*

catulinoides samples had Mg values in the middle of the range.

Mg/Ca ratios and Sr/Ca ratios are plotted against Na/Ca ratios in text-figures 5 and 6. For the different species comprising the foraminiferal assemblage in the Site 208 sample, Mg/Ca ratios and Sr/Ca ratios sympathetically increase with increasing Na/Ca ratios. Such behavior suggests that variations in each of the three atom ratios are caused by the same or at least related factors.
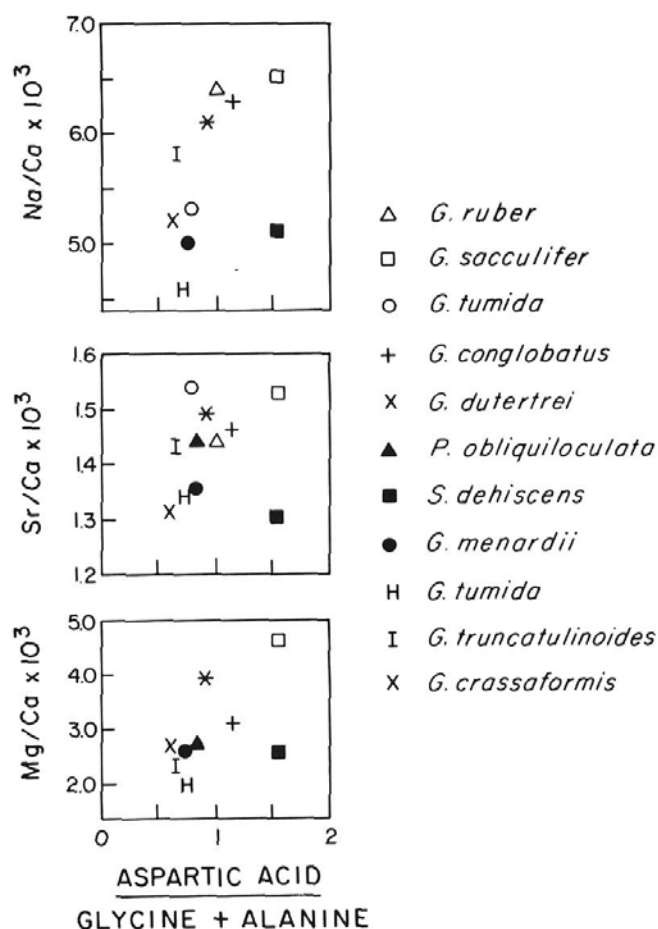
There does not seem to be any simple chemical way of accounting for the covariation of the atom ratios. If, for example, changes in elemental abundance were due to varying extents of depletion of calcium during calcification in a closed system, the variations in the Sr/Ca ratio observed would not be less than variations observed in the Na/Ca ratio. This prediction is based on the argument that for a calcite in equilibrium with a solution of a given Sr/Ca ratio, the Sr/Ca in the solid phase increases in proportion to the Sr/Ca ratio in the solution phase (Katz *et al.*, 1972), whereas the Na/Ca ratio in the solid phase increases approximately proportionally to the cube root of increases in the Na/Ca ratio of the solution (White, MS).

Perhaps there is a biochemical or physiological process which causes such a covariation in the atom ratios. There is an apparent correlation between the amino acid content of the organic matrix in the different species of

foraminifera and the atom ratio variations. King and Hare (1973) reported the amino acid composition for a variety of foraminiferal species. The principle variation occurred in the three amino acids glycine, alanine, and aspartic acid. An increase in aspartic acid content was generally associated with a decrease in glycine and alanine content. By plotting the ratio aspartic acid/(glycine + alanine) for individual species against the atom ratios of that species as determined in this paper (text-figure 7), a comparison of changes in trace element abundances and changes in the acidity of the organic matrix can be made.

Except for one species, *Sphaeroidinella dehiscens* (Parker and Jones), there is a good correlation between increases in the acidity of the matrix and increases in the Mg/Ca and Sr/Ca atom ratios. The Na/Ca correlation, although present, is not so well defined. If acidic amino acids act as nucleating sites for the crystallization of $CaCO_3$ as suggested by Matheja and Degens (1968), then perhaps an increase in such nucleating sites could cause a concomitant increase in trace metal coprecipitation due to an increased crystal growth rate.

Na/Ca, Mg/Ca, and Sr/Ca ratios also show a correlation with the relative growth depth of each species (text-figure 8). A similar correlation has been noted for magnesium and strontium by Kilbourne and Sen Gupta (1973) and for magnesium by Savin and Douglas (1973). A number of factors could be responsible for this relationship. Temperature is the most obvious one, but this notion is contradicted by our data on Na/Ca, Mg/Ca and Sr/Ca atom ratios for *G. ruber* and *G. sacculifer* from 13 samples of Recent North Atlantic sediments; these ratios do not show any clear increase with increasing surface water temperature, there may in fact be a slight decrease in the ratios with increasing temperature (text-figure 9). A second possibility is that the atom ratio variations are due to variations in the calcification rate, with higher calcification rates producing samples with higher trace element levels. Zolotarev (1975) has found this to be true for Sr and Mg in calcitic pelecypods. The decrease in Na/Ca, Mg/Ca, and Sr/Ca atom ratios with inferred increasing growth depth among the samples from Site 208 may be due to a temperature dependence on the calcification rate. Atom ratios from samples from various parts of the oceans would not necessarily follow this temperature dependency, since their calcification rates could vary from place to place according to nutrient supplies and other factors. However, according to this hypothesis atom ratios of foraminifera from various areas would be expected to covary in similar ways; compare the Mg/Ca, Sr/Ca, and Na/Ca ratios determined for tests from Site 208 in the Tasman Sea against those from the North Atlantic (text-figures 5 and 6). Sr/Ca and
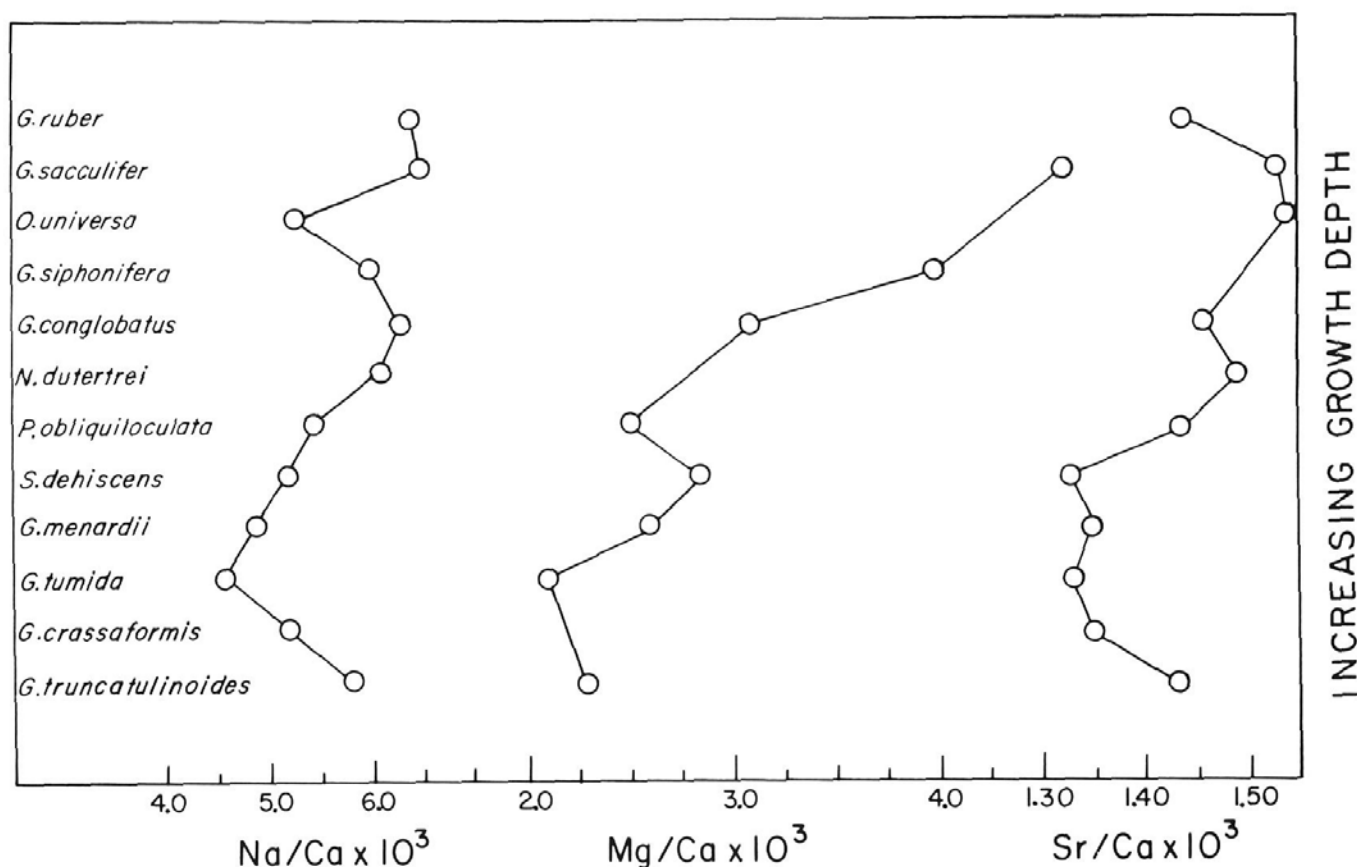

TEXT-FIGURE 7

Mg/Ca, Sr/Ca, and Na/Ca ratios for individual species from the $> 417 \mu$ size fraction of D.S.D.P. sample 21-208-2cc plotted against the ratio of the amino acids aspartic acid/(glycine + alanine) as determined for each species by King and Hare (1972).

Na/Ca ratios of Tasman Sea and Atlantic samples covary in a similar way, although the Sr/Ca ratios in the Atlantic samples appear to be systematically about 6% lower than Sr/Ca ratios in the Tasman Sea samples with similar Na/Ca ratios. While the Mg/Ca *vs.* Na/Ca data appears more scattered in the North Atlantic region, a similar trend is still evident.

SUMMARY

Na/Ca, Mg/Ca, and Sr/Ca atom ratios of planktonic foraminifera analyzed from sediments of the North Atlantic and Tasman Sea range from 4.4×10^{-3} to 7.1×10^{-3}, 1.6×10^{-3} to 4.6×10^{-3}, and 1.2×10^{-3} to 1.5×10^{-3}, respectively. Na and Sr appear, on the basis of dissolution experiments, analyses of individual tests, and our unpublished electron microprobe analyses, to be homogeneously distributed throughout the test; Mg is more variable and its disposition in the tests is unclear.

Na/Ca, Mg/Ca, and Sr/Ca atom ratios of individual species from an Upper Pleistocene core section in the

TEXT-FIGURE 8
Variation of Na/Ca, Mg/Ca and Sr/Ca atom ratios in JOIDES Site 208 sample 21-208-2cc with relative growth depth of the organisms (depth ranking derived by averaging result of Savin and Douglas, Oba (1969), Lidz *et al.* (1968), Hecht (MS), Berger (1969) and Emiliani (1971) as summarized by Savin and Douglas (1973)).

Tasman Sea decrease with increasing average growth depth of each species. Atom ratios of *G. sacculifer* and *G. ruber* samples from Recent North Atlantic sediments vary in a way generally similar to those of the Tasman Sea sample, but they do not vary with temperature in an obvious way.

Na/Ca and Sr/Ca atom ratios in the foraminiferal calcite are higher by a factor of 5 to 10 than predicted from distribution coefficient data; Mg/Ca atom ratios are however lower than predicted, assuming crystal growth occurs in a solution of composition similar to sea water.

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TEXT-FIGURE 9
Dependence of Na/Ca, Mg/Ca and Sr/Ca atom ratios of samples from North Atlantic core tops on average August temperatures. Only samples with Na/Ca > Al/Ca and Mg/Ca > Al/Ca are plotted.

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