

FLUORINE, CHLORINE, AND BROMINE IN CARBONATE ROCKS .

FLUORINE, CHLORINE, AND BROMINE IN CARBONATE ROCKS
IN RELATION TO THE CHEMICAL HISTORY OF OCEAN WATER
AND DOLOMITIZATION

By

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A Thesis

Submitted to the Faculty of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree

Doctor of Philosophy

McMaster University

May 1969

DOCTOR OF PHILOSOPHY (1969)
(Geology)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: Fluorine, Chlorine, and Bromine in Carbonate Rocks
in Relation to the Chemical History of Ocean Water
and Dolomitization

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NUMBER OF PAGES: xii, 173

SCOPE AND CONTENTS:

The purpose of this thesis is to establish possible changes in the Cl/Br ratio of ancient oceans over the past 2×10^9 years. Variations in the Cl/Br ratio of carbonate rocks are used to indicate these changes.

A secondary objective of this thesis is to determine the distribution patterns of F in limestones and dolomites. Variations in the F content of dolomites are shown to be related to environment of deposition and can be used to establish the genesis of dolomite.

The contents of the thesis include; 1) a comprehensive review of pertinent literature, 2) a discussion of the evolution of the Cl/Br ratio of the oceans, 3) application of F in paleoenvironmental reconstruction, and 4) suggestions for further research.

ABSTRACT

The geochemistries of F, Cl, and Br in the sedimentary carbonate systems from Recent to pre-Cambrian (2×10^9 years) age have been investigated. The investigation has shown:

1. The Cl/Br ratio in the water soluble and acid soluble (0.48N HNO₃) extracts show progressive increases from 15/1 in the pre-Cambrian to approximately 90/1 in Recent carbonates. This is interpreted as indicating an increase in the Cl/Br ratio of the ocean throughout geologic time. A geochemical mass balance has shown that the fractionation has occurred in the sedimentary cycle.
2. The Cl and Br occur largely in the water soluble phase, whereas, F occurs as a water insoluble phase. The order of water solubility is Cl > Br > F .
3. Absolute Cl and Br abundances in limestones and dolomites are not significantly different; however, aragonites contain significantly more Cl and Br. Fluorine is enriched in aragonites and dolomites, but is not concentrated in limestones.
4. Fluorine distributions in dolomite have been shown to be environmentally controlled. Refluxing brines and precipitation of CaF₂ in specific zones are suggested as the controlling mechanisms. Interpretation of depositional environments and dolomite genesis on the basis of F content are possible if used in conjunction with other geological data.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the following individuals for generously providing many of the samples used in this study:

Dr. M. L. Keith

Dr. H. S. Ladd

Dr. H. P. Schwarcz

Dr. E. A. Shinn

Dr. T. T. Quirke, Jr.

Dr. R. C. Harriss

Dr. Gale K. Billings

Dr. A. D. Baillie

Dr. C. Moore

Dr. F. T. Mackenzie

Dr. E. R. Jamieson and Dr. D. M. Kent of the Department of Mineral Resources, Government of Saskatchewan, assisted the author in obtaining core samples of Ordovician and Silurian carbonates.

Dr. A. D. Baillie, Dr. A. N. Petracca, and the research staff of Gulf Oil Canada Limited, Calgary, are acknowledged for their many discussions of the environmental history of the Zama dolomite.

Dr. R. C. Harriss' guidance and supervision during the early phases of the study are acknowledged.

Dr. J. R. Kramer supervised the final stages of research and thesis writing. His many useful suggestions regarding research and constructive criticisms of the manuscript were invaluable to the successful completion of the study. A large portion of the research was financially supported by Dr. Kramer.

Acknowledgements are extended to Dr. A. Corsini, Dr. C. Lock, and Dr. J. H. Crockett for critically reviewing the manuscript and acting in the capacity of committee members.

I wish to thank my wife for her patience and understanding, as well as invaluable assistance in computer programming technicalities. She also typed most of the thesis and proof read most of the manuscript.

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INTRODUCTION

The Problem

Rubey (1951), Livingstone (1963a), and Horn and Adams (1966) have shown that the principle cations of sea water (Na, K, Ca, Mg, etc.) and the major elements in sedimentary rocks (Si, Al, Fe, Ca, Mg, etc.) can be derived from the weathering of igneous rocks; while the water of the oceans, the principle anions of sea water (Cl, SO_4 , Br, and F), and a considerable part of the atmospheric gasses (N_2 , CO_2 , O_2) must have been derived from a different source. The "other source" has been attributed to degassing of the earth's interior.

The duration and degassing rate of the volatiles from the depths of the earth are still unresolved; however, it is generally accepted that the oceans have accumulated by slow degassing and that the composition of the ocean has been relatively uniform since the beginning of pre-Cambrian time. The implication is that the ocean is, and has been, in dynamic equilibrium for some time, with input balanced by removal (Holland, 1965). However, in recent years, several lines of evidence have indicated that the chemical composition of the ocean has changed. Krasintseva (1964) reported Cl/Br ratios of 50/1 for sedimentary rocks of L. Cambrian age from the Russian Platform and values of 290/1 for the Pliocene Red Beds of Turkmenia, and interprets this as representing a change in the Cl/Br ratio of sea water since Cambrian time. If the Cl/Br ratio of sea water has increased from some unknown value to the present value of 292/1, how has this change been brought

about and what was the Cl/Br ratio of the pre-Cambrian ocean?

It is proposed in this study that the Cl/Br ratio of the pre-Cambrian ocean was equal to the Cl/Br ratio of the degassing materials, which is estimated to be approximately 60/1. The value of 60/1 was selected as this value is representative of the Cl/Br ratio of igneous rocks. During crystallization of a magma, the volatile constituents accumulate in the late stage fractionates and are expelled in this gaseous and liquid residue. Assuming that magma is the only source of material for the volatiles, the ratio of Cl/Br in the primitive ocean would be equal to the Cl/Br ratio of the late stage fractionates. As discussed in a later section, geological evidence indicates that the Cl/Br ratio of igneous rocks does not vary during crystallization of a magma. It is a reasonable assumption that the ratio of 60/1 in igneous rocks is representative of the late stage fractionates, which presumably represent the degassing materials. Other models using the Cl/Br ratio of chondrite meteorites could assume a different initial Cl/Br ratio in the pre-Cambrian sea.

Several assumptions must be made: 1) the Cl/Br ratio of the degassing materials has remained constant, 2) the volume of the original ocean was small (Rubey (1951) estimates the volume to be 10% of the present ocean) and/or the Cl/Br ratio of the primitive ocean was similar to that of the degassing material, and 3) a uniform rate of degassing.

The question now arises as to how and when the fractionation occurred and how to demonstrate this fractionation in the geologic record. If the Cl/Br ratio of the ocean has increased over the past 2×10^9 years or longer, it would seem reasonable to expect the Cl/Br

ratio of interstitial water or fluid inclusions in authigenic sediments to have changed throughout geologic time. The carbonate system has been selected to define changes in the Cl/Br ratio of sea water over the past 2×10^9 years.

Carbonates are authigenic sedimentary rocks which apparently do not tend to fractionate Cl and Br, thus changes in the halogen composition of sea water should be reflected in the halogen ratios of these rocks. It is assumed that, if diagenetic alterations have not been too extensive, the Cl/Br ratio of ancient carbonates is related to the ancient seas from which they were deposited.

During deposition, sediments are slightly enriched in Br with respect to the surrounding water because many marine organisms accumulate Br which is contributed to the sediment upon their death. However, only part of the Br in organic matter is released into solution. Most of the Br remains bound in the organic matter (Shishkina, 1961). The organic matter content is further reduced by dilution with sediment and oxidation of the organic matter at the time of deposition, which will tend to minimize the enrichment of Br. The water soluble extract should give a better estimate of the Cl/Br ratio of the waters of deposition than the acid soluble fraction.

The chemistries of Cl and Br are similar and there is no mineralogical control over the distribution of these two elements in carbonates. Of the halogens, Cl is completely free of any buffering system, and Br is probably only slightly affected by organisms.

All carbonates have been subjected to varying degrees of alteration and diagenesis. The effects of diagenesis on the Cl/Br ratio of

carbonates must be known if the relationship of these ratios to sea water is to be correctly interpreted. This problem is considered in the present study by examining carbonates which have been subjected to various degrees of diagenesis.

A geochemical mass balance of Cl and Br in the sedimentary environment is presented to evaluate the possibility of fractionation within the normal sedimentary cycle.

Throughout the text, the subscripts T and W refer to the acid soluble and water soluble fractions respectively.

Source of Excess Cl and Br

It has been implied that the Cl and Br originated from the earth's interior (mantle and core). Is there a sufficiently large reservoir of Cl and Br in the mantle and core to supply the excess in the lithosphere-hydrosphere system?

Urey (1952) proposed that the earth accumulated from planetesimals of silicates and iron objects with approximately the same composition as present day meteorites. Urey's concept of planetesimal accumulation is the basis for estimating primordial earth halogen abundances.

Assuming that iron meteorites and siliceous meteorites (particularly carbonaceous chondrites) are representative of the material making up the earth's core and mantle respectively, the availability of Cl and Br may be estimated. With these assumptions, average halogen abundances in carbonaceous chondrites and iron meteorites presented in Table 1, and masses of 4×10^{27} g and 4×10^{27} g for the core

and mantle respectively, one arrives at the following halogen abundances:

	Core	Mantle *
Cl	1600×10^{20} g	2000×10^{21} g
Br	4×10^{20} g	62×10^{21} g

* Data of Reed and Allen (1966) and Goles et al. (1967).

The masses of Cl and Br present in the lithosphere-hydrosphere system are 290×10^{20} g and 170×10^{20} g respectively (Table 21). The amounts of Cl and Br contributed to the lithosphere-hydrosphere system by weathering of igneous rocks are 5×10^{20} g Cl and 8×10^{18} g Br, resulting in an excess of 290×10^{20} g Cl and 160×10^{18} g Br. It would take less than 3% of the mass of the mantle to supply all the excess Cl and Br. The choice of carbonaceous chondrites or ordinary chondrites as representative of the mantle has no effect on the amounts of Cl and Br available.

TABLE 1

Halogen Abundances in Meteorites

Type	N	Cl ppm	Br ppm	Cl/Br	Reference
Carbonaceous chondrites	2	285	65	4.4	Reed and Allen (1966)
Type 1 carbonaceous	4	772	4.0	197	Goles <u>et al.</u> (1967)
Type 2 carbonaceous	4	335	1.9	180	Goles <u>et al.</u> (1967)
Enstatite chondrites	20	131	0.9	152	Goles <u>et al.</u> (1967)
Iron meteorites	4	40	0.09	426	Goles <u>et al.</u> (1967)

N = number of samples.

TABLE 2

Equilibrium Reactions Controlling pH and Distribution of Br Species in Sea Water

Reaction	T (°C)	Equilibrium Constant *	Reference
1. $3\text{Br}_2(\text{g}) + 3\text{H}_2\text{O} \rightleftharpoons 5\text{Br}^- + \text{BrO}_3^- + 6\text{H}^+$	25	$K = \frac{[\text{Br}^-]^5 [\text{BrO}_3^-] [\text{H}^+]^6}{[\text{P}_{\text{Br}_2}]^3} = 10^{-33.19}$	Latimer (1952)
2. $2\text{Br}_2(\text{g}) + 2\text{H}_2\text{O} \rightleftharpoons 4\text{Br}^- + 4\text{H}^+ + \text{O}_2(\text{g})$	25	$K = \frac{[\text{Br}^-]^4 [\text{H}^+]^4 [\text{P}_{\text{O}_2}]}{[\text{P}_{\text{Br}_2}]^2} = 10^{9.9}$	Latimer (1952)
3. $\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	5	$K_c = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] = 10^{-8.09}$	Kramer (1964)
4. $\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2(\text{aq}) + \text{H}_2\text{O}$	5	$K_o = \frac{[\text{CO}_2(\text{aq})]}{[\text{P}_{\text{CO}_2(\text{g})}]} = 10^{1.19}$	Kramer (1964)
5. $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	5	$K_2 = \frac{[\text{H}^+] [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10^{-10.6}$	Kramer (1964)
6. $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	5	$K_1 = \frac{[\text{H}^+] [\text{CO}_3^{2-}]}{[\text{CO}_2(\text{aq})]} = 10^{-6.52}$	Kramer (1964)

* All concentrations in moles/litre except $\text{O}_2(\text{g})$, $\text{Br}_2(\text{g})$, and $\text{CO}_2(\text{g})$ which are given in atmospheres.

Oxidation State of Br in the Oceanic System

The chemical behavior of Br in the oceanic system is of considerable importance in the discussion of the Cl/Br ratio in the pre-Cambrian seas. Because Br is present as a minor constituent, small changes in its absolute abundance will have a significant effect on the Cl/Br ratio, particularly if the conditions are favorable for the existence of Br₂. The species present in the aqueous phase are dependent upon reactions of Br with H⁺, H₂O, and O₂. It is critical to establish the limits of pH and P_{O₂} in the system under consideration, and to determine the relative abundances of the various Br species.

The reactions controlling the pH of sea water and the oxidation state of Br are summarized in Table 2. The upper and lower limits of pH, P_{O₂}, and P_{CO₂} are summarized in Table 3.

TABLE 3

pH, P_{O₂}, P_{CO₂}, and Predominant Br Species

	P _{CO₂} (atm)	P _{O₂} (atm)	pH	Predominant Br Species (> 99%)	Reaction (Table 2)
Recent	10 ^{-3.5}	10 ^{-0.7}	8.20	Br ⁻	2
pre-Cambrian	1	?	*6.07	BrO ₃ ⁻ and Br ⁻	1
pre-Cambrian	1	10 ⁻⁶⁸	6.07	Br ⁻	2

$$* [H^+] = \sqrt[3]{\frac{K_2 K_1^2 (P_{CO_2})^2}{2K_o^2 K_c}} \quad (\text{Reactions 3, 4, 5, and 6 of Table 2}).$$

This model assumes no other ions present, therefore, [Ca²⁺] is replaced by $([CO_3^{2-}][H^+]/2) K_2$.

The upper limit of 1 atmosphere P_{CO_2} is the limit determined by the gravitational constant and the limit at which life forms can exist. The abundance of algae in the time interval considered indicates that the P_{CO_2} was probably lower than 1 atmosphere. The lower limit of P_{O_2} has been taken as the P_{O_2} necessary to oxidize magnetite to hematite (10^{-68} atmospheres). The pre-Cambrian iron ores indicate a P_{O_2} of at least 10^{-68} . The pH of the pre-Cambrian seas is calculated to be 6.07 at a P_{CO_2} of 1 atmosphere.

The predominant species of Br present under varying conditions of pH and P_{O_2} are summarized in Table 3. The species of Br_2 is important only below a pH of about 5.9. The Br in the present ocean is in the form of Br^- , which is also the predominant form of Br in the pre-Cambrian seas.

PREVIOUS GEOCHEMICAL DATA FOR THE HALOGENS

The published data on halogen geochemistry are briefly reviewed. Only the data which are pertinent to the models and concepts developed in the present study are discussed. This includes halogen data on the following: 1) carbonate rocks, 2) igneous rocks, and 3) biogeochemistry. A review of the previous investigations of chemical changes in the ancient oceans is also included as these are pertinent to the concept of a steady state oceanic system since pre-Cambrian time.

Investigations of the geochemistry of the halogens up to 1961 have been summarized by Correns (1961). Fleischer and Robinson (1963) reviewed the geochemistry of F. The most recent summary of the geochemistry of Cl has been presented by Johns and Huang (1967).

The percentage abundances of the halogens in the earth's crust, in order of abundance, are Cl (0.20%), F(0.08%), and Br(0.001%) (Walters, 1967). Abundances of the halogens in various materials of the earth's crust are given in Table 4.

The geochemical cycle of F is essentially transportation to the sea and deposition as CaF_2 or CO_2 -F-apatite (Rankama and Sahama, 1950). The bulk of the Cl carried to the sea remains in solution as the Cl^- ion. Br remains largely in solution in sea water with partial re-incorporation into sediments by means of organic mechanisms. The concentrations of F, Cl, and Br in sea water are 1.35 ppm, 19,000 ppm, and 65 ppm respectively (Mason, 1964).

TABLE 4

Halogen Abundances in Various Materials of the Earth's Crust

Rock Type	F (ppm)	Cl (ppm)	Br (ppm)	Reference
Deep-Sea Sediments	693			Shepherd (1940)
Sandstones and Quartzites	357	60	2.0	Hansen (1961) Correns (1961)
Globigerina Ooze	387			Correns (1961)
Greywacke	211	63	6.2	Seraphim (1951) Fleischer and Robinson (1963)
Bentonite	5980			Fleischer and Robinson (1963)
Shale	732	255	4.4	Correns (1961) Barth and Bruun (1945)
Coal	80	77	4.7	Crossley (1944)
Phosphorites	20950			Kuroda and Sandell (1953)
Bauxite	90	686	2.3	Behne (1953)
Gypsum	658	300		Stewart (1963) Correns (1961)
Anhydrite	500	10000	20	Stewart (1963) Correns (1961)
Sea Water	1.4	19000	65	Hoering and Parker (1961) Mason (1964)

Geochemistry of the Halogens in Carbonate Rocks

The geochemistry of Cl in calcareous sediments is largely that of soluble chloride salts (Correns, 1961). Correns reports averages of 745 ppm and 152 ppm Cl in dolomites and limestones respectively. Johns and Huang (1967) report averages of 659 ppm and 131 ppm Cl for dolomites and limestones respectively. Sample sizes in both cases are less than ten, and both authors use essentially the same sources of data. Correns (1961) suggested that the difference in Cl content may give an indication of the nature of the solutions active in bringing about dolomitization. Johns and Huang (1967) point out that it is still not known whether the Cl in carbonates is present in fluid inclusions, within the carbonate lattice, or in the clay mineral impurities.

The mode of occurrence of Br and F in carbonates is not known. The average of reported Br values in dolomites and limestones are 11.3 ppm and 4.8 ppm respectively (Correns, 1961).

The average of reported F values in dolomites and limestones are 244 ppm and 345 ppm respectively (averages from Table 5). Averages reported by various workers are summarized in Table 5.

Considerable overlap exists between the limestones and dolomites. The variation is not surprising in view of the fact that little information is given about the mineralogy of the samples. Averages given are arithmetic means which may not represent the best estimate of the F content. The large variations are difficult to explain without more details regarding the nature of the samples analyzed. It is not known if the samples labelled "limestone" contain appreciable amounts of clay mineral, or how much dolomite is present in the carbonate fraction.

TABLE 5
F Content of Carbonate Rocks:
A Comparison of Averages of Various Investigators

	Reference	Sample Size	Average F (ppm)
Limestone	Fleischer and Robinson (1963)	98	220
	Danilova (1949)	9	227
	Jeffries (1951)	28	340
	Kokubu (1956)	30	98
	Koritnig (1951)	12	240
	Eberius and Kowalski (1952)		
	Michael and Blume (1952)	7	940
	Seraphim (1951)	6	90
Dolomite	Fleischer and Robinson (1963)	14	200
	Danilova (1949)	10	250
	Jeffries (1951)	2	390
	Koritnig (1951)	2	180

Geochemistry of the Halogens in Igneous Rocks

The majority of the published data for the halogens in igneous rocks has been for F and Cl. Johns and Huang (1967) report an average of 185 ppm Cl in igneous rocks, based on 2 parts felsic and 1 part mafic. Kuroda and Sandell (1953) report averages of 220 ppm, 210 ppm, and 140 ppm Cl in granitic rocks, gabbros, and basalts and diabases respectively. Farley (1958) reports an average of 200 ppm Cl in igneous rocks including gabbros, basalts, and diabases. The range reported by these authors is from 50 ppm Cl to greater than 3,000 ppm Cl. The Br content of igneous rocks reported by Correns (1961) is 3.0 ppm. Kuroda

and Sandell (1953) and Greenland and Lovering (1966) have shown that there is no marked trend for Cl in differentiation of common igneous rocks. Because of the similarity of the chemical characteristics of Cl and Br, it is reasonable to assume that Br follows Cl in its behavior in igneous rocks. Although there is no apparent halogen fractionation within the solid phases, there must be a fractionation between the solid and liquid phases resulting in increasing halogen concentration in the residual fluids. It is assumed that there is no fractionation of Cl and Br in the liquid phase, and that the Cl/Br ratio in the solid phase is the same as the Cl/Br ratio in the liquid phase.

Kogarko and Gulyayeva (1965), in a study of the alkaline rocks of the Lovozero massif, found the halogens to occur in the following modes; 1) independent minerals (villiaumite, sodalite), 2) isomorphous substitution of F^- and Cl^- for OH^- and O^{2-} in silicate minerals, 3) Br substitution for Cl in sodalite and eudialyte, and 4) F substitution for OH^- and O^{2-} in amphiboles and apatite. The governing factor is ionic radius, which are (for six-fold coordination) (Pauling, 1960):

Ion	Radius (Å)
O^{2-}	1.40
OH^-	1.40
F^-	1.36
Cl^-	1.81
Br^-	1.95

Greenland and Lovering (1966) have also demonstrated the isomorphous substitution of Cl^- and F^- for OH^- and O^{2-} in a differentiated

tholeiitic magma. No fractionation of Cl was found; however, F was found to be enriched in the more mafic differentiates.

The F concentration of igneous rocks is variable, generally being enriched in basalts and ultramafic rocks (Correns, 1961), reflecting F enrichment in ferromagnesian silicates. Correns reports an average F content of 700 ppm for igneous rocks.

Biogeochemistry of the Halogens

Organisms are known to concentrate the halogens, the degree of concentration being dependent on; 1) species, 2) halogen content of soil, and 3) halogen content of surrounding media (gaseous and liquid). Data of halogen abundances in various organisms are summarized in Table 6.

The mode of occurrence of F in the skeletal material is thought to be CaF_2 or $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. The carbonate shells of marine organisms are generally poor in phosphate. Shells of 17 species of lamellibranchs from the Black Sea contained between 0.004% and 0.02% P_2O_5 (Glagoleva, 1961). On the basis of these low P_2O_5 contents, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ may not be the most important form of F in shells. Lowenstam and McConnell (1968) have identified CaF_2 in statholiths of Recent marine mysid crustaceans and tectibranch gastropods. CaF_2 may be the predominant form of F in skeletal material for the major taxonomic groups.

Fluorine occurs as a salt of fluoroacetic acid or as fluo-oleic acid in Dichapetalum cynosum; however, the form of F in plants is otherwise unknown (Fleischer and Robinson, 1963).

Chlorine is present to some extent in most plants and animals, being more concentrated in organisms from the marine environment. Only

TABLE 6
Halogen Abundances in Various Organisms

Organism	F (ppm)	Cl (ppm)	Br (ppm)	Reference
Theacea (tea plant)	758-3060			Rankama and Sahana (1950)
*Dichapetomycosum	150			Rankama and Sahana (1950)
**Molluscs				
Lingula	15200			Correns (1961)
Ostrea	30-120			Chatin and Muntz (1895)
Mytilus	30-120			Chatin and Muntz (1895)
Limnaea stagnalis			25.8	Selivanov (1939)
**Helix (land snail)	30			Chatin and Muntz (1895)
**Corals		400-2000 (dry matter)	2300- 26000 (soft parts)	Vinogradov (1953), McCance and Masters, (1937), Low (1951), Correns (1961)
Sponges		4 - 5% (ash)		Vinogradov (1953)
Seaweed			480-1200	Vinogradov (1953)
Algae			46-1300	Walters (1967)

* - a plant.

** - data are for skeletal material unless otherwise noted.

limited data are available on the Cl contents of the soft parts of shelled organisms, and data are non-existent for Cl in calcareous skeletal material. The soft parts of marine organisms contain 0.05% to 1.0% Cl in the living matter (Vinogradov, 1953; McCance and Masters, 1937).

The occurrence of the halogens in the soft parts of various organisms is well established; however, the mode of occurrence is not. Craigie and Gruenig (1967) identified 3,5-dibromo-p-hydroxybenzyl alcohol and 2,3-dibromo-4,5-dihydroxybenzyl alcohol in both Ondonthalia dentata and Rhodomela confervoides. Ashworth and Cormier (1967) isolated 2,6-dibromophenol from the marine hemichordate Balenoglassus biminensis. Dibromophenols appear to be important organic compounds in the soft parts of marine organisms. Bromine occurs in the form of 6,6-dibromo-indigo in the skin of the Mediterranean gastropod Murex brandaris, in Purpura aperta from the west coast of Mexico, and in widely distributed species of Purpura lapillus (Friedlander, 1909; 1922).

The mode of occurrence of Br in hard parts of shelled organisms has not been definitely established, although its occurrence as bromo-organic compounds has been suggested by Vinogradov (1953). Walters (1967) found that a large portion of the Br and lesser amounts of Cl in several marine organisms are insoluble in dilute NH_4NO_3 and distilled water. The tyrosines and phenols of Br are very soluble in water which would suggest that the soluble organic compounds are not present to any large extent in the shells. However, insoluble Br compounds may be important.

Evidence of Changes in the Chemical Composition of Sea Water

Several lines of evidence suggest small, but real, changes in the chemical composition of the oceans throughout geologic time.

Lane (1908) thought that connate waters of sediments would represent the composition of the original water in which the sediments were deposited. However, many physical and chemical processes have been modifying sediments since deposition, modifying the connate waters, and tending to establish sediment-water equilibrium. These processes include base exchange, dolomitization, evaporation, sulphate reduction, hydration and recrystallization of clay minerals, adsorption, and mixing of foreign waters.

Chave (1960) investigated the chemistry of connate brines of ancient basins as indicators of the chemical composition of ancient sea water. The dissolved solid content of subsurface brines ranges from 0 ppm to more than 3×10^5 ppm. Chave investigated only those brines containing more than 19,000 ppm dissolved solids, as these brines would probably not have been diluted by meteoric waters. Chave concluded that there is no evidence from subsurface waters to suggest changes in the relative proportions of the major dissolved ions in sea water since pre-Cambrian time. Reactions of carbonate, sulfate, and clay minerals with water can explain the observed differences from sea water. He also concluded that no evidence concerning the absolute concentrations of ions in ancient sea water could be obtained from subsurface waters.

Clayton et al. (1966) studied the isotopic composition of oil-field brines from Illinois, Michigan, Alberta, and the Gulf Coast.

They concluded that most of the brines were probably of local meteoric origin and did not represent true fossil sea water.

Sedimentary rocks of certain ages appear to have distinctive chemical and mineralogical characteristics over wide areas. The most notable is the abundance of stratiform siliceous iron formations of pre-Cambrian age and their general absence in post pre-Cambrian rocks. Govett (1966) suggests that the pre-Cambrian banded iron formations were formed in a lacustrine or closed-basin environment. Weathering processes and a change in the character of the earth's crust are suggested as being responsible for the formation of the iron formations of pre-Cambrian age and their absence in post pre-Cambrian.

Vinogradov and Ronov (1956) investigated the changes in the chemical composition of clays from the Russian Platform with geologic age. They report a two-fold decrease in K and a slight increase in Na in younger rocks, an increase in the Ca/Mg ratio, and a decrease in Si and Ti since pre-Cambrian time. Weaver (1967) found the same general trend for K and Na in clays, and suggested that a change from K to Na fixation occurred at the end of the Paleozoic. Weaver attributes this change to an increase in Na and possibly Mg in sea water, caused by the rapid development of plant life and an increase in soil acidity.

Holser and Kaplan (1966) have summarized previous sulfur isotope data and have shown that the isotopic composition of oceanic sulfate has varied since late pre-Cambrian time. Their $^{34}\text{S}/^{32}\text{S}$ vs. time curve shows a general trend toward increasing ^{34}S in the oceanic system with younger rocks.

Keith and Weber (1963) investigated the changes in δC^{13} and δO^{18}

vs geologic age in marine limestones. They reported that "no great change has occurred in the carbon isotopic composition of marine bicarbonate over geologic time, and that oxygen isotopic compositions of marine limestones exhibit a progressive increase in average δO^{18} content from the oldest to youngest age groups." Scatter in their data is due mainly to post-depositional recrystallization and oxygen exchange in the presence of waters different from those of the original environment. Mean δO^{18} varied from -9.7 per mil to -1.2 per mil for Cambrian and Quaternary respectively.

Weber (1967) attempted to show, "small but possibly real variations in the carbon isotopic composition of the active exchange reservoir throughout geologic time". The development and distribution of land plants are suggested as being responsible for this fractionation.

Krasintseva (1964) proposed that the Cl/Br ratio of oceanic water has increased throughout geologic time. Release of excess amounts of Cl during volcanic activity and Cl/Br fractionation in soils are the mechanisms proposed by Krasintseva to bring about the increased Cl/Br ratio of the oceans. Krasintseva found the Cl/Br ratio of Pliocene Red Beds to be 270/1 (two analyses) compared to a ratio of 52/1 for Lower Cambrian rocks. However, only limited data are available.

The investigations cited above demonstrate that changes in the chemical composition of the oceans over the past 2×10^9 years are possible, and have probably occurred. The ocean may not be in dynamic equilibrium with respect to all its chemical constituents. Each chemical component must be considered separately. Mineral-water reactions will have little effect on the contents of Cl and Br in sea water.

SAMPLING AND SAMPLE PREPARATION

Sampling

Recent marine and fresh water shelled organisms were collected from a variety of widespread locations in the eastern United States and along the Atlantic coast. All the fresh water organisms were collected alive; however, several of the marine shells were collected after the organism had died. The Halimeda sp. was collected alive. Sample descriptions are given in Appendix I.

The carbonate rocks were obtained from several sources and include outcrop and core samples from widespread geographic locations. About 70% of the samples analyzed were collected by the author. During outcrop sampling, only fresh and visibly unweathered samples were taken. Sample size ranged from 500 g to 1000 g.

All the core samples, except those of the X-series, were chip samples. Chips were taken approximately every foot over the core interval recorded for each sample. Samples were approximately 100 g in size.

Core samples of the X-series were sampled by means of a specially constructed grinding wheel which cut a continuous groove over the core interval recorded for each sample. The 5 - 10 g sample obtained was -300 mesh in grain size. Each sample was blended in a Wig-L-Bug blender for 10 minutes to ensure homogeneity.

Seventy control samples of dolomites from the X-series representing supratidal, intertidal, turbulent subtidal, and quiet lagoonal

environments have been selected to determine the environmental control on F distribution in carbonates. The dolomites selected were dolomitized by refluxing brines, similar to processes forming recent dolomite (Geological staff, Gulf Oil Canada, Calgary; personal communication).

Sources of samples, other than those collected by the author, are as follows:

- Recent - Pleistocene shell material - Dr. F. T. Mackenzie
- Recent carbonates - Dr. A. D. Baillie and E. A. Shinn
- X-series core samples and Halimeda sp. - Dr. A. D. Baillie
- Midway core material - Dr. H. S. Ladd
- Cambrian and Ordovician outcrop samples - Dr. M. L. Keith
- pre-Cambrian D-series samples - Dr. H. P. Schwarz
- pre-Cambrian marbles - Dr. T. T. Quirke, Jr.
- Cretaceous samples - Dr. Gale K. Billings and Dr. C. Moore
- Shell material - Dr. R. C. Harriss.

Complete details of all samples are presented in Appendix I.

Selection of Samples

The major criterion was to obtain a single phase (calcite or dolomite) so as to observe fractionation of Cl and Br in the one phase only. The carbonate samples investigated were divided into two groups: dolomites and limestones. Those samples classified as dolomites contain greater than 90% dolomite, and the samples classified as limestones contain greater than 90% calcite in their respective carbonate fractions. No quantitative mineralogy determinations were made. Mineral abundance estimates were based on visual examination of X-ray diffractograms and

are qualitative.

Sample Preparation

The samples were first crushed to approximately 66 mm size in a Chipmunk grinder. Each shell and carbonate sample was then ground in a Specs Shatter Box grinder and sieved to remove particles larger than +200 mesh grain size. Core samples of the X-series were prepared by a different method as discussed under the section on sampling. No further treatment was made after grinding. The marine shells were rinsed in distilled water before grinding to remove obvious sea salt contamination.

ANALYTICAL METHODS

Halide Analyses

Instrumentation

Bromide and F activities were determined by means of Orion Specific Ion Electrodes coupled with a Fisher double junction reference calomel electrode. Chloride activity measurements were made with a Beckman Ag/AgCl electrode and a Fisher double double junction calomel reference electrode. A Carey vibrating reed electrometer was used to detect EMF changes.

Electrode Theory

The halide electrodes develop a potential defined by the Nernst equation:

$$E = E_a + 2.3 \frac{RT}{F} \log A$$

where E = the measured potential of the system

E_a = a constant at constant temperature and includes the potential of the reference electrode

$2.3 \frac{RT}{F}$ = the Nernst factor (59.16 mv at 25°C)

R = the gas constant (1.98726 cal/deg mole)

F = the Faraday constant (23062 cal/volt equiv)

T = temperature in degrees Kelvin

A = the activity of the ion in the solution being measured.

The potential developed is proportional to the logarithm of the activity of the halide ion for which the particular electrode is sensitive.

A comprehensive discussion of the theory of anion electrode response is presented by Frant and Ross (1966), Rechnitz and Kresz (1966), Rechnitz et al. (1966), Eisenman (1967), Pungor (1967), and Rechnitz (1967).

Halide Ion Concentration Determinations

Halide ion concentrations can be determined directly by comparison of the EMF of an unknown solution to a calibration curve of EMF vs concentration prepared from a series of standard solutions of known concentrations.

Halide ion activity is related to concentration by the relationship:

$$A_{X^-} = \gamma_{X^-} \cdot C_{X^-}$$

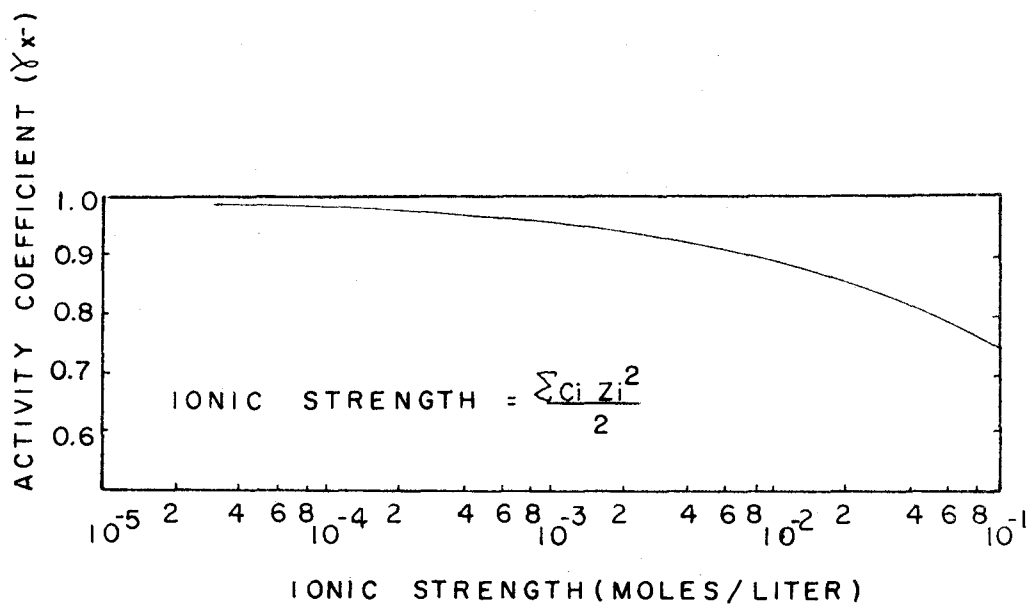
where A_{X^-} = activity of the halide ion

γ_{X^-} = activity coefficient

C_{X^-} = concentration of halide ion

and γ_{X^-} is related to the total ionic strength of the solution. The relationship of activity to ionic strength is shown in Fig. 1. As activity depends on ionic strength in dilute solutions, it is critical that the ionic strength of the unknown solution be equal to that of the standards to which it is being compared. Alternatively, if the ionic strength of the unknown solution is determined, then the appropriate correction factor γ need only be applied (ie. $A_{X^-} = \gamma_{X^-} \cdot C_{X^-}$).

The ionic strength of most natural fresh waters is sufficiently low ($< 10^{-3}$) that activity corrections are not necessary. This has been assumed to be the case for the water leach solutions analyzed in



SINGLE ION ACTIVITY COEFFICIENTS OF Cl^- AND Br^-
(IN SODIUM HALIDE SOLUTIONS) AS A FUNCTION
OF THE TOTAL IONIC STRENGTH.

Fig. 1

this study. Maximum error introduced by this assumption is $\pm 3\%$ (see Fig. 1).

Shell material and carbonate rocks were analyzed for acid soluble halogen content by using concentration vs EMF curves. Ionic strength of the sample solutions was calculated on the basis of two g CaCO_3 in 100 ml HNO_3 (0.24 N for shell material and 0.48 N for carbonate rocks). The ionic strength of the standards was adjusted by adding two g CaCO_3 per 100 ml solution to equal the ionic strength of the sample solutions, thus enabling direct concentration determinations.

Electrode Selectivity, Sensitivity, and Interferences

The selectivities of the particular anion electrode over other anions are listed below. Selectivity ratios are used to quantitatively measure the electrode's preference for its common anion compared to other anions. For example, the bromide Specific Ion Electrode's

Table of Selectivity Ratios

Interfering Ion	Br Electrode	F Electrode	Cl Electrode
Br^-			0.003
* OH^-	3×10^4	10^{-9}	
Cl^-	400		
I^-	2×10^{-4}		5×10^{-7}
S^{2-}	must be absent		must be absent
CN^-	8×10^{-5}		2×10^{-7}
HCO_3^-			3000
SO_4^{2-}			3000
** H^+		10^{-4}	

Note - Ratios are expressed as molar concentration of interfering ion / molar concentration of X^- (halide).

* - OH^- reacts with the F electrode in a manner analogous to F^- (Fig. 2).

** - H^+ reacts with F^- to form the HF_2^- complex in acidic solutions (Fig. 2).

selectivity ratio relative to chloride is 400/1, which means that the bromide electrode is 400 times more selective to Br^- than to Cl^- .

Electrode potentials are affected by changes in temperature, as illustrated by the factor $2.3 RT/F$ in the Nernst equation. The absolute potential of the electrode changes with temperature because of the change in solubility equilibria which are the basic mechanisms governing the operation of the electrodes.

Effect of Temperature on Electrode Potential

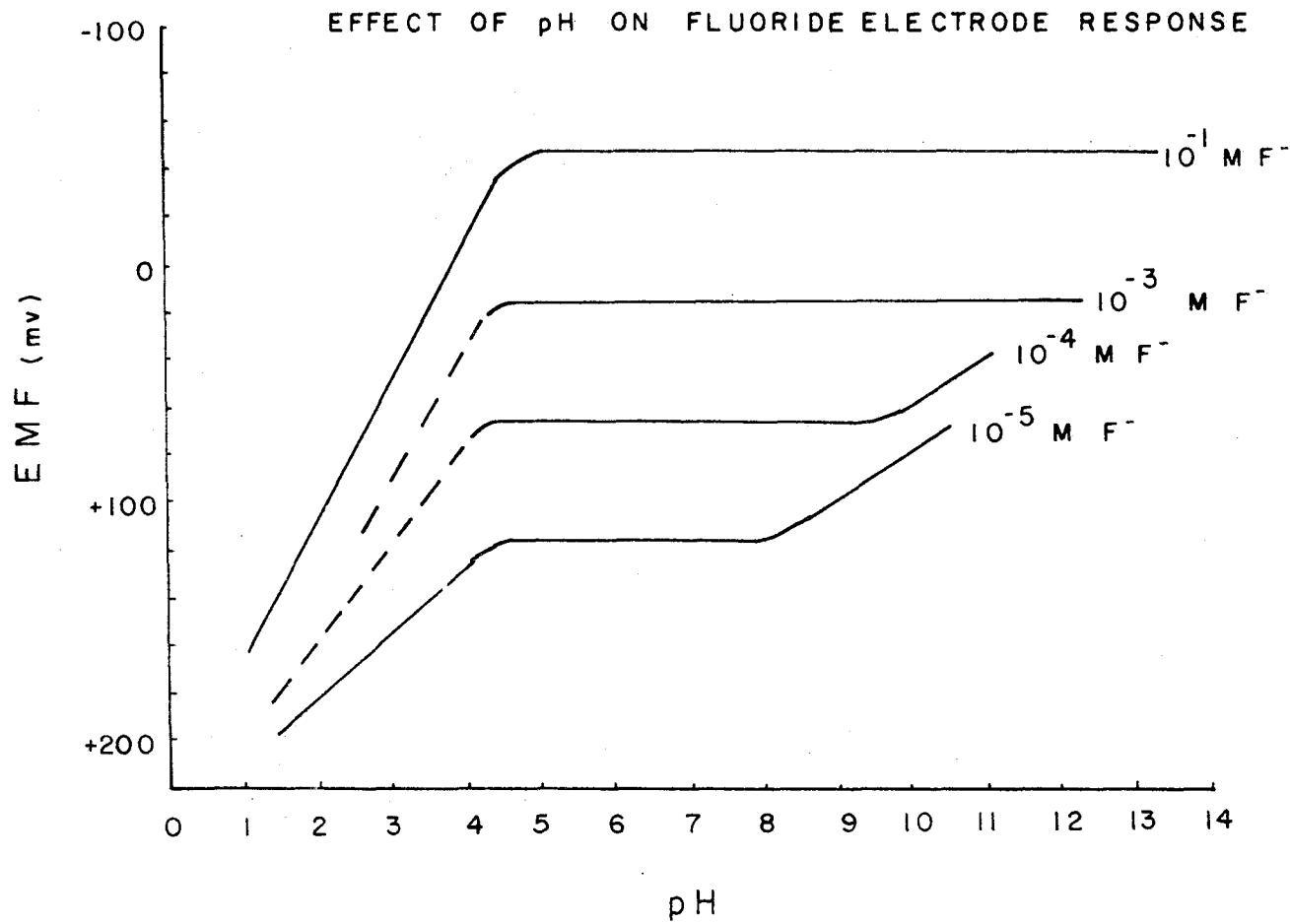
T ($^{\circ}C$)	*AgCl	*AgBr	F Electrode ($2.3 RT/F$)
0	4.5×10^{-6}	1.8×10^{-7}	54.20
25	1.4×10^{-5}	7.1×10^{-7}	59.16
50	4.5×10^{-5}	2.8×10^{-6}	64.11
75	7.9×10^{-5}	8.9×10^{-6}	-
100	1.6×10^{-4}	2.0×10^{-5}	74.04

* - Solubility in moles per liter.

Thus it is critical to maintain a constant temperature for standard and sample solutions.

Detectability for the F, Cl, and Br electrodes are 0.02 ppm,

Fig. 2



0.1 ppm, and 0.04 ppm respectively. The electrodes follow Nernstian behavior up to concentrations in excess of 10,000 ppm. However, since activity vs EMF is a logarithmic function, small changes in halide activity cannot be accurately detected at high activities. A precision of ± 0.5 mv can be expected with a high precision electrometer.

Halogens in the Acid Leach

The technique used to analyze acid soluble halogen contents in the shells and carbonate rocks was developed by modifying the methods of Nardoizzi and Lewis (1961) and Shapiro (1960) for F analyses in rocks. The apparatus used is illustrated in Fig. 3.

Reagents used are:

0.24 N HNO_3 - dilute 100 ml of 70% reagent grade HNO_3 to a volume of 1000 ml.

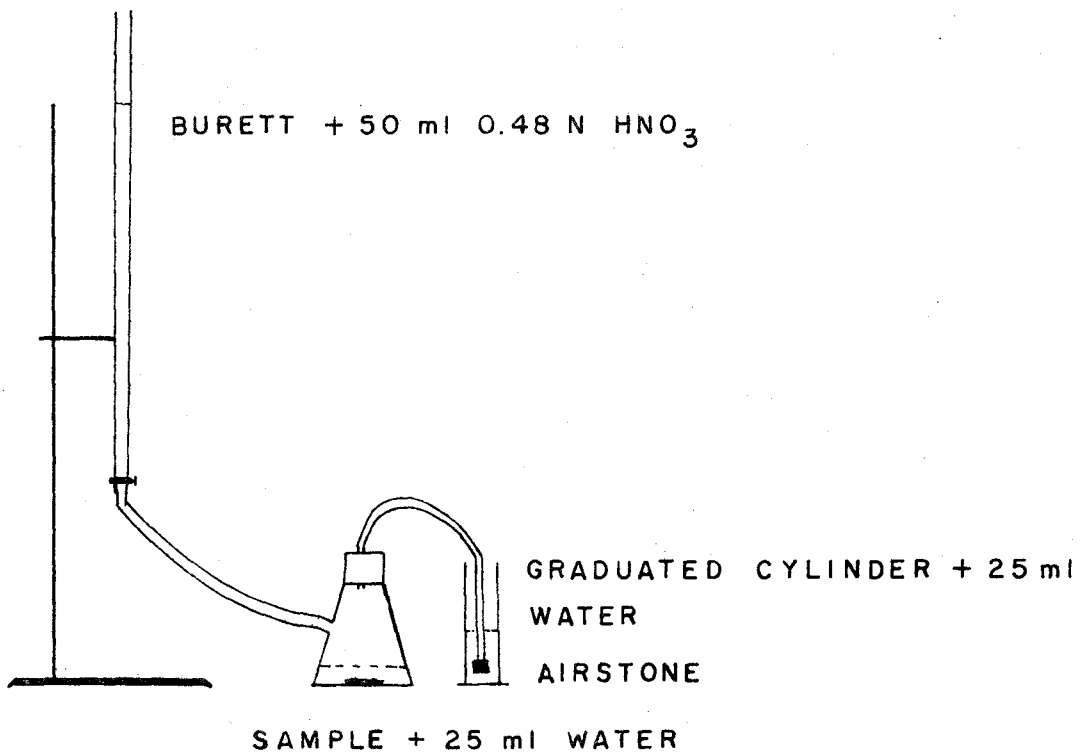
Standard Stock Solutions - solutions of 1000 ppm X (X = F, Cl, and Br) are prepared.

Standards - Prepare a series of standards from the stock solutions by diluting with distilled, deionized water to cover the expected range of concentration. Dilute 25 ml of each standard to 50 ml by adding 25 ml of solution A.

Solution A - dissolve 20 g reagent grade CaCO_3 in 500 ml 0.24 N HNO_3 .

The procedure is as follows.

A 2.0 g portion of finely ground sample (-200 mesh) was placed in the vacuum flask and 25 ml of distilled, deionized water were added. Twenty-five ml of distilled, deionized water were placed in the graduated cylinder. Fifty ml of HNO_3 from the burett were then released



POLYETHYLENE APPARATUS FOR ACID DISSOLUTION
OF CARBONATES

Fig. 3

into the flask. The acid strength was 0.24 N HNO_3 for shell material and 0.48 N HNO_3 for carbonate rocks (standards and reagents are adjusted accordingly). By having the system entirely closed, the released CO_2 could be bubbled through the water in the graduated cylinder, allowing any halogen escaping with the CO_2 to be collected in the water. An airstone was used to decrease bubble size. Blank runs indicated no contamination from the airstone. When the reaction ceased, the two solutions were mixed and the final solution filtered through 0.45 μ filter paper. Samples were stored in polyethylene bottles for subsequent analyses.

Halogens in the Water Leach

The water soluble halide fraction was determined by leaching a 0.5 g sample (~200 mesh) in 25 ml distilled, deionized water for 12 hours. A wrist-action shaker was used to gently agitate the slurry to ensure thorough leaching. The solution was then filtered through 0.45 μ filter paper. The samples were stored in polyethylene bottles for subsequent analyses.

Phosphate Analyses

A modification of the method of Shapiro and Brannock (1962) was used for phosphate analyses of the acid soluble fraction in the carbonate rocks and calcareous marine shells. The P_2O_5 content was determined by measuring the light absorbed at 420 m μ by a solution containing the yellow molybdivanado-phosphoric acid complex. A Bausch and Lomb Spectronic 20 was used to measure transmittance.

Reagents

Molybdivanadate solution - Dissolve 1.2 g of sodium metavanadate in 400 ml of 1 + 1 (volume) HNO_3 . Dissolve 75.0 g of sodium molybdate in 400 ml of distilled, deionized water. Mix the two solutions and dilute to 2 liters.

Standard P_2O_5 solution - Weigh 1.9290 g of KH_2PO_4 (potassium metaphosphate) into a beaker. Add 40 ml 1 + 1 (volume) HNO_3 and 32 ml 1 + 1 (volume) H_2SO_4 . Dilute to 1 liter. The concentration of P_2O_5 is 0.10%. Standards may be made by appropriate dilutions of this standard stock solution. Use a solution of 40 ml 1 + 1 (volume) HNO_3 and 32 ml 1 + 1 (volume) H_2SO_4 diluted to a volume of 1 liter with distilled, deionized water to prepare diluted standards.

H_2SO_4 solution - Mix 136 ml 1 + 1 (volume) HNO_3 and 109 ml 1 + 1 (volume) H_2SO_4 and dilute to 2 liters.

Procedure

Approximately 2 g of carbonate rock sample (-200 mesh) were weighed out into a tared beaker. The weight was adjusted to 100 g by adding 0.48 N HNO_3 and the mixture was allowed to stand until the reaction ceased, generally 30 minutes, then filtered through 0.45 μ millipore filter paper. The filter paper was washed with dilute HNO_3 before filtering to minimize phosphate contamination from filter paper. Solutions were stored in polyethelene bottles for subsequent analyses.

Ten ml of each sample solution were transferred to a series of beakers. Fifteen ml of the H_2SO_4 - HNO_3 solution and 25 ml of molybdivanadate solution were added to each sample. Each sample was mixed

and allowed to stand for 5 minutes. This was repeated for 2 or 3 aliquots of water which were used as blanks. The percent transmittance was determined at $420\text{ m}\mu$ for each sample and for a series of standards.

Calculations

Percent transmittance was converted to absorbance by the relationship:

$$\text{absorbance} = 2 - \log (\text{transmittance}).$$

A graph of absorbance vs $\% \text{P}_2\text{O}_5$ for the standards was constructed. The absorbance of the sample was compared directly to the working curve to obtain $\% \text{P}_2\text{O}_5$ in the sample solution. The P_2O_5 content of the rock was obtained by multiplying the P_2O_5 content of the sample solution by the appropriate dilution factor.

Precision Estimates

Precision for Br by the acid treatment is 6.6%. Recovery tests indicate that Br recovery is 105%, which is well within the analytical error. Time tests indicated that 12 hours were sufficient to thoroughly water leach the samples. Precision estimates for the materials analyzed are given in Table 7.

A sample of phosphate rock previously analyzed at 37.4% P_2O_5 (Kramer, personal communication) was analyzed to estimate the accuracy and precision of the method. A value of 37.8% P_2O_5 was obtained, in good agreement with the previous independent analysis.

ADDENDUM

The possibility of Cl^- interference with the bromide electrode was checked by the following tests:

- 1) Standard chloride solutions containing up to 50 ppm Cl^- were analyzed with the bromide electrode and compared to a set of standard bromide solutions containing no detectable Cl^- . No measurable interference was detected.
- 2) A 50 ppm Cl^- solution was spiked with 0.40 ppm Br^- and analyzed for Br^- . The measured Br^- was 0.43 ppm, which is within the limits of analytical error. The Cl/Br ratio of this solution was 125/1.

No further checks were made as the Cl/Br ratios of 97% of the solutions analyzed were less than 100/1. The limit of 50 ppm Cl^- was selected as the solutions analyzed were diluted to maintain Cl^- below 50 ppm, generally in the range of 1 - 10 ppm.

TABLE 7

Analytical Precision Estimates

Precision for Shell Analyses

Element	Method	\bar{x} (ppm)	s_x	N	C.V.(%)	Sample
F _T	Electrode	15.7	0.43	4	0.3	22
F _W	Electrode	3.8	0.17	4	4.5	22
Br _T	Electrode	55.4	3.69	6	6.6	13
Br _W	Electrode	15.5	2.85	3	18.0	22
Cl _T	Electrode	114.0	11.00	4	9.7	13
Cl _W	Electrode	28.0	1.40	3	5.0	22

Precision for Carbonate Rock Analyses

Element	Method	\bar{x} (ppm)	s_x	N	C.V.(%)	Sample
F _T	Electrode	56.8	4.73	6	8.3	9
F _W	Electrode	2.3	0.02	6	0.7	15
Br _T	Electrode	120.4	9.97	6	8.3	9
Br _W	Electrode	3.5	0.41	6	11.6	15
Cl _T	Electrode	2875	199.4	6	6.9	9
Cl _W	Electrode	101.7	2.37	6	2.3	15

\bar{x} arithmetic mean

s_x standard deviation

N number of samples

C.V. coefficient of variation (%) at one s_x given by $(s_x/\bar{x}) \times 100$

RESULTS AND INTERPRETATIONS

Introduction

The results of the analyses of water soluble and acid soluble F, Cl, and Br in all samples analyzed are shown in Appendix II. The data are arranged in groups according to geologic age. Mineralogy is denoted by Ar, C, D, and Ay for aragonite, calcite, dolomite, and anhydrite respectively.

Correlation coefficients and linear regression analyses were used to study the interrelations between the halogens. Simple linear regression was used to establish relationships between pairs of variables. Linear equations of "best fit" were calculated by the reduced major axis method proposed by Imbrie (1956). Scatter diagrams of the data verified the assumption of linearity.

Results of the regression analysis are presented in Tables 8 and 9. The number of samples (N), arithmetic mean (\bar{x}), median (\tilde{x}), and standard deviation (S_x) of each group are given in Table 8. The pertinent correlation coefficients (r) and regression equations are listed in Table 9. The ratio of water soluble halide / acid soluble halide in the various groups are shown in Table 10.

The complex interactions between the variables were determined by means of R-mode factor analysis using a varimax rotation criterion (Miller and Kahn, 1962).

TABLE 8
Basic Statistics

Variable	N	\bar{x}	\tilde{x}	s_x	Variable	N	\bar{x}	\tilde{x}	s_x
Recent Fresh Water Shells					Recent Marine Shells				
F_T	21	4.6	4.6	2.4	F_T	18	474	42.0	495
CL_T		58.5	60.0	36.3	CL_T		2062	820	2277
Br_T		22.9	21.0	9.4	Br_T		48.4	36.0	44.4
CL/Br_T		2.5	2.3	1.4	CL/Br_T		35.0	35.7	18.4
F_W		2.9	2.6	1.8	F_W	17	13.1	9.4	10.9
CL_W		44.9	42.0	21.5	CL_W		1824	820	2150
Br_W		5.9	6.0	2.2	Br_W		26.4	19.5	21.8
CL/Br_W		10.0	6.8	17.4	CL/Br_W		49.6	42.1	25.2
Recent Aragonites					Recent Dolomites				
F_T	2	1279		122	F_T	2	675		100
CL_T		3681		2356	CL_T		13750		1750
Br_T		69.3		26.3	Br_T		180		20.0
CL/Br_T		47.0		16.2	CL/Br_T		76.3		1.3
F_W		23.5		4.0	F_W		11.0		2.0
CL_W		2875		1750	CL_W		12625		875
Br_W		29.1		17.1	Br_W		100		7.5
CL/Br_W		96.9		3.2	CL/Br_W		126		0.8
Pleistocene Limestones					Miocene Aragonites				
F_T	3	321		107	F_T	2	900		150
CL_T		106		52.6	CL_T		3519		1394
Br_T		20.5		26.2	Br_T		57.1		10.1

TABLE 8 (continued)

Variable	N	\bar{x}	\tilde{x}	s_x	Variable	N	\bar{x}	\tilde{x}	s_x
Pleistocene Limestones (continued)					Miocene Aragonites (continued)				
CL/Br _T	3	26.5		18.3	CL/Br _T	2	59.6		14.4
F _W		11.6		3.0	F _W		26.1		10.3
CL _W		84.6		34.3	CL _W		3213		1288
Br _W		4.2		2.1	Br _W		37.5		10.0
CL/Br _W		21.4		6.1	CL/Br _W		83.4		13.4
Miocene Limestones					Miocene Dolomites				
F _T	2	138		46.8	F _T	2	426		239
CL _T		4426		580	CL _T		5002		3546
Br _T		54.2		6.6	Br _T		55.3		38.1
CL/Br _T		81.6		0.8	CL/Br _T		88.2		3.5
F _W		11.2		2.2	F _W		9.7		2.4
CL _W		3788		463	CL _W		4594		3156
Br _W		38.4		4.9	Br _W		44.8		30.3
CL/Br _W		98.6		0.2	CL/Br _W		101		2.1
Cretaceous Limestones					Cretaceous Dolomites				
F _T	10	42.5	35.0	12.6	F _T	2	392		10.2
CL _T		61.3	50.9	22.6	CL _T		2535		2348
Br _T		5.9	5.1	2.8	Br _T		117		96.5
CL/Br _T		13.5	9.5	10.7	CL/Br _T		15.9		6.8
F _W		2.7	2.6	1.1	F _W		5.6		1.7
CL _W		22.4	14.0	20.9	CL _W		1946		1854
Br _W		0.8	0.6	0.6	Br _W		18.7		18.4
CL/Br _W		36.7	20.0	24.8	CL/Br _W		205		102

TABLE 8 (continued)

Variable	N	\bar{x}	\tilde{x}	s_x	Variable	N	\bar{x}	\tilde{x}	s_x
Triassic Limestones					Triassic Dolomites				
F_T	9	173	170	71.7	F_T	7	827	869	443
CL_T		504	140	508	CL_T		1733	1245	1546
Br_T		8.4	4.7	6.2	Br_T		24.9	16.2	18.2
CL/Br_T		51.7	50.0	18.7	CL/Br_T		69.9	78.6	22.3
F_W	8	4.4	2.5	2.9	F_W	6	10.7	5.8	5.9
CL_W		444	140	397	CL_W		1317	825	1153
Br_W		6.9	4.7	3.6	Br_W		20.2	17.5	11.9
CL/Br_W		53.1	45.0	23.2	CL/Br_W		60.5	45.7	28.4
U. Devonian Limestones					Mississippian Dolomites				
F_T	6	54.5	46.0	29.3	F_T	10	348	371	130
CL_T		1535	1093	824	CL_T		330	357	112
Br_T		49.5	21.3	39.8	Br_T		13.6	13.5	4.0
CL/Br_T		37.4	32.7	11.0	CL/Br_T		24.9	21.7	8.1
F_W		5.3	3.5	3.1	F_W		10.0	8.1	4.3
CL_W		1255	830	731	CL_W		219	220	69.2
Br_W		20.2	18.5	8.6	Br_W		8.0	8.0	2.3
CL/Br_W		59.0	59.3	9.9	CL/Br_W		30.0	28.2	11.7
M. Devonian Limestones					M. Devonian Dolomites				
F_T	11	113	115	33.6	F_T	3	263		167
CL_T		1795	1750	488	CL_T		385		219
Br_T		31.0	31.5	7.1	Br_T		15.5		3.9
CL/Br_T		57.6	58.7	5.6	CL/Br_T		25.7		12.2
F_W		12.9	10.0	6.7	F_W		2.7		0.9

TABLE 8 (continued)

Variable	N	\bar{x}	\tilde{x}	s_x	Variable	N	\bar{x}	\hat{x}	s_x
M. Devonian Limestones (continued)					M. Devonian Dolomites (continued)				
CL _W	11	1791	1700	307	CL _W	3	215		120
Br _W		23.2	23.5	1.9	Br _W		6.7		4.5
CL/Br _W		76.9	76.3	9.6	CL/Br _W		35.5		7.6
M. Ordovician Limestones					L. Ordovician Dolomites				
F _T	8	39.6	28.6	32.8	F _T	4	30.9		7.0
CL _T		23.0	18.2	13.1	CL _T		107		31.4
Br _T		4.7	4.3	1.4	Br _T		7.8		2.0
CL/Br _T		4.7	4.5	1.1	CL/Br _T		13.7		1.5
F _W		8.0	4.9	6.2	F _W		6.3		2.7
CL _W		24.6	23.8	8.1	CL _W		66.3		14.8
Br _W		2.1	2.0	0.3	Br _W		2.6		0.7
CL/Br _W		11.9	10.8	4.2	CL/Br _W		26.3		5.4
Cambrian Limestones					L.U. Ordovician Dolomites				
F _T	3	56.9		4.1	F _T	7	318	335	116
CL _T		264		63.6	CL _T		2640	1521	2808
Br _T		23.9		6.5	Br _T		35.0	23.3	28.5
CL/Br _T		11.1		0.6	CL/Br _T		67.1	65.2	11.4
pre-Cambrian (Waterton) Limestones					U. Silurian Dolomites				
F _T	8	36.8	28.1	15.5	F _T	7	145	131	43.6
CL _T		134	76.1	107	CL _T		2966	2770	791
Br _T		6.0	4.5	2.5	Br _T		43.8	41.8	10.9
CL/Br _T		21.3	20.1	10.5	CL/Br _T		70.4	70.8	4.9
F _W		5.8	1.6	7.6					
CL _W		33.6	34.0	7.6					

TABLE 8 (continued)

Variable	N	\bar{x}	\tilde{x}	s_x	Variable	N	\bar{x}	\tilde{x}	s_x
pre-Cambrian (Waterton) Limestones (continued)									
Br _W	8	2.1	1.9	0.7					
Cl/Br _W		17.1	17.5	5.1					
pre-Cambrian (Bruce) Limestones					M. Silurian Dolomites				
F _T	3	62.9		6.5	F _T	8	143	151	42.4
Cl _T		33.8		3.8	Cl _T		1480	1459	572
Br _T		7.3		0.6	Br _T		40.6	33.5	15.4
Cl/Br _T		4.6		0.4	Cl/Br _T		42.8	42.0	20.0
F _W		2.1		0.3					
Cl _W		13.3		0.9					
Br _W		1.9		0.6					
Cl/Br _W		6.7		1.8					
pre-Cambrian (Waterton) Dolomites					L. Silurian Dolomites				
F _T	5	61.8		14.5	F _T	9	168	170	47.4
Cl _T		168		63.8	Cl _T		538	420	177
Br _T		9.3		4.4	Br _T		20.5	18.5	6.4
Cl/Br _T		20.3		8.5	Cl/Br _T		26.5	26.7	4.3
F _W		3.1		1.4	F _W	2	5.9		1.0
Cl _W		42.4		20.0	Cl _W		487		137
Br _W		2.7		1.2	Br _W		20.8		11.8
Cl/Br _W		15.4		2.3	Cl/Br _W		29.1		9.9

TABLE 8 (continued)

Variable	N	\bar{x}	\tilde{x}	s_x	Variable	N	\bar{x}	\tilde{x}	s_x
pre-Cambrian Marbles					pre-Cambrian Dolomites - D series				
F_T	6	28.5	25.5	18.6	F_T	7	120	112	61.0
CL_T		833	695	659	CL_T		184	133	110
Br_T		37.5	24.3	26.5	Br_T		12.4	10.2	5.6
CL/Br_T		21.0	21.4	5.6	CL/Br_T		13.9	14.3	2.9
Aragonites					Limestones				
F_T	5	995	1050	282	F_T	64	90.4	60.4	82.0
CL_T		6096	4912	5285	CL_T		720	140	1035
Br_T		86.5	67.2	50.2	Br_T		17.9	8.2	21.0
CL/Br_T		60.5	63.1	20.7	CL/Br_T		31.0	25.0	24.0
F_W		22.5	19.5	8.4	F_W	59	6.8	4.0	6.1
CL_W		4785	4500	3747	CL_W		647	84.0	951
Br_W		49.6	46.2	35.2	Br_W		9.6	3.0	10.8
CL/Br_W		92.5	96.8	11.6	CL/Br_W		41.7	32.5	29.5
Limestones and Aragonites					Dolomites				
F_T	69	156	66.0	259	F_T	307	381	240	359
CL_T		1110	175	2227	CL_T	75	1589	494	2656
Br_T		22.8	10.6	30.2	Br_T		31.0	18.3	38.1
CL/Br_T		33.2	30.8	25.0	CL/Br_T		40.5	30.5	26.0
F_W	64	8.0	4.5	7.6	F_W	46	8.7	7.2	5.3
CL_W		971	105	1779	CL_W		1492	260	2801
Br_W		12.7	3.5	17.9	Br_W		17.1	9.0	22.3
CL/Br_W		45.7	35.0	31.6	CL/Br_W		60.0	37.8	54.6

TABLE 9
Linear Regression Analyses

Group	Variables	r*	N	Linear Regression Equation**
Recent Fresh Water Shells	Cl _T Br _T	0.63	21	Br _T = 1.31 + 0.10 Cl _T
	F _T Cl _T	0.61	21	Cl _T = 7.75 + 0.26 F _T
Recent Marine Shells	Cl _T Br _T	0.87	18	Br _T = 8.19 + 0.02 Cl _T
	Cl _W Br _W	0.99	17	Br _W = 7.91 + 0.01 Cl _W
Cretaceous Limestones	Cl _T Br _T	0.78	10	Br _T = -1.69 + 0.12 Cl _T
	Cl _W Br _W	0.84	10	Br _W = 0.16 + 0.03 Cl _W
Triassic Limestones	Cl _T Br _T	0.97	9	Br _T = 2.25 + 0.01 Cl _T
	Cl _W Br _W	0.98	8	Br _W = 2.88 + 0.01 Cl _W
Triassic Dolomites	Cl _T Br _T	0.76	7	Br _T = 4.50 + 0.01 Cl _T
Mississippian Dolomites	Cl _T Br _T	0.57	10	Br _T = 1.78 + 0.04 Cl _T
U. Devonian Limestones	Cl _T Br _T	0.95	6	Br _T = -24.64 + 0.05 Cl _T
	Cl _W Br _W	0.98	6	Br _W = 5.44 + 0.01 Cl _W
M. Devonian Limestones	Cl _T Br _T	0.91	11	Br _T = 4.86 + 0.01 Cl _T
	Cl _W Br _W	0.74	11	Br _W = 12.10 + 0.01 Cl _W
M. Ordovician Limestones	Cl _T Br _T	0.98	8	Br _T = 2.24 + 0.11 Cl _T
	Cl _W Br _W	0.74	8	Br _W = 1.19 + 0.04 Cl _W
U. Silurian Dolomite	Cl _T Br _T	0.83	7	Br _T = 2.91 + 0.01 Cl _T
L.U. Ordovician Dolomites	Cl _T Br _T	0.99	7	Br _T = 8.21 + 0.01 Cl _T
pre-Cambrian (Waterton) Dolomites	Cl _T Br _T	0.86	5	Br _T = -2.25 + 0.07 Cl _T
	Cl _W Br _W	0.98	5	Br _W = 0.16 + 0.06 Cl _W

TABLE 9 (continued)

Group	Variables		r*	N	Linear Regression Equation**
pre-Cambrian (Waterton) Limestones	F_T	Cl_T	0.60	8	$Cl_T = 7.99 + 3.43 F_T$
	Cl_T	Br_T	0.72	8	$Br_T = 2.87 + 0.02 Cl_T$
pre-Cambrian (D - series) Dolomites	Cl_T	Br_T	0.98	7	$Br_T = 3.06 + 0.05 Cl_T$
pre-Cambrian Marbles	Cl_T	Br_T	0.96	6	$Br_T = 4.01 + 0.04 Cl_T$
Aragonites	Cl_T	Br_T	0.99	5	$Br_T = 28.59 + 0.01 Cl_T$
	Cl_W	Br_W	0.99	5	$Br_W = 4.65 + 0.01 Cl_W$
Limestones	Cl_T	Br_T	0.77	64	$Br_T = 3.29 + 0.02 Cl_T$
	Cl_W	Br_W	0.97	59	$Br_W = 8.27 + 0.01 Cl_W$
Dolomites	Cl_T	Br_T	0.86	75	$Br_T = 2.25 + 0.01 Cl_T$
	Cl_W	Br_W	0.97	46	$Br_W = 5.22 + 0.01 Cl_W$

* - coefficient of correlation.

** - calculated by the reduced major axis method (Imbrie, 1956).

TABLE 10

Ratio of Water Soluble Halogen Content / Acid Soluble Halogen Content

Age	Material	F_W/F_T (%)	Cl_W/Cl_T (%)	Br_W/Br_T (%)
Recent	Fresh water shells	63.0	76.7	25.8
Recent	Marine shells	2.1	88.5	54.5
Recent	Aragonite	1.1	72.1	42.0
Recent	Dolomite	1.6	91.8	55.6
Pliocene	Limestone	3.6	80.0	20.5
Miocene	Aragonite	2.9	91.3	65.7
Miocene	Limestone	8.1	85.6	70.8
Miocene	Dolomite	2.3	91.8	81.0
Cretaceous	Limestone	6.4	36.5	1.4
Cretaceous	Dolomite	1.4	76.8	16.0
Triassic	Limestone	2.5	88.1	82.1
Triassic	Dolomite	1.3	76.0	81.1
Mississippian	Dolomite	3.2	66.3	59.0
U. Devonian	Limestone	9.7	81.8	40.8
M. Devonian	Limestone	11.4	99.8	74.8
M. Devonian	Dolomite	1.0	55.9	43.2
L. Silurian	Dolomite	4.1	75.2	78.8
M. Ordovician	Limestone	2.0	100.0	44.6
L. Ordovician	Dolomite	20.4	61.7	33.3
pre-Cambrian (Waterton)	Limestone	15.8	25.0	35.0
pre-Cambrian (Waterton)	Dolomite	5.0	25.3	29.3
pre-Cambrian (Bruce)	Limestone	3.3	39.3	26.0

Halogens in Carbonate Rocks

A total of 64 limestones and 75 dolomites from Recent to pre-Cambrian age were analyzed for acid soluble (0.48 N HNO₃) Cl and Br. The water soluble F, Cl, and Br contents of 46 dolomites and 64 limestones were also determined. A total of 307 dolomites and 64 limestones were analyzed for total F. Data for the acid soluble F, Cl, and Br have been recalculated to 100% carbonate. The acid soluble halide content will be referred to throughout the thesis as total halide.

The F, Cl, and Br contents, both water soluble and acid soluble, were determined for six carbonates with aragonite contents ranging from 5% to 100%. The results are shown in Table 11. The samples included inorganically precipitated ooliths, aragonite muds of probable inorganic origin, and mixed organic-inorganically derived material. Samples were obtained from Recent carbonate sediments, Pleistocene carbonate rocks, and essentially unconsolidated Miocene sediments.

The average Cl_T, Cl_W, Br_T, and Br_W contents of the limestones and dolomites of all ages are:

	Cl _T ppm	Cl _W ppm	Br _T ppm	Br _W ppm
Limestone	1109	971	22.8	12.7
Dolomite	1589	1482	31.0	17.1

Histograms of the Cl_T and Cl_W contents are shown in Fig. 4. The distributions of Cl_T and Cl_W in both the limestones and dolomites are lognormal, with the mean and median values being higher in the dolomites than in the limestones. The aragonite samples are included in the limestone histogram. The median value gives a better estimate of the most

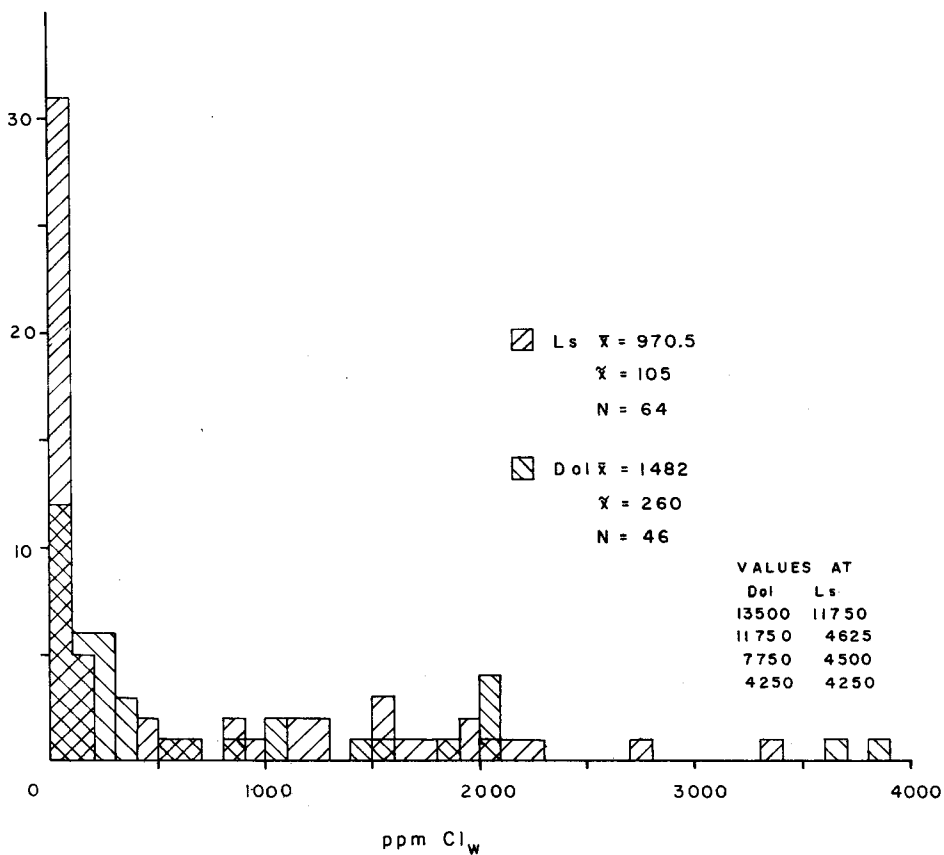
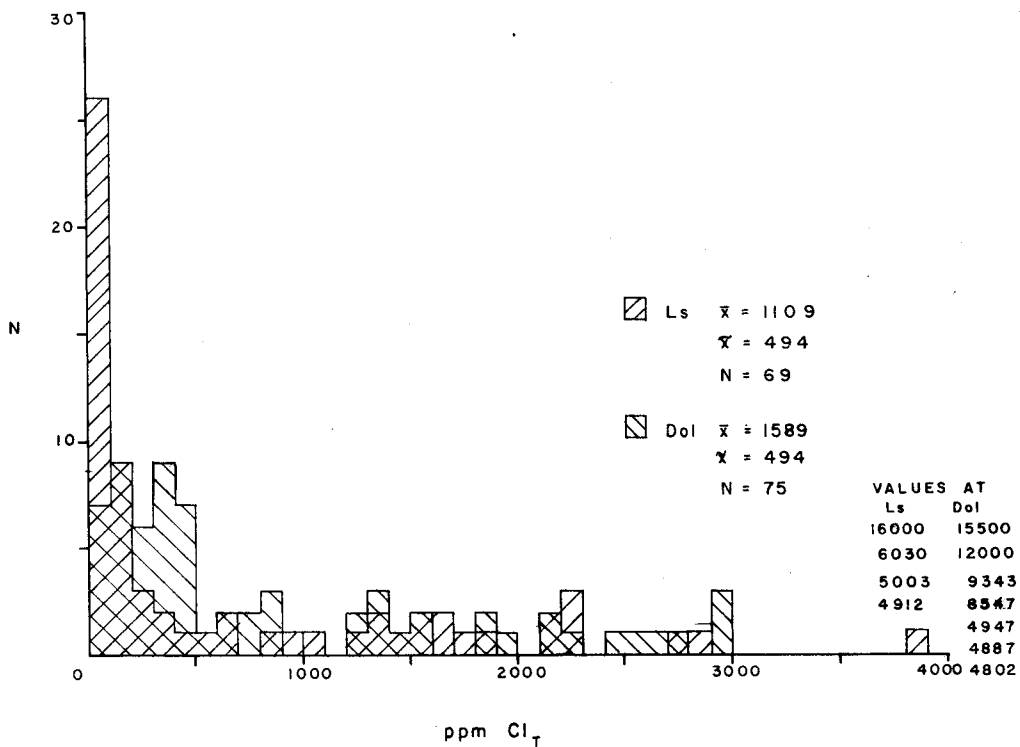


Fig. 4

TABLE 11

Halogen Distributions During Diagenesis
and Metamorphism

		Increasing Diagenesis —————→ Metamorphism			
		Aragonite	Calcite	Dolomite	Marbles*
F_T	\bar{x}	995	90.4	381	28.5
	s_x	282	82.0	359	18.6
	N	5	64	307	6
F_W	\bar{x}	22.5	6.8	8.0	
	s_x	8.4	6.1	7.6	
	N	5	59	46	
Cl_T	\bar{x}	6096	720	1589	833
	s_x	5284	1035	2656	659
	N	5	64	75	6
Cl_W	\bar{x}	4785	647	970	
	s_x	3747	951	1770	
	N	5	59	46	
Br_T	\bar{x}	86.5	17.9	31.0	37.5
	s_x	50.2	21.1	38.1	26.5
	N	5	64	75	6
Br_W	\bar{x}	49.6	9.6	12.7	
	s_x	35.2	10.8	17.9	
	N	5	59	46	

* -- metamorphosed sedimentary carbonates.

probable value of Cl_T and Cl_W in limestones and dolomites. There is no significant difference in the Cl_T (or Cl_W) content of the limestones and dolomites at the 10% confidence level. However, the difference is significant between aragonites and limestones, and between aragonites and dolomites.

There is considerable variation in the amount of Cl_T which is water soluble (25% - 100%). The pre-Cambrian carbonates contain less Cl_W than the younger carbonates (Table 10). The Cl_T contents of the pre-Cambrian carbonates are also correspondingly lower.

The Br_T and Br_W distributions in limestones and dolomites of all ages are shown in Fig. 5, the aragonites being included with the limestones. Dolomites, with a mean of 31.0 ppm Br_T , are enriched in Br_T relative to limestones which have an average Br_T content of 22.2 ppm. The difference is not significant at the 10% confidence level, but is significant at the 20% confidence level. Both the Br_T and Br_W contents of the aragonites are significantly higher than in the dolomites or limestones. There is considerable variation in the amount of Br_W in the various age groups (1.4% - 82.1%); however, the Br_W follows the same pattern as Cl_W and is less soluble in the pre-Cambrian carbonates (Table 10). Acid soluble Br contents are also lower in the pre-Cambrian carbonates.

The lower percentages of Cl_T and Br_T which are water soluble may be due to post-lithification leaching. The low Cl_T and Br_T contents in the pre-Cambrian carbonates could indicate that the pre-Cambrian sea had a lower salinity than modern ocean water as proposed by Kramer (1965).

The average F_T content of limestones (including aragonites) is

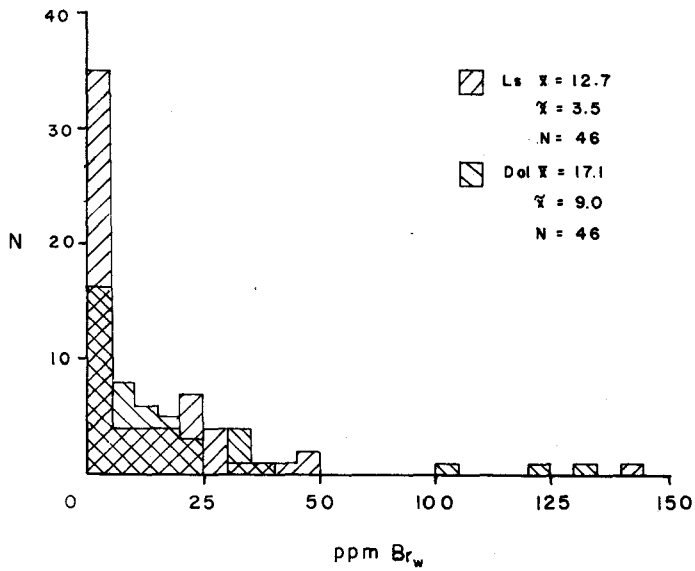
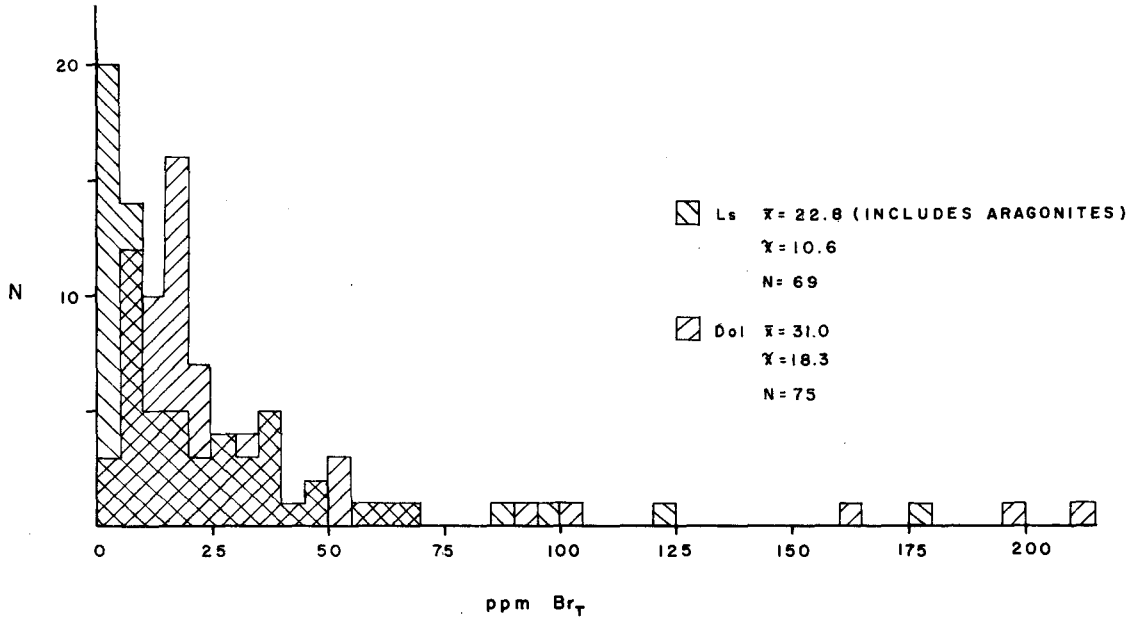


Fig. 5

156 ppm compared to an average of 381 ppm for dolomites. The difference is significant at the 1% confidence level. The F_W content of limestones (including aragonites) is 8.0 ppm compared to an average of 8.7 ppm for dolomites, the difference not being significantly different. Histograms of the F_T and F_W distributions in limestones and dolomites are shown in Fig. 6.

The regression analysis indicates that there is a strong correlation between Cl and Br in both the acid and water soluble phases, and that the water soluble contents are dependent upon the acid soluble contents. The F_W does not show a relationship to F_T in either the limestones or dolomites.

Relationships between Cl and Br for all samples are shown in Figs. 7 and 8. The linear relationship of Cl_W to Br_W is

$$\log Br_W = -0.86 + 0.70 \log Cl_W$$

with a coefficient of correlation of 0.94 (N = 103). The relationship of Cl_T to Br_T is

$$\log Br_T = -0.50 + 0.65 \log Cl_T$$

with a coefficient of correlation of 0.88 (N = 150).

The results of an R-mode factor analysis of the limestones and dolomites are shown in Tables 12 and 13 respectively. The geochemistries of Cl and Br are strongly correlated, while F reacts independently. The behavior of each element is essentially the same in both limestones and dolomites.

Factor 1, in both cases, accounts for the major variance of Cl_W , Cl_T , Br_W , and Br_T . This factor is attributed to a combination of fluid inclusions and water soluble intergranular salts. The F_T distribution

Fig. 6

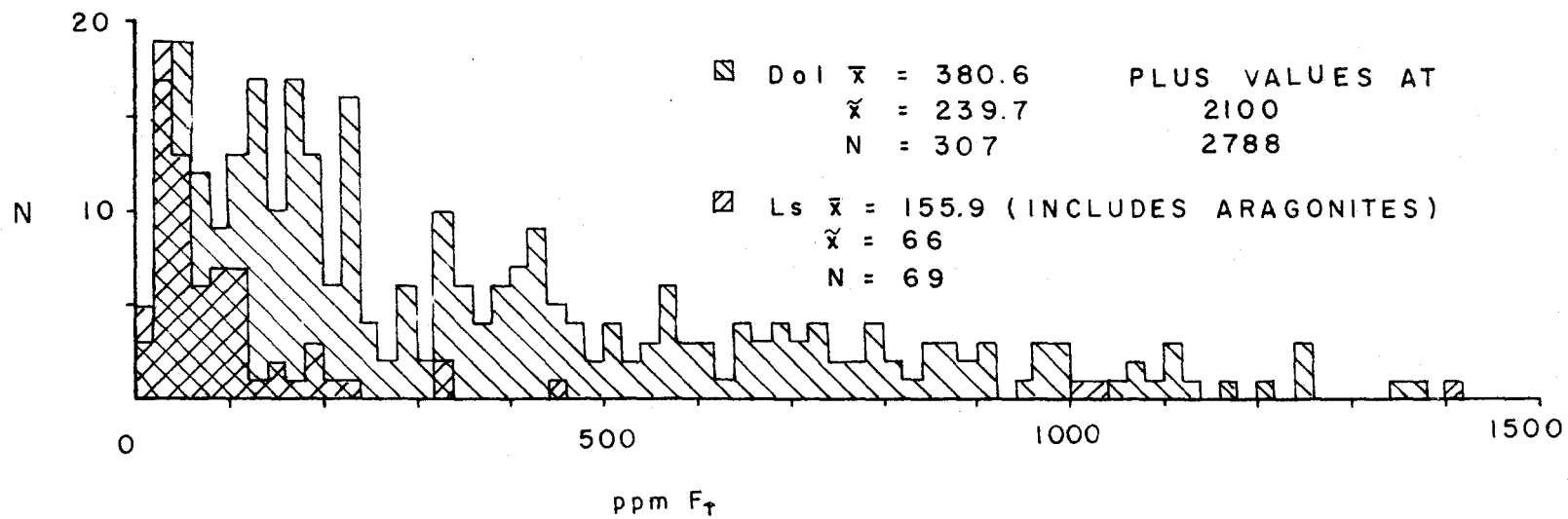
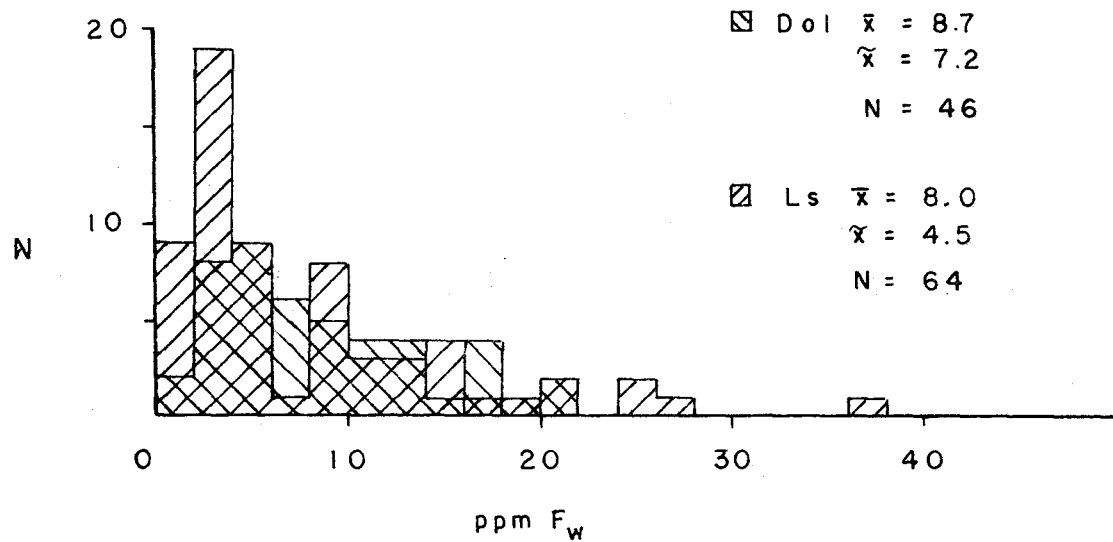
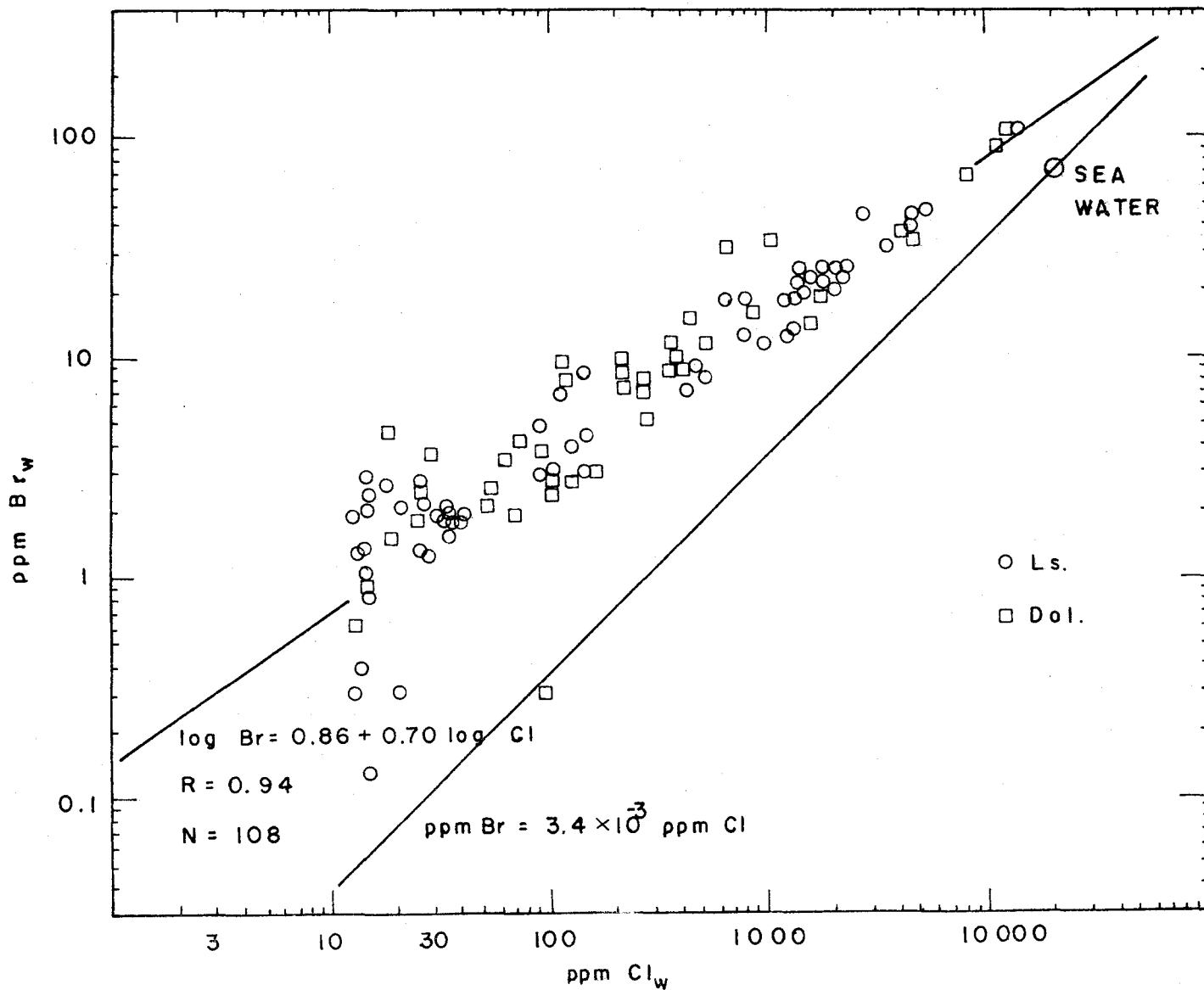
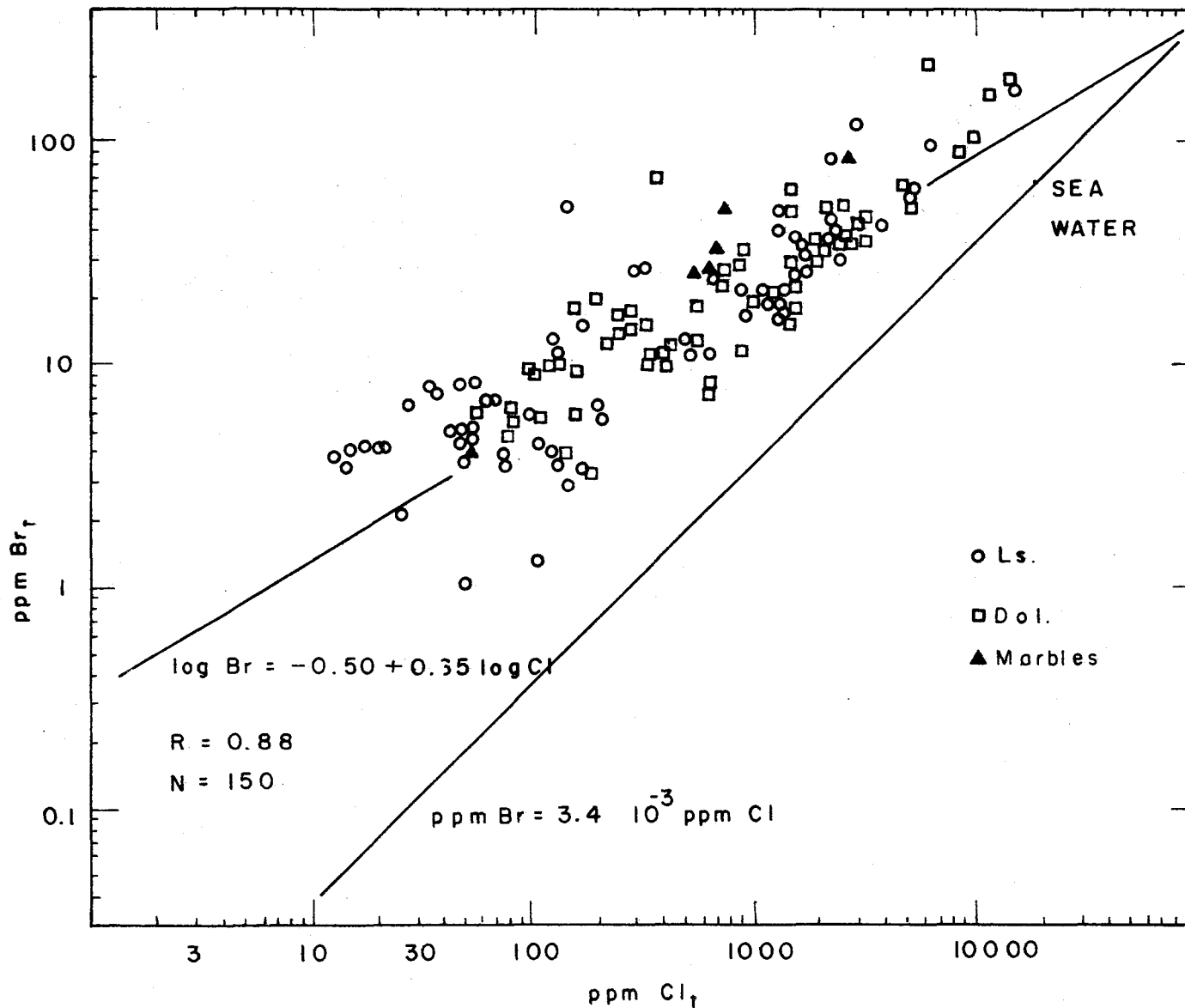


Fig. 7



RELATIONSHIP OF Cl_w TO Br_w FOR ALL SAMPLES

Fig. 8



RELATIONSHIP OF Cl_T TO Br_T FOR ALL SAMPLES

in the carbonates is controlled by a single factor independent of Cl_T and Br_T . A factor independent of F_T controls F_W . This suggests that the F_W is controlled by a simple mineral-water equilibrium reaction.

TABLE 12
R-Mode Factor Analysis of Limestones

Rotated Normalized Factor Loadings				
Factor Variate	1	2	3	4
Br_T	<u>-0.73</u>	0.07	0.09	-0.67
Br_W	<u>-0.92</u>	0.32	0.17	-0.13
Cl_T	<u>-0.94</u>	0.05	0.22	-0.25
Cl_W	<u>-0.96</u>	0.12	0.22	-0.13
F_T	-0.16	<u>0.98</u>	0.15	-0.04
F_W	-0.24	0.16	<u>0.96</u>	-0.05
Percent of variance explained by factors				
	66.65	16.58	11.09	3.68
Cumulative percent of variance				
	66.65	83.23	94.32	98.00

The extremely high water soluble content of Cl in the limestones and dolomites indicates that intergranular salts and/or fluid inclusions are the major modes of occurrence of Cl. The water insoluble Cl is probably contained within the carbonate lattice. The Br_T is much less water soluble than Cl_T , being only 54% and 55% water soluble in the limestones and dolomites respectively (Table 10). The water insoluble Br is either contained within the carbonate lattice or in the form of water

insoluble bromo-organic compounds.

E. Roedder (personal communication) believes that, although fluid inclusions will contribute part of the Cl_W and Br_W , intergranular salts will be more important. Lamar and Shrode (1953) studied the nature of water soluble salts in limestones and dolomites and concluded that the soluble ions are contained largely in fluid inclusions. The relative importance of these two mechanisms cannot be resolved in the present study.

TABLE 13

R-Mode Factor Analysis of Dolomites

Rotated Normalized Factor Loadings				
Factor Variate	1	2	3	4
Br_W	<u>-0.71</u>	0.22	-0.24	0.62
Cl_W	<u>-0.87</u>	0.24	-0.32	0.30
Cl_T	<u>-0.91</u>	0.24	-0.24	0.25
Br_T	<u>-0.97</u>	0.17	-0.15	0.04
F_T	-0.23	<u>0.95</u>	-0.18	0.10
F_W	-0.25	0.19	<u>-0.94</u>	0.11
Percent of variance explained by factors				
	72.25	12.87	9.68	3.35
Cumulative percent of variance				
	72.25	85.12	94.80	98.15

The occurrence of F as a water insoluble phase in the carbonates suggests the possibility of separate phases of CaF_2 , CO_2 -F-apatite,

or solid solution of CaF_2 in the CaCO_3 . If the F is in the form of CO_2 -F-apatite, there should be a strong correlation of F to P_2O_5 , with a $\text{P}_2\text{O}_5/\text{F}$ molar ratio of 10/1 (Correns, 1961). Analyses of the P_2O_5 content of 20 of the Zama dolomites indicated an average of 0.00629% P_2O_5 resulting in a $\text{P}_2\text{O}_5/\text{F}$ weight ratio of 0.16/1. The P_2O_5 contents of 48 other Zama dolomites were on the same order of magnitude but were not determined precisely. Analysis of sample B-5.2, a Recent dolomite, yielded a value of 0.0775% P_2O_5 which agrees very well with the values of 0.06% - 0.08% reported by Friedman (1968) for Recent carbonates from the Trucial Coast. It is concluded that F does not occur primarily in the form of CO_2 -F-apatite in the carbonates analyzed.

X-ray analyses were unable to detect CaF_2 in the samples. If all the F were present as CaF_2 , less than 0.3 weight percent CaF_2 would be present in the carbonates; well below the detectability of the x-ray technique.

Indirect evidence on the form of the F may be obtained from a consideration of the F_w . There are several possible sources of the F_w , the following being the most important: 1) F exchange from clay mineral impurities, 2) fluid inclusions, and 3) F dissolved from a fluoride mineral such as CaF_2 or CO_2 -F-apatite.

A small amount of the water soluble halogens may be contributed by exchange reactions with clay minerals. The limited data available in the literature and the pH dependence of the anion exchange capacity of clay minerals makes any estimate of contamination from clay mineral exchange reactions tenuous. Weiss *et al.* (1956) determined the anion exchange capacity of kaolinite and montmorillonite to be 1 - 12 meq

F / 100 g (approximately 200 - 2000 ppm) in concentrated F solutions (up to 1.5 molar). Bower and Hatcher (1967) studied the reactions of soils and minerals with dilute F solutions which more closely resemble the F concentrations of sea water. They report that two different kaolinites adsorbed 70 and 100 ppm F from solutions containing 2 ppm F. A bentonite adsorbed only traces of F from a 16 ppm F solution. Carpenter (1968) has shown that F exchange between sea water and clay minerals is negligible.

The average content of insoluble residue in all the samples analyzed for F_T is 6.4 weight percent. Samples analyzed for F_W averaged 7.3 weight percent insoluble residue. Scatter diagrams indicated that there is no correlation between either F_T or F_W and insoluble residue content.

Samples of API illite, montmorillonite, and kaolinite as well as a sample of mica from pegmatitic granite were treated by the methods outlined for the acid and water leach treatments of carbonates to obtain an estimate of the F contamination from clay minerals. The results are shown in Table 14.

Kaolinite and montmorillonite are not present in sufficient quantity in any of the carbonates analyzed to make a significant contribution to the F_T or F_W . Illite would not be expected to be a source of F contamination on the basis of the experimental results. The acid leach does not appear to have removed much F from the clays. The F_W is not the result of exchange from clay mineral impurities in the carbonates.

TABLE 14

Water and Acid Soluble F Contents of Phyllosilicates

Sample	F_W (ppm)*	F_T (ppm)**
Kaolinite	25.0	25.0
Illite	n.d.	n.d.
Montmorillonite	80.0	33.3
Mica	140.0	17.0

Note - 2 g of sample were treated seperately in 100 ml of water and in 100 ml 0.48 N HNO_3 .

* A 12 hour water leach.

** A 30 minute acid leach.

Description of Samples:

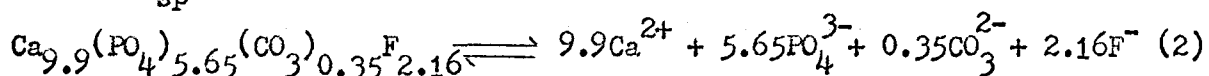
1. Kaolinite #5 Lamar pit, Bath, South Carolina.
2. Montmorillonite #23 (bentonite) Chambers, Arizona.
3. Illite #36 Morris, Illinois.
4. Mica Preisscue-Lacorne Batholith, Abitibi Co., Quebec.

If the F_W were contributed by fluid inclusions, there should be a great deal of scatter in the data. The relatively small amount of scatter in the data suggests that fluid inclusions are not an important source of F_W .

The other possible source of F_W is from the solution of fluorine bearing minerals, of which CaF_2 and CO_2 -F-apatite are the most probable. The solubility of CaF_2 and CO_2 -F-apatite are given by the following reactions:



$$K_{\text{sp}} = 4.0 \times 10^{-11} \text{ (Butler, 1964)}$$



$$K_{\text{sp}} = 1.0 \times 10^{-107} \text{ (Kramer, 1965).}$$

The F_W contents of the carbonate phases analyzed and the equilibrium F_W contents predicted by the above reactions are shown in Table 15. It can be seen that the water leach is saturated in F with respect to CO_2 -F-apatite in the limestones, dolomites, and aragonites. The water leach of aragonites is saturated in F with respect to CaF_2 ; however, the limestones and dolomites have F_W contents predicted by equilibrium reaction (1). A simple mineral equilibrium between water and CaF_2 is suggested as the factor controlling the F_W content in the carbonates.

TABLE 15

Calculated Solubilities of Fluoride Minerals
Compared to the Observed F_W of Carbonates

	m/l F
$\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$ $K_{sp} = 4.0 \times 10^{-11}$ <p>predicted F =</p>	4.3×10^{-4}
$\text{Ca}_9.9(\text{PO}_4)_5.65(\text{CO}_3)0.35\text{F}_{2.16} \rightleftharpoons$ $9.9\text{Ca}^{2+} + 5.65\text{PO}_4 + 0.35\text{CO}_3 + 2.16\text{F}^-$ $K_{sp} = 1.0 \times 10^{-107}$ <p>predicted F =</p>	0.19×10^{-4}
Limestones - observed F_W	1) 3.6×10^{-4} 2) 2.1×10^{-4}
Dolomites - observed F_W	1) 4.6×10^{-4} 2) 2.4×10^{-4}
Aragonites - observed F_W	1) 11.8×10^{-4} 2) 10.2×10^{-4}

1) - calculation based on mean F_W .

2) - calculation based on median F_W .

DISCUSSION

Incorporation of the Halogens in Carbonates

The incorporation of F, Cl, and Br into carbonates can take place by inorganic mechanisms or indirectly through biogenic contributions.

Inorganic Incorporation

The incorporation of Cl and Br in the carbonates is predominantly by fluid inclusions and intergranular salts derived from pore waters. The difference $X_T - X_W$ (where $X = \text{Cl}$ or Br), is interpreted as an estimate of the Cl and Br contained in the carbonate lattice. However, it must be remembered that fluid inclusions in the -300 mesh fraction are possible. The amount of Cl in the lattice amounts to about 70 - 100 ppm in the limestones and dolomites and about 1200 ppm in the aragonites. Approximately 8 - 15 ppm Br would occur in the lattices of limestones and dolomites compared to 30 - 40 ppm Br in the lattice of aragonite. A co-precipitation mechanism of CaCl_2 and CaBr_2 is probably responsible for high Cl and Br incorporation in the aragonite lattice with partial loss upon subsequent alteration to calcite and/or dolomite.

There is an anomalously high F_T content in the aragonites (corals and sediments) compared to the limestones and dolomites. The high F_T content of the aragonitic corals may be attributed to co-precipitation of CaF_2 intracellularly, but an inorganic mechanism must be responsible for the high F_T in the oolites and inorganic aragonite muds.

Ooliths are believed to form inorganically (Illing, 1954; Ginsberg et al., 1963).

In inorganic precipitation, neither orthorhombic aragonite nor rhombohedral calcite should show a preference for incorporation of body centered cubic fluorite as fluorite is not isomorphous with either of these two minerals. If the solid phase were pure CaF_2 , the activity of CaF_2 would be equal to 1. If it were a solid solution of CaF_2 and CaCO_3 , the activity of CaF_2 would be equal to its mole fraction (X_{CaF_2}) times its activity coefficient (γ_{CaF_2}). This is illustrated for aragonite as follows:

$$A_{\text{CaF}_2} = X_{\text{CaF}_2} \times \gamma_{\text{CaF}_2} \quad (1)$$

where A_{CaF_2} = the activity of CaF_2

X_{CaF_2} = the mole fraction of CaF_2 in the CaCO_3

γ_{CaF_2} = the activity coefficient of CaF_2 .

A_{CaF_2} = ion product of $(\text{Ca}^{2+})(\text{F}^-)^2$ in sea water/ K_{sp}

$$= \frac{8.8 \times 10^{-12}}{4.0 \times 10^{-11}} = 2.2 \times 10^{-1}$$

$X_{\text{CaF}_2} = 6.0 \times 10^{-4}$ for 300 ppm F and 3.0×10^{-3} for 1600 ppm F.

Activities of 75 and 370 for F concentrations of 1600 ppm F and 300 ppm F respectively calculated from (1) above, are unrealistic (Garrels and Christ, 1965). The F does not likely occur as CaF_2 in solid solution in the CaCO_3 .

It is proposed that CaF_2 co-precipitates as a separate phase when the aragonite precipitates during the formation of ooliths. Ooliths are typical of beach sands and form in areas subjected to strong tidal

currents. The warm waters in the intertidal zone are supersaturated with respect to CaCO_3 which facilitates the precipitation of aragonite on moving particles. It is in this zone that wide variations in salinity occur and concentration of sea water would favor the co-precipitation of CaF_2 with aragonite.

Carbonate - F mineral-water equilibrium reactions carried out over a period of one year have shown that aragonite (-300 mesh) from ground skeletal material removed F^- (an increase of 20 - 100 ppm F in the aragonite) from solutions undersaturated with respect to CaF_2 (2 ppm F^-). Reagent grade calcite (precipitated) in contact with F^- solutions of the same concentration used for the aragonite had no effect on the F^- content of the solution. In both cases CaF_2 should not have precipitated, suggesting that an adsorption reaction between the aragonite and F^- must have taken place. The mechanism involved is not known; however, the results indicate that F^- adsorption is possible. More experimental work on the uptake of F by carbonates is needed.

Organic Incorporation

One of the factors controlling the distribution of the elements in carbonate rocks is the geochemical activity of shelled organisms, in particular their selective capacity to accumulate specific elements. The role of various shelled organisms in the formation of sedimentary rocks of biogenic origin is well established. Species and environmental variations in skeletal composition are well known for the cation trace elements (Glagoleva, 1961; Filkey and Harriss, 1966); however, no such studies have been reported for the halides.

The geochemistry of F, Cl, and Br in several species of Recent marine and fresh water shelled organisms was investigated to determine: 1) the environmental effects on the concentration of F, Cl, and Br, 2) the mode of occurrence of the halides in the shells, 3) the role of shelled organisms in fractionating the halogens, particularly with respect to carbonate rocks, and 4) the role of shelled organisms in incorporating halides in carbonates.

Twenty-one fresh water lamellibranchs collected from the Finger Lakes, New York included five species; Nitocris carinata, Andonta cataraeta, Elliptio complanatus, Goniobasis liviscens, and Lampsilis radiata. All the shells were composed of aragonite.

Seventeen Recent calcareous marine organisms analyzed included 6 species of corals, 5 species of pelecypods, 2 species of gastropods, and 1 species of algae.

Complete details of all samples, including mineralogy, are given in Appendix I.

Shells of Fresh Water Organisms

Results of the analyses of the fresh water shells are presented in Appendix II. All three halogens are enriched in the shells relative to their concentrations in fresh water (0.26 ppm F, 8.3 ppm Cl, and 0.006 ppm Br; Livingstone, 1963b). The water leach analyses indicate that 97.6% of the Cl_T , 63.0% of the F_T , and 25.8% of the Br_T are in a water soluble form. The average Cl/Br_T ratio of the shells is 2.5/1 compared to a value of 1200/1 for average fresh water. The Cl/Br_W ratio of the shells is 10/1, reflecting the higher solubility of Cl over Br.

A complete variable correlation matrix is shown in Table 16.

TABLE 16

* Correlation Matrix - Fresh Water Shells						
F_T	1.00					
Cl_T	0.69	1.00				
Br_T	0.42	0.75	1.00			
F_W	0.78	0.75	0.41	1.00		
Cl_W	0.65	0.86	0.76	0.66	1.00	
Br_W	-0.39	-0.14	0.07	0.53	-0.13	1.00

* \log_{10} transformation on raw data. Sample size is 21.

Several points are significant: 1) Cl_T and Br_T are highly correlated; however, they show no strong relationship to F_T , 2) of the water soluble extracts, only Cl_W and F_W are related to their corresponding total element contents.

Results of an R-mode factor analysis are shown in Table 17. The first four factors account for 95.5% of the total variance. The most significant points are the general coherence of Cl and Br and the independence of F.

Both Cl and Br are essential for the metabolic functions of the organisms and their concentrations in the shells must be largely dependent on an organic uptake. The high concentrations of Cl and Br in the shells relative to fresh water demonstrates that organic functions are important in the incorporation of the halogens in the skeletal material.

Cl and Br appear to occur in different forms in the shells, Cl

TABLE 17

Rotated Factor Analysis of Fresh Water Shells

Rotated Normalized Factor Loadings				
Factor	1	2	3	4
Cl _T	<u>-0.66</u>	0.04	-0.33	-0.67
Cl _W	<u>-0.76</u>	0.05	-0.30	-0.58
Br _T	<u>-0.98</u>	-0.05	-0.16	-0.14
F _W	-0.24	0.42	-0.47	<u>-0.73</u>
Br _W	-0.06	<u>-0.98</u>	0.16	0.12
F _T	-0.29	0.23	<u>-0.87</u>	-0.33
Percent of variance explained by factors				
	63.38	21.63	6.50	4.01
Cumulative percent of variance				
	63.38	85.01	91.50	95.51

being more soluble than Br. The Br may be in the form of water insoluble organic compounds. Chlorine is probably contained in small fluid inclusions or as soluble organic compounds such as chlorophenols. The concentration of Cl in body fluids of shelled organisms is high (Vinogradov, 1953) and inclusions of such fluids in the shell could account for the Cl.

The acid soluble F is not as concentrated in the shells relative to its average content in fresh water as are Cl_T and Br_T. The high water solubility of F cannot be explained as a simple mineral solubility equilibrium and cannot be explained on the basis of the data obtained

in this study.

Shells of Marine Organisms

Results of the analyses of the marine organisms are given in Appendix II. In contrast to the fresh water shells, the halogens are not enriched in the shells of the marine organisms relative to sea water. The ratios of Cl/Br_T and Cl/Br_W are 35/1 and 49.6/1 respectively compared to the ratio of 300/1 in sea water. The percentages of Cl_T , Br_T , and F_T which are water soluble are 88.5%, 54.5%, and 2.1% respectively. Chlorine is less water soluble than in the fresh water shells, whereas, Br is approximately 2 times more water soluble in the marine shells than in the fresh water shells. The F in the marine shells is very insoluble in water compared to the fresh water shells.

Acid soluble halogen concentrations are higher in the marine shelled organisms than in the fresh water shells, reflecting environmental influences. The absolute Br contents are not very different considering the large salinity gradient between fresh water and sea water, indicating the metabolic control of shelled organisms in incorporating Br in the skeletal material. The higher percentage of water soluble Br in the marine shells can be attributed to the higher Br concentration of 65 ppm in sea water. A large portion of the Cl_T is present in an insoluble form, possibly incorporated in the carbonate lattice as a result of higher Cl contents in the body fluids of the marine organisms.

A correlation analysis indicates a strong coherence between Cl and Br and only a weak coherence of Br and Cl to F (Table 18). The water soluble extracts of all three halogens are strongly correlated to their respective total element contents, which is in sharp contrast

to the fresh water shells.

TABLE 18

* Correlation Matrix - Marine Shells						
F_T	1.00					
Cl_T	0.65	1.00				
Br_T	0.57	0.95	1.00			
F_W	0.90	0.39	0.34	1.00		
Cl_W	0.62	0.97	0.96	0.33	1.00	
Br_W	0.55	0.95	0.95	0.24	0.97	1.00

* \log_{10} transformation on raw data. Sample size is 17.

An R-mode factor analysis indicates that 2 factors account for 97.4% of the total variance (Table 19). Factor 1 is a Cl and Br factor and is attributed to the high salinity of sea water. In contrast to the fresh water shells, only one factor controls the Cl and Br distributions. Factor 2 is essentially a F factor accounting for most of the variance of F_T and F_W . It is significant that both F_T and F_W are controlled by the same factor, which is not the case for the fresh water shells.

Factor 2 is believed to indicate that the F in the marine shells occurs as an insoluble fluoride mineral. The recent discovery of CaF_2 in statholiths of Recent marine mysid crustaceans and tectibranch gastropods substantiates the validity of the occurrence of CaF_2 in the skeletal portions of marine organisms (Lowenstam and McConnell, 1968).

Six corals analyzed contained an average of 0.0067% P_2O_5 and 3

TABLE 19

R-Mode Factor Analysis of Marine Shells

Rotated Normalized Factor Loadings		
Factor Variate	1	2
Cl _T	-0.94	0.30
Br _T	-0.96	0.23
Cl _W	-0.97	0.24
Br _W	-0.98	0.15
F _W	-0.11	0.99
F _T	-0.41	0.90
Percent of variance explained by factor		
	75.93	21.45
Cumulative percent of variance		
	75.93	97.38

pelecypods contained an average of 0.008% P₂O₅. If the F_T were present in the form of CO₂-F-apatite, the P₂O₅/F molar ratio should be 10/1. The ratios observed for the corals and pelecypods are 0.08/1 and 4.3/1 respectively. The P₂O₅ contents of the corals and pelecypods analyzed in this study are within the range of 0.004% to 0.02% P₂O₅ reported in lamellibranchs by Glagoleva (1961). CO₂-F-apatite is not the predominant form of F in the marine shells investigated.

Since early Cambrian time, shelled organisms have become increasingly more important contributors to carbonate deposition. These biogenic

skeletal contributions can have a definite influence on the relative abundance of the halogens in carbonate rocks. The effect will be relatively insignificant for Cl; however, Br and F distributions could be altered significantly if the biogenic fraction is large. The Cl/Br ratios in carbonates can be altered by the influence of skeletal material.

The environment in which the organism lives will have a strong influence on the uptake of halogens by the organism, and will be reflected in the carbonate rock. Of the various taxonomic groups analyzed, corals and algae concentrate F to a greater extent than the other organisms. Bromine is concentrated to about the same extent by all taxonomic groups, apparently not affected by environment as much as Cl and F.

Diagenesis

Presumably all marine carbonates were originally aragonites and/or calcites which have undergone recrystallization and diagenesis to the new phases, calcite and/or dolomite. The distribution of the halogens will be affected to varying degrees as diagenesis proceeds. This redistribution will be critical to an understanding of halogen abundances in carbonate rocks.

Five samples of Recent to Miocene carbonates containing variable amounts of calcite and aragonite were analyzed and compared to limestones and dolomites. Six samples of pre-Cambrian marbles derived from metamorphism of sedimentary carbonates were included for comparison. The results are shown in Table 11.

A detailed discussion of the distribution of F_T in dolomites

will be presented in a later section. The Cl_T and Br_T contents are the same in the marbles, limestones, and dolomites, indicating that Cl and Br are not lost during metamorphism of sedimentary carbonates. The marbles are extremely depleted in F, the F either being expelled during diagenesis or initially low in the original carbonate.

The Cl and Br contents of the aragonitic samples show no relationship to the abundance of aragonite, although the absolute abundances are higher in aragonites than in limestones or dolomites. During recrystallization of aragonite, a large portion of the Cl and Br are removed. The general pattern of distribution of Cl and Br during diagenesis is a reduction in the abundance of both water and acid soluble phases during conversion of aragonite to calcite. No further effects were observed. The Cl/Br ratio is not significantly altered by diagenesis.

Fluorine shows a very strong relationship to the aragonite content, as shown in Fig. 9, and is expressed by the equation:

$$F \text{ (ppm)} = 523.16 + 9.93 \text{ Ar (\%)}$$

The coefficient of correlation is 0.88 (N = 6). Carpenter (1968) analyzed two Recent oolites (100% aragonite) from Miami and Key West, Florida and found F contents of 1507 and 1640 ppm, in agreement with the value of 1500 ppm F found in pure aragonite (sample R-1) in this study.

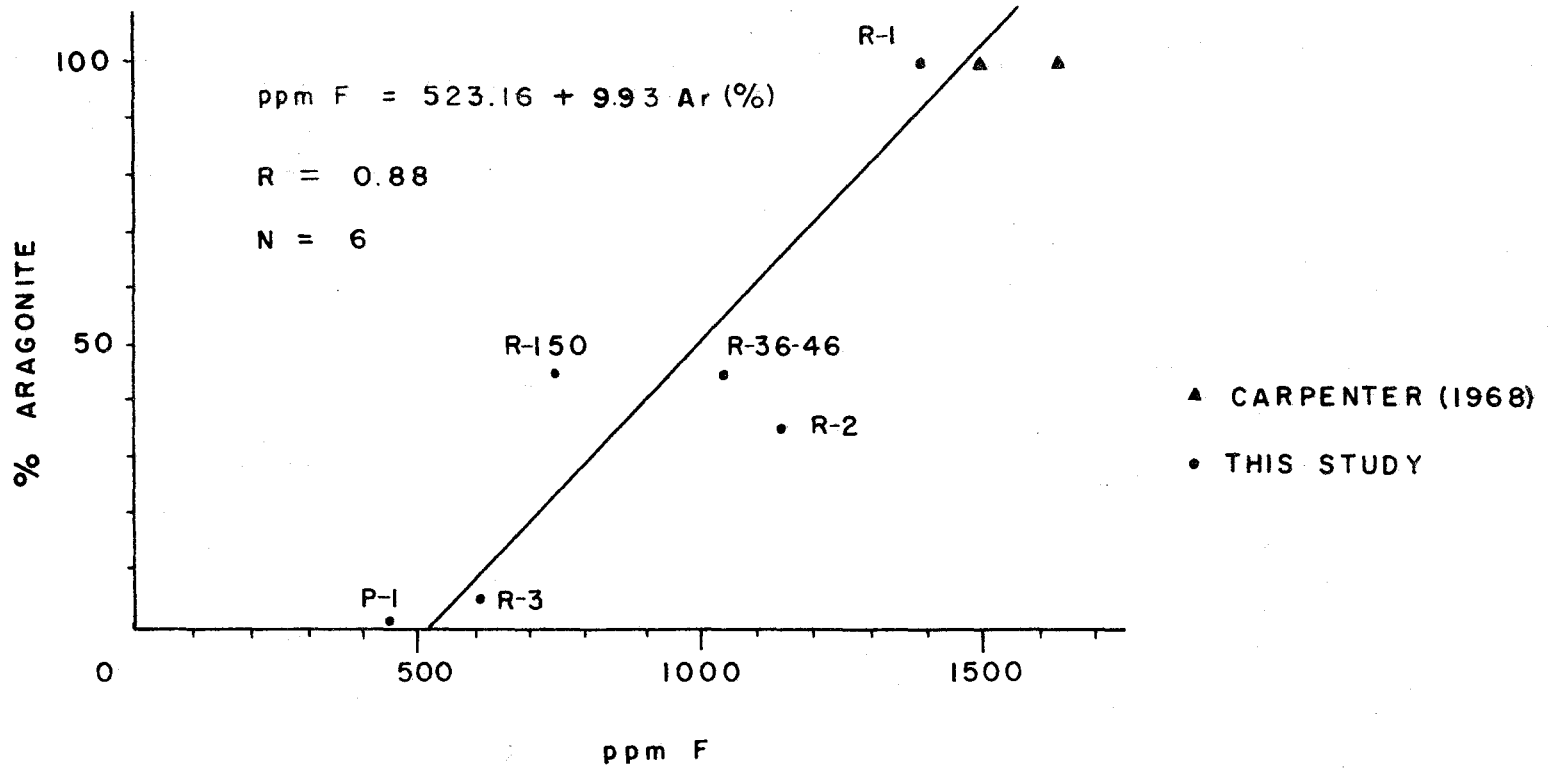
Meteoric waters are responsible for altering aragonites to calcite (Ladd *et al.*, 1967). If the F is present in the aragonites as CaF_2 , the acidic meteoric waters would tend to dissolve the CaF_2 .

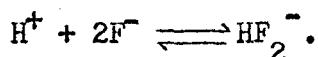
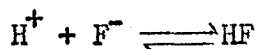
The reaction is: $CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$.

An increase in H^+ results in the formation of HF and HF_2^- complexes by the reactions:

% ARAGONITE vs ppm F

Fig. 9





Complexing of the F results in greater solubility of the CaF_2 with a resulting decrease in the F content of the material as the aragonite alters. No mineralogical control is necessary to explain the F content of aragonite. The same process which alters the aragonite also favors the solution of CaF_2 .

The effects of diagenesis of skeletal material was investigated by analyzing two species of Recent marine pelecypods and their Pleistocene analogs. The results are shown in Table 20.

The Pleistocene sample of Spondylus sp. has been completely altered to calcite from aragonite, while Cittarium pica has only been partially altered. There is an erratic but general trend to increasing F_T in both species and considerable loss of water soluble Cl and Br with increasing diagenesis. The Br_T increases slightly in Spondylus sp. and decreases slightly in Cittarium pica during diagenesis.

The most significant result of diagenesis of skeletal material is the loss of Cl_W , Cl_T , and Br_W . The Cl_W is more readily removed than Br_W . Loss of Cl_W results in low Cl/ Br_W ratios.

It is possible to lower the Cl/Br ratios in sedimentary carbonates by two fractionations: 1) an initial fractionation by the shelled organism, and 2) fractionation during diagenesis of the skeletal material by preferential loss of Cl. These effects will be important in carbonates only if the biogenic fraction is relatively large. Diagenesis of the non-biogenic fraction has no apparent effect on the Cl/Br ratio.

TABLE 20

Halogen Contents of some Recent Marine Pelecypods and their Pleistocene Fossil Analogs

	Recent*		Pleistocene		Recent*		Recent**		Pleistocene	
	Spondylus sp.		Spondylus sp.		Cittarium pica		Cittarium pica		Cittarium pica	
	T-1		U-94		Pr-2		U-133		U-48	
	T	W	T	W	T	W	T	W	T	W
F	34.0	9.2	48.0	6.0	21.5	4.8	125	11.0	95.0	19.0
Cl	250	250	50.0	57.5	850	650	2500	2250	575	450
Br	24.5	2.0	44.0	1.4	25.5	10.8	39.0	30.0	20.0	7.3
Cl/Br	10.2	125	1.1	41.1	33.3	60.5	64.1	75.0	28.8	62.1
Mineralogy	Aragonite		Calcite		Aragonite		Aragonite		Aragonite >> Calcite	

* - collected living

** - > 200 years old

Variations in the Cl/Br Ratios of Carbonates During Geologic Time

The average Cl/Br ratio of each age group vs geologic time are shown in Figs. 10 and 11. Both water soluble and acid soluble ratios are shown. For both limestones and dolomites, the Cl/Br_T and Cl/Br_W ratios show a definite trend to increasing values in younger carbonates. The Cl/Br ratio remains relatively constant at about 15/1 throughout the pre-Cambrian, then increases to approximately 90/1 in the Recent carbonates.

Two fractionations of Cl and Br have occurred in the carbonate rocks: 1) a fractionation across the mineral-water interface, and 2) a fractionation throughout geologic time.

Fractionation Across the Mineral-Water Interface

The most likely factors contributing to the fractionation of Cl and Br across the mineral-water interface are contributions of organic matter and skeletal material to the sediment. If organic mechanisms are responsible for the fractionation, the relationship of the Cl/Br ratio of sea water to carbonate rocks may well have changed throughout geologic time because of the increased activity of organisms. It has been previously shown that skeletal material in carbonate rocks can lower the Cl/Br ratio significantly if the biogenic contribution is large. The effects of organic matter are more difficult to evaluate; however, as pointed out in the introduction, these effects are probably small.

If the role of organisms is the major factor in the fractionation of Cl and Br across the sediment-water interface, the amount of Br_W should be higher in the pre-Cambrian carbonates. The data in Table 10

indicates that this is not the case. It is possible that Cl_w may have been removed from the pre-Cambrian carbonates by post-lithification leaching with ground water. If secondary leaching were important, a great deal of scatter would be expected in the data. This is not observed in the data.

The problem of Cl and Br fractionation across the mineral-water interface cannot be satisfactorily explained by the data obtained in this study; however, the above evidence suggests that the relationship of the Cl/Br ratio of sea water to the Cl/Br ratio of carbonates has remained constant. This is assumed throughout the remaining discussion.

Fractionation of Cl and Br Throughout Geologic Time

The Cl/Br ratio vs time curves shown in Figs. 10 and 11 have an exponential form. Plots of the \log_{10} Cl/Br ratio vs time are linear, verifying the exponential form of the curve (Fig. 12).

The variations in the Cl/Br ratios of carbonates throughout geologic time are interpreted as reflecting changes in the Cl/Br ratio of sea water over the past 2×10^9 years. The relationship of the Cl/Br ratio of sea water to the Cl/Br ratio of carbonate rocks is given by:

$$R_{ot} = R_{rt}/K$$

where R_{ot} = the Cl/Br ratio of the ocean at time t (calculated).

R_{rt} = the Cl/Br ratio of the carbonate rock at time t. This value is the analytical value of the Cl/Br ratio of the rock.

K = the distribution coefficient = 0.27.

The constant K is analogous to the distribution coefficient

Fig. 10

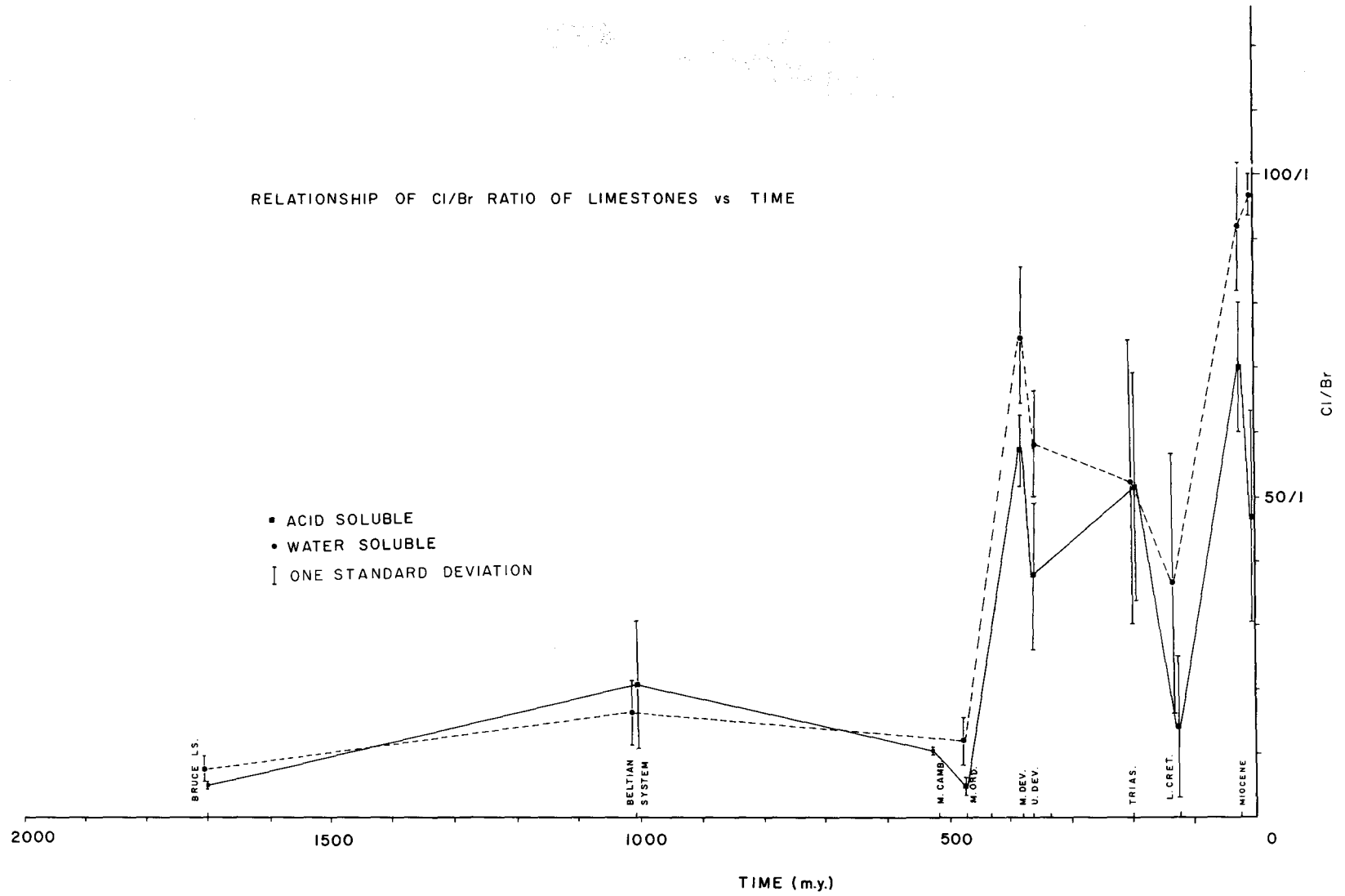
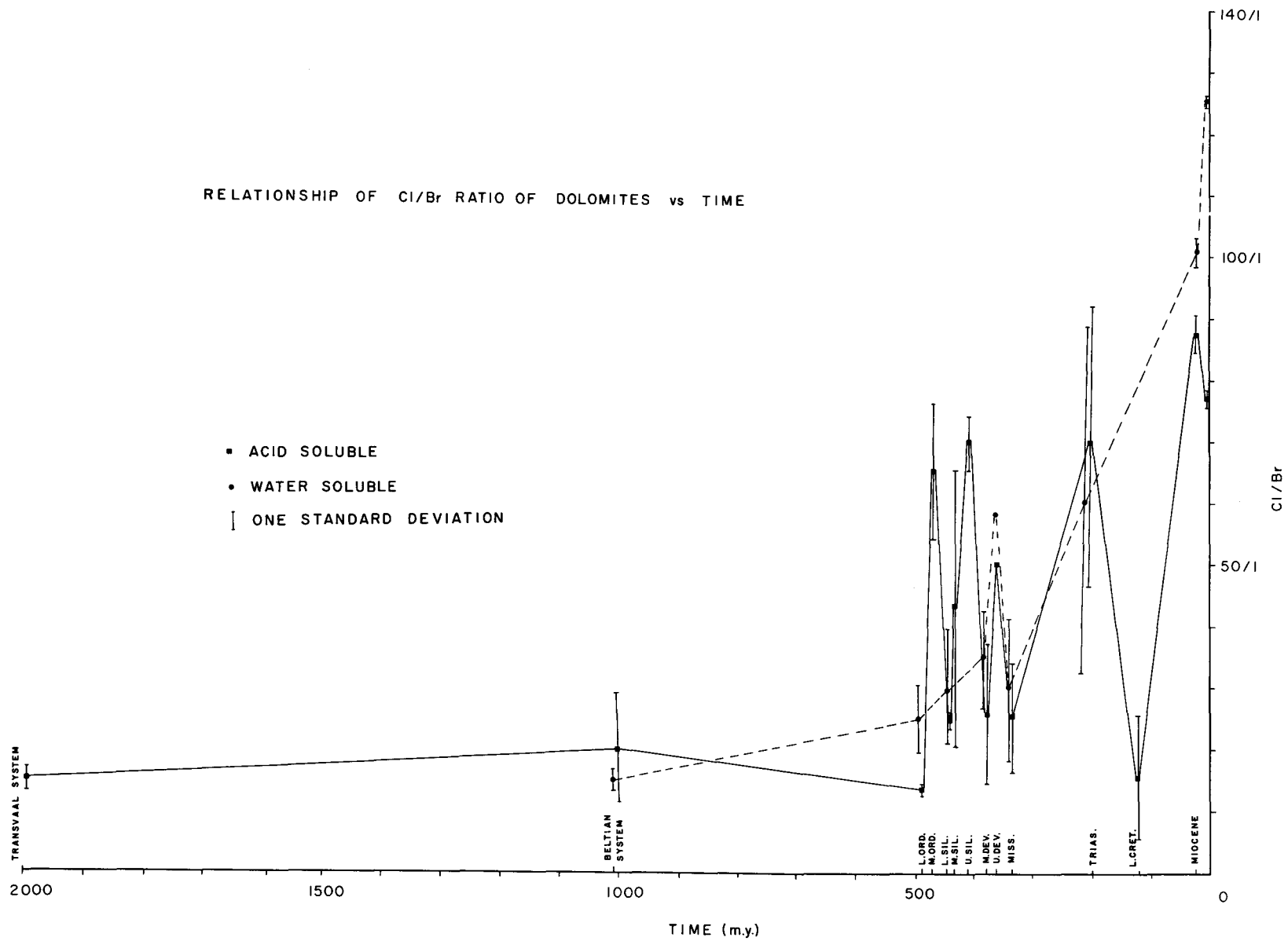
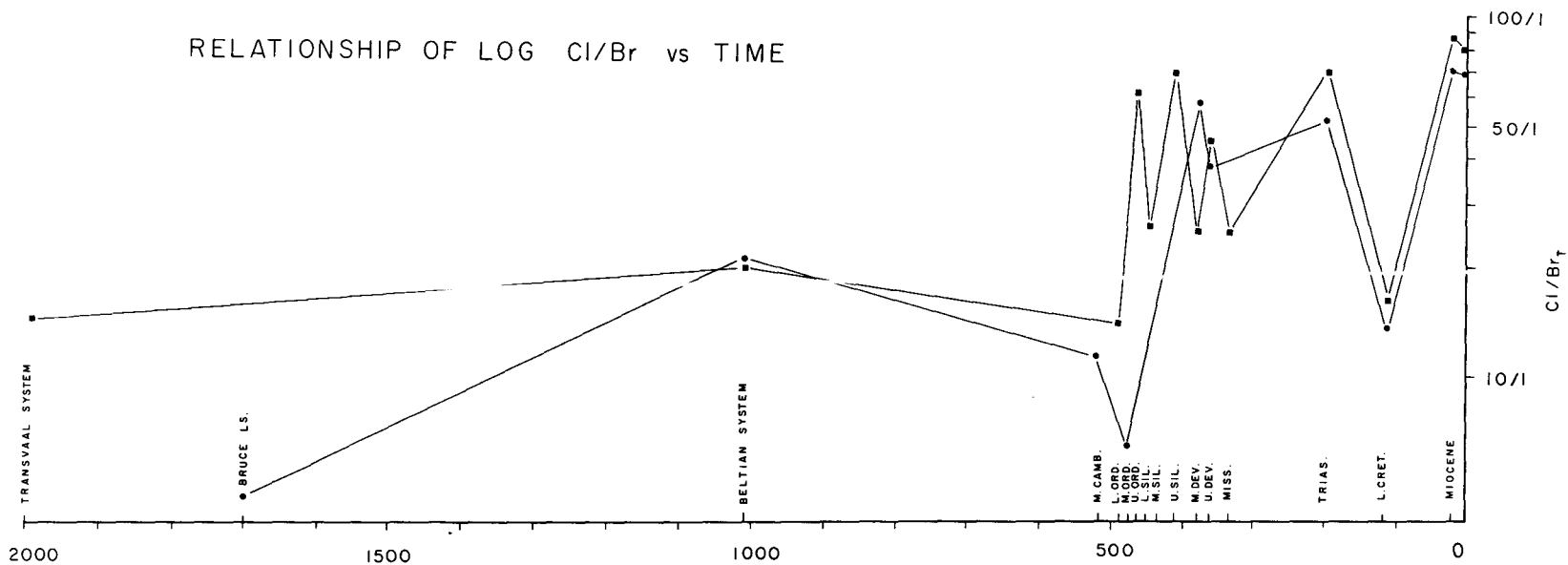


Fig. 11



RELATIONSHIP OF LOG Cl/Br vs TIME



▪ DOLOMITE
• LIMESTONE

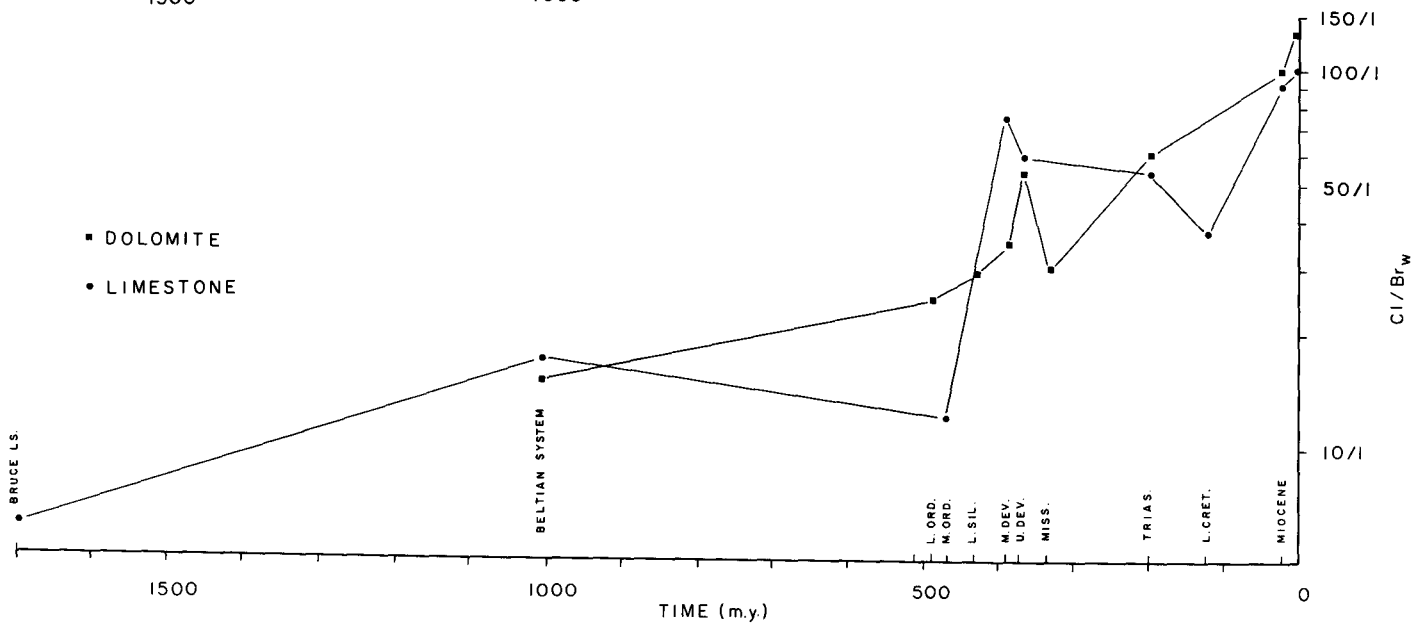


Fig. 12

$$K = \frac{r_c}{r_l} = \frac{\text{Cl/Br}_c}{\text{Cl/Br}_l} \quad \begin{array}{l} \text{(solid phase)} \\ \text{(liquid phase)} \end{array}$$

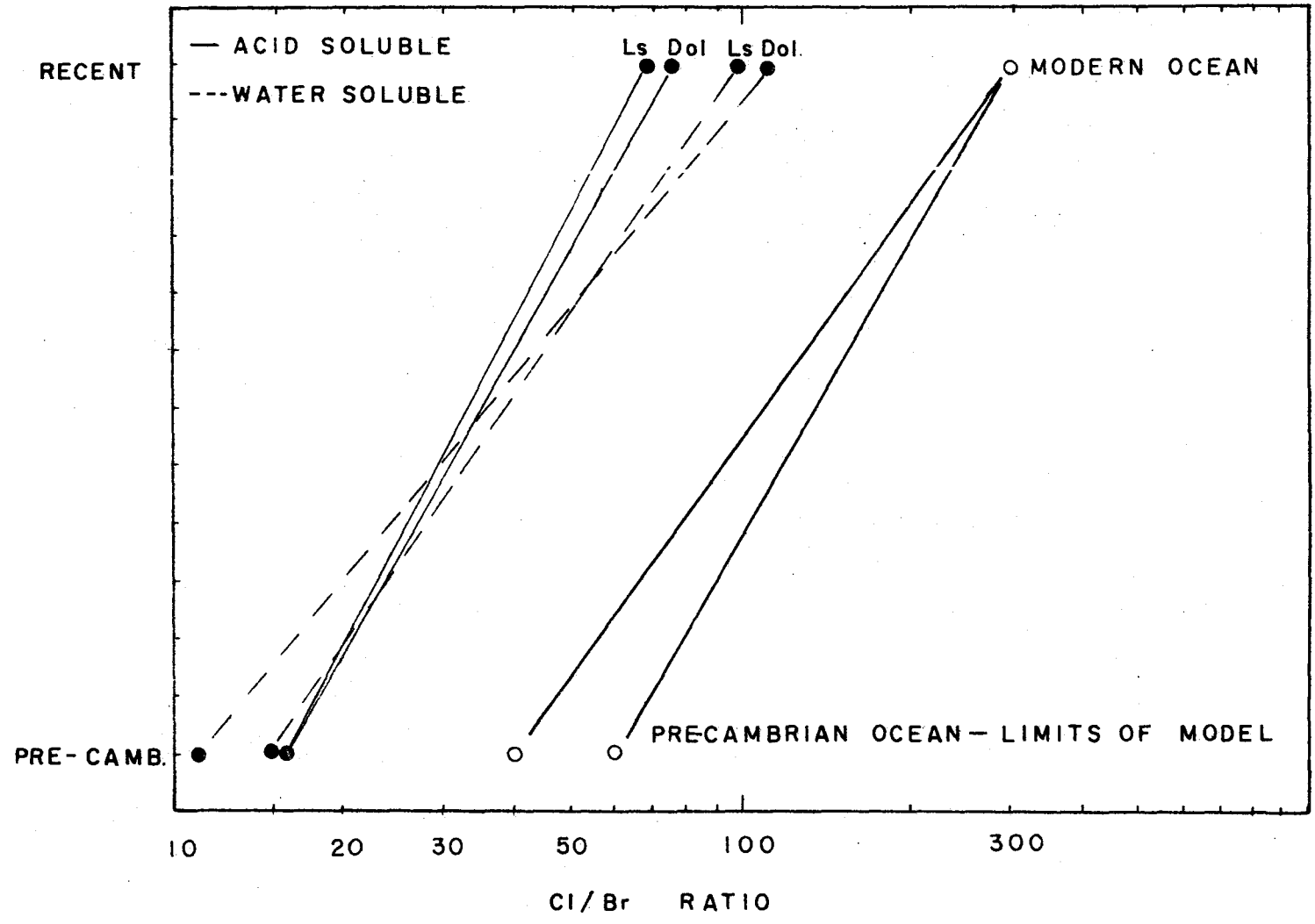
For the Recent carbonates $K = (80/1)/(292/1) = 0.27$. For simplicity, it is assumed that the value of K is constant throughout geologic time. The validity of this assumption may be seen in Fig. 13 which shows the relationship of the theoretical changes in the Cl/Br ratio of sea water to the changes in the Cl/Br ratio in the carbonate rocks. The slopes of the Cl/Br ratios in the carbonates lie within the limits of the slope of the oceanic model, indicating no significant change in the value of K .

The only major deviation from the general trend of the Cl/Br ratio vs time curve occurs in the Lower Cretaceous; however, the samples analyzed for this age group consist of biogenic reef material and would be expected to have low Cl/Br ratios. Other samples of the Lower Cretaceous should be investigated before any definite conclusions are made regarding the Cl/Br ratio of the Cretaceous seas.

The fractionation of Cl and Br may occur in several phases in the sedimentary cycle (Fig. 14). The following chemical mass balance is an attempt to account for the masses of Cl and Br in the lithosphere-hydrosphere system and to explain the processes responsible for the fractionation of Cl and Br in the oceans from a value of 60/1 in the pre-Cambrian to the present value of 292/1.

Weathering of igneous rocks has contributed 5×10^{20} g Cl and 80×10^{17} g Br to the lithosphere-hydrosphere system (Rubey, 1951). Table 21 shows that there is a total of 293×10^{20} g Cl and 170×10^{18} g Br in the lithosphere-hydrosphere system, most of which must have been derived from sources other than weathering of igneous rocks. Table 22

Fig. 13



RELATIONSHIP OF OBSERVED CI/Br RATIO IN CARBONATES TO PROPOSED OCEAN CI/Br RATIOS

GEOCHEMICAL CYCLE OF THE HALOGENS

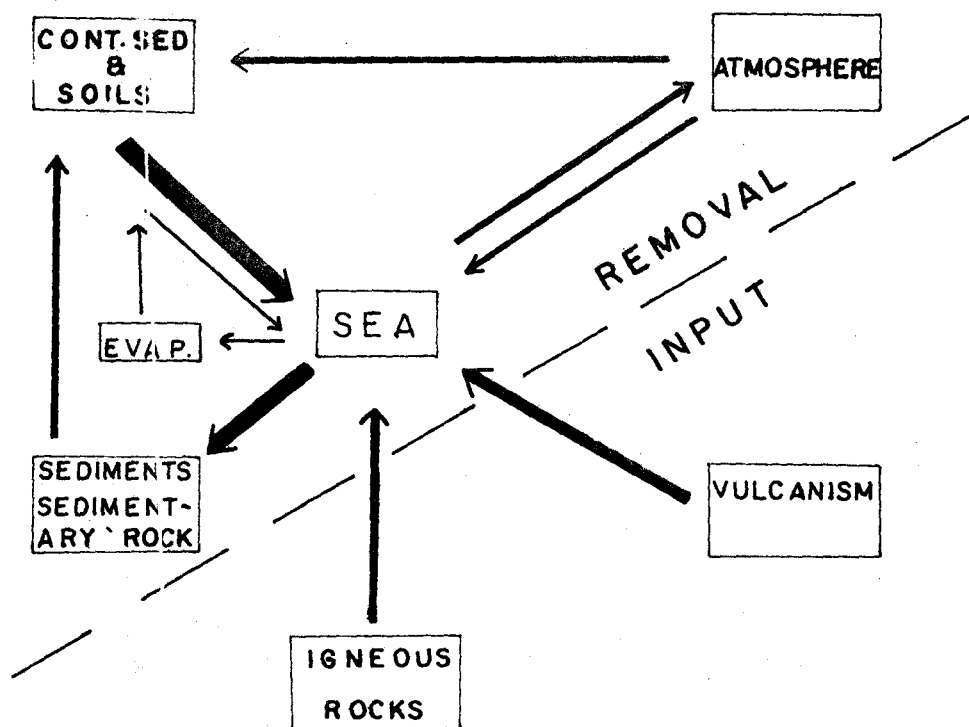


Fig. 14

TABLE 21

Geochemical Mass Balance for Cl and Br

	Cl x 10 ²⁰ g	Br x 10 ¹⁸ g	Reference	Cl/Br
Lithosphere	27 *	75	Vinogradov (1959)	36/1
Atmosphere	n.s.	n.s.	Poldervaart (1955)	
Oceans	270	90	Correns (1961)	292/1
Fresh water	0.002	n.s.	Livingstone (1963b)	
Subsurface water	-	n. s.	White <u>et al.</u> (1963)	
Biosphere	n.s.	n.s.	Kalle (1943)	
SUBTOTAL	290	170		
Crustal recycling	100	260		
TOTAL	400	430		93/1

* - calculations assumed a value of 1000 ppm Cl in shales
(Billings and Williams, 1967).

n.s. - not significant.

gives the Br in the various phases considered in the mass balance.

Assuming that the Cl and Br accumulated from degassing, and in the proportion of 60/1 as discussed earlier, 490×10^{18} g Br should have accumulated. The total mass of Br which can be accounted for in the present hydrosphere-lithosphere system is 170×10^{18} g, thus, 320×10^{18} g Br must have been removed from the system to give the Cl/Br ratio of 292/1 in the present ocean. The mass balance of Table 21

TABLE 22

Br in the Lithosphere-Hydrosphere System

	Mass (g)	Br (ppm)	Reference	Mass Br (g)
Shale	45×10^{22}	45	Poldervaart (1955) Billings and Williams (1967)	2×10^{19}
Sandstone	1×10^{23}	2	Poldervaart (1955)	20×10^{16}
Carbonate	23×10^{22}	15	Poldervaart (1955)	35×10^{17}
Pelagic Sediments	11×10^{23}	45	Poldervaart (1955)	50×10^{18}
Subsurface Waters	5×10^{20}	36	White <i>et al.</i> (1963)	20×10^{15}
Organic Carbon	250×10^{20}	10	Kalle (1943)	25×10^{16}
SUBTOTAL				75×10^{18}
Ocean				90×10^{18}
TOTAL				170×10^{18}

is unable to account for the missing Br.

Possible sources of unaccounted Br are petroleum deposits and sediments re-incorporated into the crust as igneous and metamorphic rocks. Recycled sediments would be the most important factor.

The ratio of metamorphosed sediments / sediments is between 4/1 and 6/1 (Livingstone, 1963a). The total mass of sediments is 2600×10^{21} g. Using the ratio of 4/1, one arrives at a mass of 10600×10^{21} g of metamorphic rocks. There are no data on the Br content of metasediments; however, a lower limit of 3 ppm Br (average for igneous rocks) would account for 30×10^{18} g Br, or about 1/10 of the total missing Br.

Six pre-Cambrian marbles analyzed in this study, have an average Br content of 37.5 ppm. Using this value for metasediments, 360×10^{18} g of the 3×10^{20} g missing Br can be accounted for. This compares favorably with the estimate of 3×10^{20} g Br arrived at by assuming a crustal recycling of four times the total volume of sediments which contain 75×10^{18} g Br; the assumption being that there is no loss of Br during metamorphism.

Approximately 108×10^{20} g Cl would also have been recycled if we assume no loss of Cl during metamorphism. As shown in Table 21, the ratio of Cl/Br added to the lithosphere-hydrosphere system and re-incorporated in metamorphic rocks is 93/1, which agrees very well with the Cl/Br ratio of 60/1 proposed for the degassing materials.

If the ocean is a steady state system, Br should be removed as fast as it is added. The yearly budget of Br in the oceans has been calculated on the basis of available data in the literature. In many cases data are insufficient or non-existent, necessitating approximations. The results of the balance are shown in Table 23. The balance indicates that the removal of Br from the oceans exceeds input by 16×10^{10} g per year. Over a period of 2×10^9 years, 320×10^{18} g Br would be removed from the ocean. The ocean is not a steady state system with respect to Br.

Sedimentary processes can account for the fractionation of Cl and Br in the oceanic system over the past 2×10^9 years.

TABLE 23

Yearly Budget of Br in the Modern Ocean

	Reference	Mass Br (g)
INPUT		
1. Continental Drainage 3.3 x 10 ¹⁹ g water/year Average of 0.006 ppm Br	Livingstone (1963b)	20 x 10 ¹⁰
2. Sediment load (assume 50% shale). Assume 3 ppm Br (average for igneous rock) Mass of 1.7 x 10 ¹⁶ g / 2	Livingstone (1963b)	2 x 10 ¹⁰
3. Volcanic sources - Assume excess is volcanic in origin (4.9 x 10 ²⁰ g / 3 x 10 ⁹ years)		16 x 10 ¹⁰
REMOVAL		
1. Shales (assume 50% of the sediment load forms shales) Average Br content of shales is 4.4 ppm. Mass of 1.7 x 10 ¹⁶ g / 2	Fleischer and Robinson (1963), Correns (1961), Barth and Bruun (1945)	4 x 10 ¹⁰
2. Carbonates Average of 30 ppm Br. Mass of 2.3 x 10 ²³ g / 6 x 10 ⁸ yr	This study	1 x 10 ⁹
3. Organic Carbon Reservoir Average of 10 ppm Br. Mass of 250 x 10 ²⁰ g / 2 x 10 ⁹ yr.	Kalle (1943)	1 x 10 ⁸
4. Pelagic Sediments Assume 45 ppm Br. Mass of 11 x 10 ²³ g / 10 ⁸ yr.		50 x 10 ¹⁰
TOTAL REMOVAL		54 x 10 ¹⁰
TOTAL INPUT		37 x 10 ¹⁰
NET DIFFERENCE		16 x 10 ¹⁰

Effect of Major Periods of Evaporite Deposition on the Cl/Br Ratio

A close examination of the Cl/Br ratio vs time curves shows that there is cyclic behavior of the curve throughout the Ordovician, Silurian, and Devonian periods. A detailed Cl/Br ratio vs time curve covering this time interval is shown in Fig. 15. Major periods of evaporite deposition are also plotted on the curve and can be seen to correspond to Cl/Br lows. Deposition of evaporites may possibly account for part of this variation. It is also interesting to note that the basal halite in most salt deposits have lower Br contents (30 - 50 ppm) than the value of 75 ppm predicted on the basis of experimental work on the distribution coefficient of Br in halite (Holser, 1965). Holser has suggested that during certain periods more rock salt may have been eroded than deposited, resulting in an increase in the Cl/Br ratio of sea water and consequently a lower Br content in the first halite crystals precipitated. Holser (1966) looked for but was unable to find any conclusive evidence in the Br content of basal halites which would indicate an increase in the Cl/Br ratio of sea water since the Cambrian.

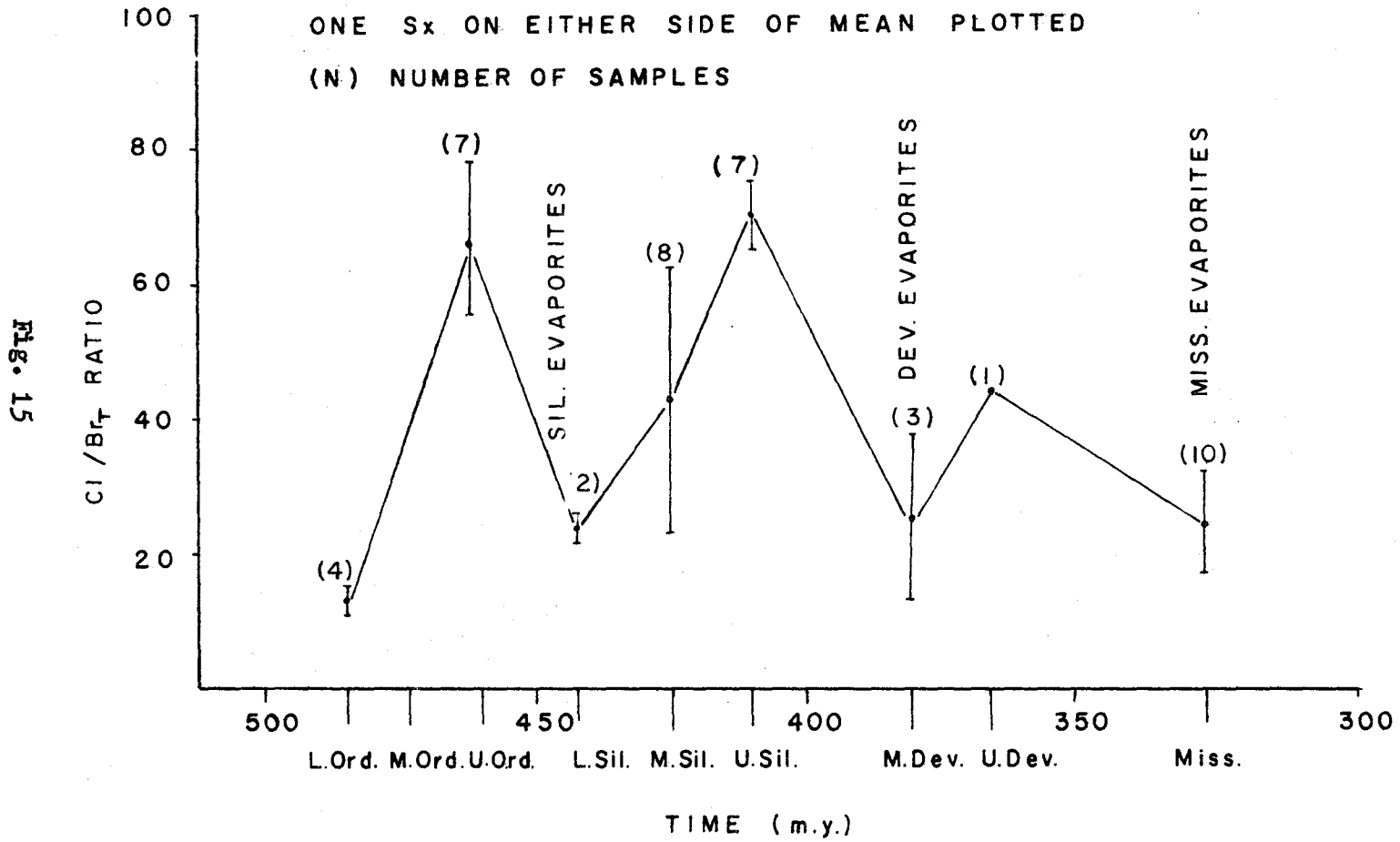
The Zechstein evaporite sequence from continental Europe has been examined to determine the effect of evaporite deposition on lowering the Cl/Br ratio of sea water. Considerable data are available on the extent and composition of this deposit (Borchert and Muir, 1964).

The Zechstein evaporites average 600 m in thickness over an area of $0.04 \times 10^8 \text{ km}^2$ and contain a total volume of $0.024 \times 10^8 \text{ km}^3$ of salts, or a mass of $58 \times 10^{20} \text{ g}$ of salts (assuming an average density of 2.4; Stewart, 1963). Complete evaporation of the present oceans would produce a layer of salts 60 m thick over an area of $3.6 \times 10^8 \text{ km}^2$, or a total

Cl_T / Br_T RATIO vs TIME (m.y.) - DOLOMITES

ONE Sx ON EITHER SIDE OF MEAN PLOTTED

(N) NUMBER OF SAMPLES



volume of $0.22 \times 10^8 \text{ km}^3$ of salts of which 80% would be halite. About 11% of the present ocean salts would have been removed by the Zechstein evaporites in approximately 5×10^5 years (Richter-Bernburg, 1938). Borchert and Muir (1964) estimate that 80% of the Zechstein evaporites consist of NaCl.

If we assume that the Br content of 280 ppm, representative of the kieserite-carnallite phase is an estimate of the Br content of evaporites, and a composition of 80% NaCl, we can estimate the quantities of Cl and Br removed from sea water during the Zechstein period. The total NaCl in the evaporites is 460×10^{19} g, or 300×10^{19} g Cl. The mass of Br amounts to 130×10^{16} g. There will also be some input of Cl and Br into the oceans from volcanic activity and continental drainage. Using average Cl and Br contents of 8.3 ppm and 0.006 ppm respectively in river water and a volume of 3.3×10^{16} liters runoff per year (Livingstone, 1963b), a total of 130×10^{19} g Cl and 100×10^{15} g Br would be added to the ocean during the Zechstein period. An estimate of the input from volcanic activity has been derived by assuming a uniform input of Cl and Br by degassing for the past 3×10^9 years. An estimate of the yearly Cl and Br input by volcanic activity is given in Table 4. The total balance of input - removal is presented in Table 24. If a volume of NaCl equal to the NaCl content of the Zechstein deposits were removed from the present oceans, the Cl/Br ratio of the ocean would decrease from 292/1 to 264/1, or a decrease of 9.5%. It is possible for large scale evaporite deposition to account for some fluctuation of the Cl/Br ratio in ancient oceans.

TABLE 24

Effect of the Permian Zechstein Evaporites
on the Cl/Br Ratio of Sea Water

	Cl (g)	Br (g)
Present Ocean	27×10^{21}	9×10^{21}
Removed by Zechstein	3×10^{21}	130×10^{16}
*Volcanic Input	50×10^{17}	8×10^{16}
Continental Drainage	130×10^{21}	10×10^{16}
Net Removal	30×10^{20}	1×10^{18}
New System	24×10^{21}	9×10^{19}

Note - All calculations are based on a time interval of
 5×10^5 years.

$$\begin{aligned}
 * \text{ Volcanic Cl} & - (290 - 5) \times 10^{20} \text{ g} / 3 \times 10^9 \text{ years} = \\
 & 96 \times 10^{11} \text{ g/year for } 5 \times 10^5 \text{ years} = \\
 & 48 \times 10^{17} \text{ g.}
 \end{aligned}$$

* Volcanic Br - see Table 23

$$\begin{aligned}
 & 16 \times 10^{10} \text{ g/year for } 5 \times 10^5 \text{ years} = \\
 & 80 \times 10^{15} \text{ g.}
 \end{aligned}$$

GEOLOGIC APPLICATION OF F_T IN ENVIRONMENTAL RECONSTRUCTIONS

Dolomitization and Environmental Interpretations

The origin of dolomite is one of the most perplexing problems in geology. It is now well established that dolomite is being formed today in the supratidal flats of arid and semi-arid regions in association with waters that have been highly concentrated (Shinn et al., 1965; Deffeyes et al., 1965). A mechanism of refluxing brines has been invoked to explain the dolomitization of Recent carbonates (Deffeyes et al., 1965). Adams and Rhodes (1960) explained the dolomitization of the Permian Basin reef complex by refluxing of hypersaline brines.

The distribution of a given trace element within a dolomite sequence formed by a refluxing brine must be dependent on the physical and chemical characteristics of the system. If such a relationship could be established for F, the interpretation of the genesis of other dolomites would be greatly facilitated. Dolomites analyzed in this study contain an average of 381 ppm F with a standard deviation of 359 ppm. The distribution of F in dolomites shown in Fig. 6 appears to be multimodal with peaks occurring at 50 ppm, 200 ppm, 350 ppm, and 450 ppm. The average F content of limestones is 90 ppm with a standard deviation of 82 ppm.

The variable distribution of F in the dolomites and the consistently low F contents in the limestones suggests that the chemistry of the dolomitizing fluids and/or the physical mechanisms involved may be the factors which control the distribution of F in the dolomites.

A suite of 70 samples of dolomites from cores of the Zama member, Middle Devonian Muskeg formation, from four oil wells in Northern Alberta were analyzed for F. Petrologic interpretations of the cores had outlined four depositional environments: 1) supratidal, 2) intertidal, 3) turbulent subtidal, and 4) quiet subtidal to lagoonal. Environmental interpretations and correlations based on the petrologic data are shown in Fig. 16 (Interpretations by V. Jenik, Gulf Oil Canada, Calgary).

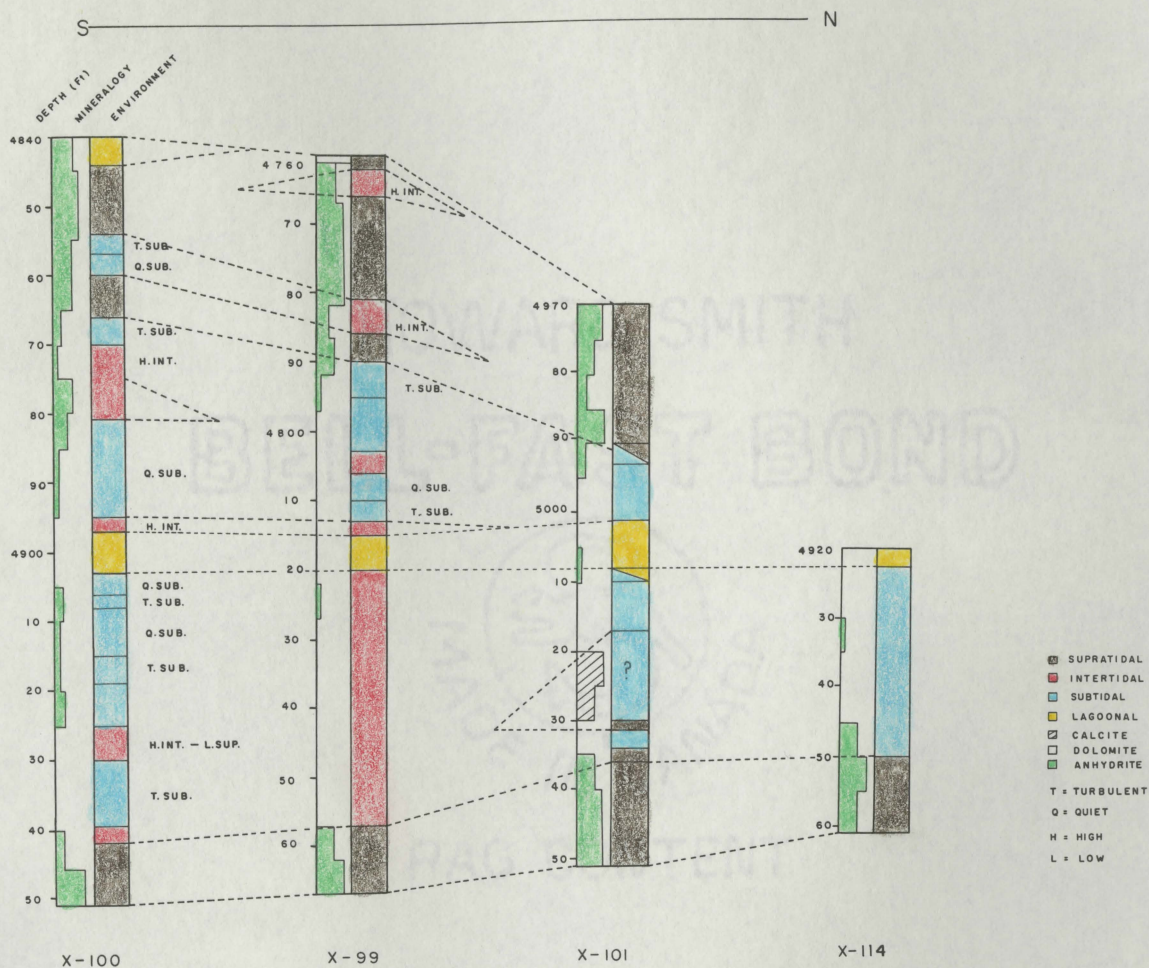
The Zama member is a 60 to 120 foot thick carbonate unit of the Middle Devonian Muskeg formation. The detailed stratigraphy of the Devonian of Alberta is shown in Fig. 17. Details of the four well locations and cored intervals are presented in Table 25. Locations of all the X-series wells are shown in Fig. 18.

TABLE 25

Well Locations and Cored Intervals - Zama Member Dolomites

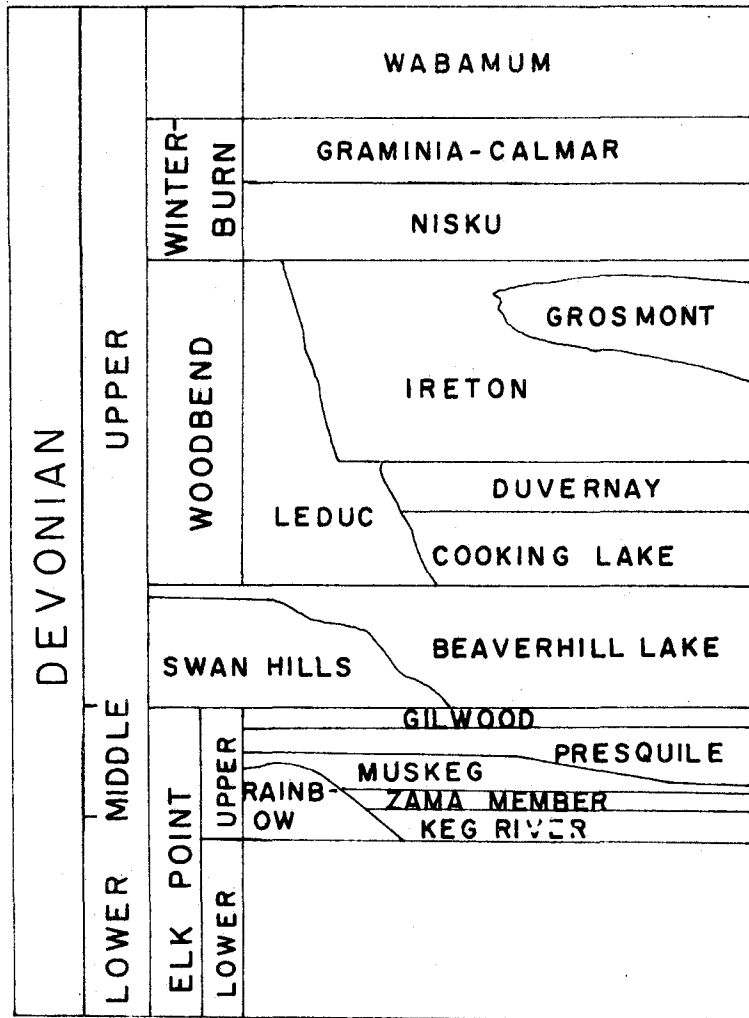
Well	Location	Cored Interval (feet)
X-99	16-19-116-446	4761-4883
X-100	4-19-116-446	4840-4950
X-101	5-30-116-446	4970-5051
X-114	2-25-117-546	4922-4960

The assumption of dolomitization of the Zama member by a reflux mechanism is supported by several lines of evidence. The cyclic nature of the dolomites is remarkably similar to the sabkha-wadi complex of the Trucial Coast and to the Recent carbonates of the Bahamas where dolomites are forming today. Ordovician Stoney Mountain and Silurian Interlake



ENVIRONMENTAL INTERPRETATION AND CORRELATIONS — ZAMA MEMBER
(N-S X-SECTION)

Fig. 16



DEVONIAN STRATIGRAPHY OF ALBERTA

Fig. 17

LOCATION MAP - ZAMA LAKE AREA, ALBERTA

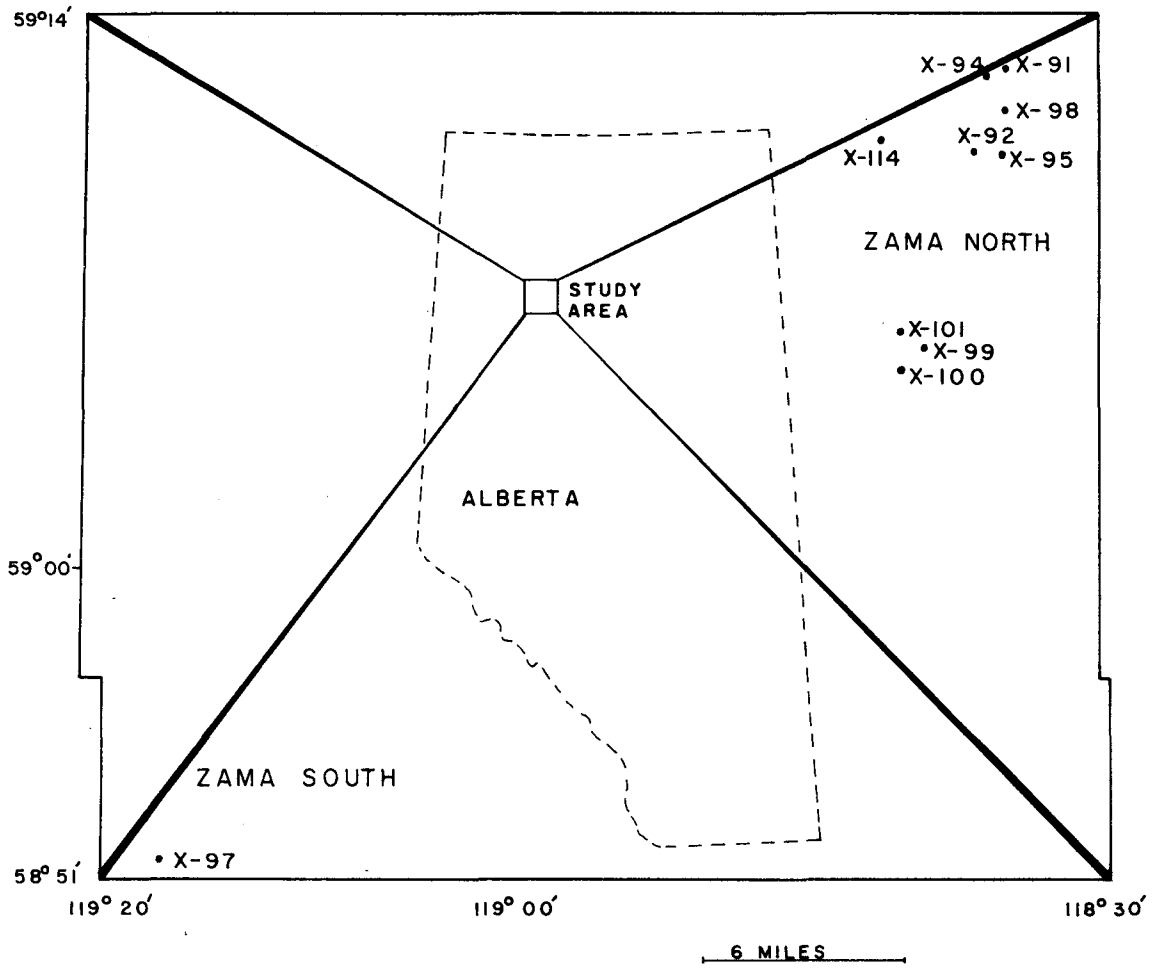


Fig. 18

carbonate analogs of the Bahamian carbonates, dolomitized by refluxing brines, are similar to the Zama dolomites (Roehl, 1967). W. D. Shearman (personal communication, 1966) has confirmed the similarity of the Zama dolomites to the Recent sabkha-wadi complex of the Trucial Coast.

A typical sabkha-wadi type cycle present in the Zama member is shown in Fig. 19. These cycles are characteristically 2 to 3 feet in thickness, but may be up to 120 feet thick. The complete cycle is not always preserved and numerous oscillations within a cycle are common. The cycles represented in wells X-99, X-100, X-101, and X-114 do not show complete cycles on the scale used. Minor variations on a scale of several inches are not shown because each sample covered an interval of 5 feet.

The vertical F distribution in the four wells are shown in Fig. 20. There is a definite relationship of F to environment in all four wells. The average F contents in the four environments are:

Environment	\bar{x} (ppm)	S_x (ppm)	N
Supratidal	302	235	21
Intertidal	411	188	12
Turbulent Subtidal	556	290	26
Quiet Subtidal to Lagoonal	124	36	11

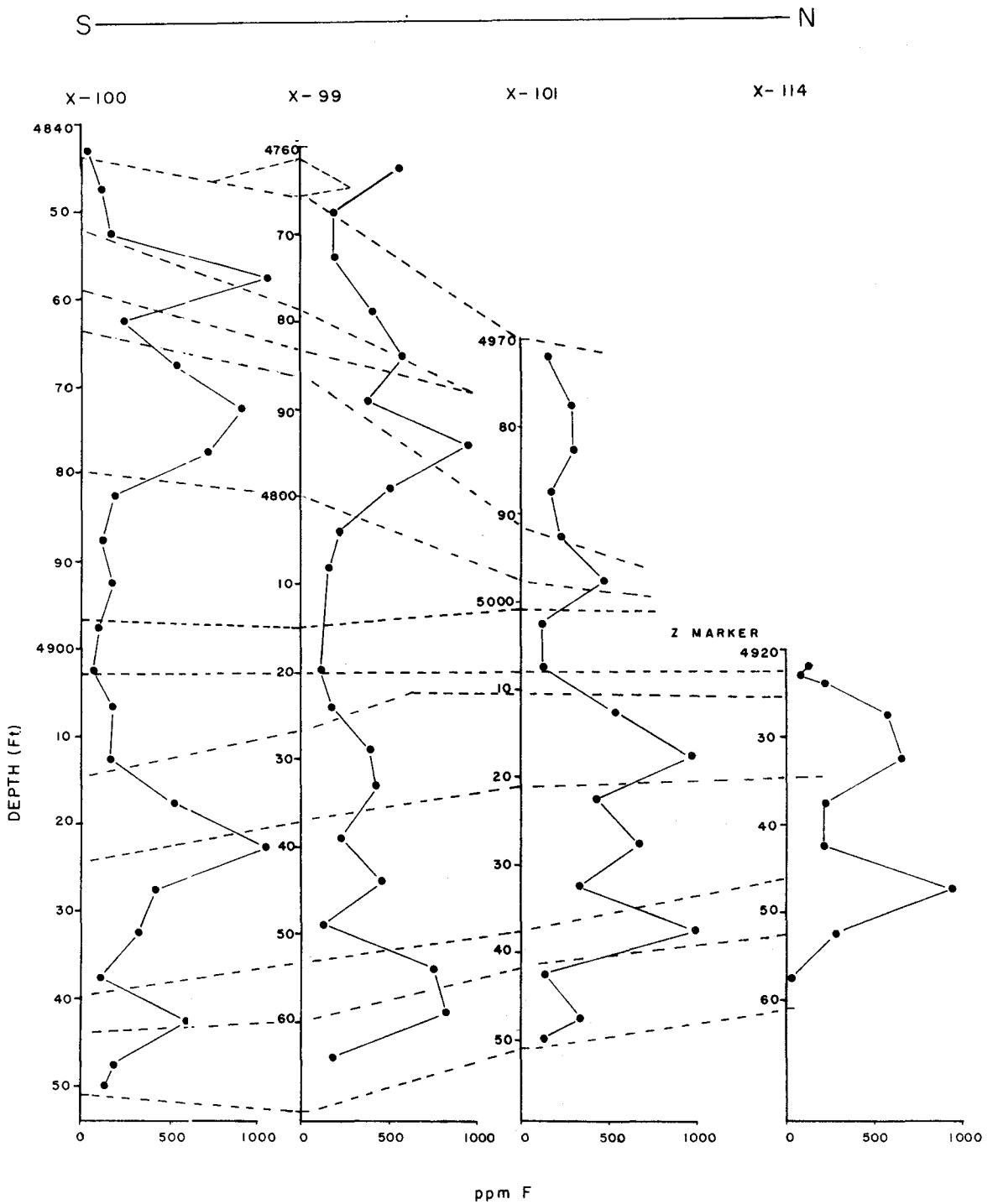
A Student-t test indicates that the differences between the groups are significant at the 99% confidence level.

It is believed that the F distributions in the dolomites are not a primary feature of their limestone precursors. Two lines of evidence support this view. 1) Of 58 limestones analyzed for F, only 3 had F

TYPICAL SABKHA WADI-CYCLIC CARBONATE FABRICS

ENVIRONMENT	DIAGNOSTIC FEATURES
SUPRATIDAL	<p data-bbox="828 451 1341 506">Flat pebble conglomerate and breccia.</p> <p data-bbox="828 566 1273 590">Algal mat – stromatolites.</p> <p data-bbox="828 721 1159 747">Nodular anhydrite.</p>
LOW SUPRATIDAL HIGH INTERTIDAL	Breccia.
INTERTIDAL	<p data-bbox="828 985 1311 1060">Burrows, borings, mudcracks, breccia fragments, laminae,</p> <p data-bbox="828 1110 1207 1137">algal mats, reworking.</p>
TURBULENT SUBTIDAL	Extensively reworked, burrow traces, mud, pellets, bioclasts.
LAGOONAL	Fine laminae, organic matter, dark.

Fig. 19



F DISTRIBUTION IN THE ZAMA MEMBER AND CORRELATIONS BASED ON F CONTENTS. (N-S X-SECTION)

Fig. 20

contents in excess of 100 ppm. If the F distributions in the dolomites are controlled by primary F contents of the original limestones, more of the limestones should have high F contents. 2) A suite of ten samples of Lower Cretaceous limestones, from environments analogous to the Zama environments, all had low F contents. Two tidal flat dolomites associated with these limestone samples had high F contents, very similar to the F contents in the Zama intertidal dolomites.

If dolomitization of the Zama member is assumed to be the result of refluxing brines, the F distributions must be a function of the hydrologic system and the brine chemistry. An idealized model illustrating the hydrologic system is shown in Fig. 21. With each tidal pulse, sea water is added to the system in the intertidal zone. Evaporation in this zone results in formation of a dense brine. The dense brine sinking through the sediments into the intertidal and subtidal zones is forced down by each tidal influx. Brine moves into the supratidal zone, predominantly by capillary action. Further additions to the supratidal zone are made by storm action and spring tides.

As the sea water concentrates in the intertidal zone, CaF_2 will begin to precipitate. The highest concentrations of F are observed in the turbulent subtidal zone, because of two factors. 1) A kinetic effect. The precipitation of CaF_2 initiated in the intertidal zone may not have had sufficient time to go to completion before the brine moves into the turbulent subtidal zone. The bulk of the precipitation would take place in the turbulent subtidal zone. 2) Tidal influx may dilute the brine sufficiently to retard the precipitation of CaF_2 , resulting in lower F values in the intertidal zone than in the turbulent subtidal zone. The

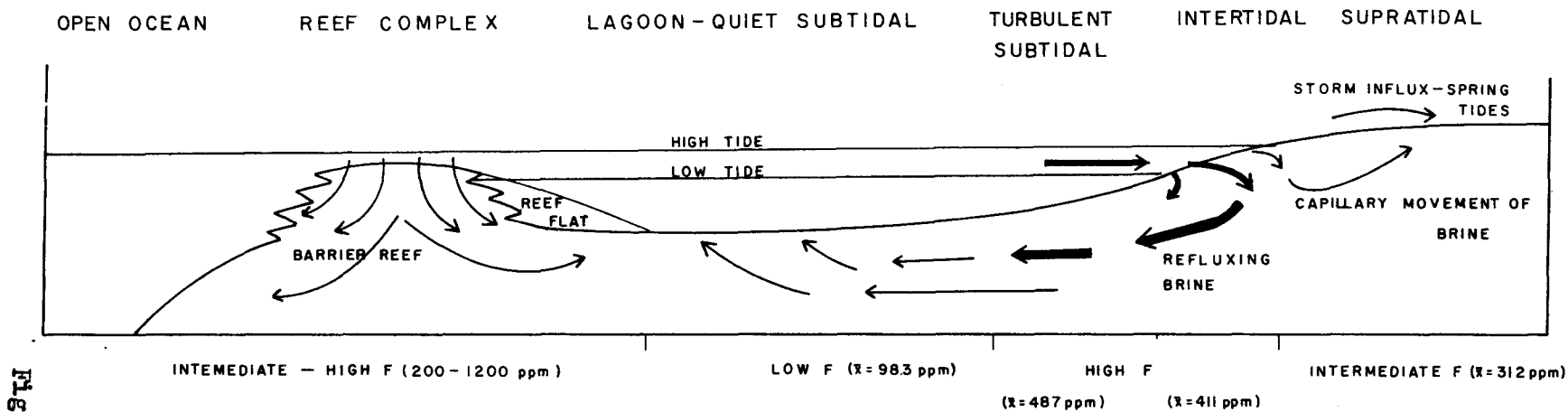


Fig. 21

SCHEMATIC RELATIONSHIP BETWEEN REFLEXING BRINES, FLUORINE DISTRIBUTION, AND DEPOSITIONAL ENVIRONMENT

low F contents in the supratidal zone are the result of two factors.

1) The F would be removed from the brine in the high intertidal - low supratidal zone. This is verified by the high F in the high intertidal samples and a generally high F at the transitional boundary of the intertidal - supratidal zones. 2) There would also be a smaller volume of brine moved by capillary action through the supratidal zone.

The occurrence of significant quantities of anhydrite in the supratidal carbonates may result in a simple dilution effect. Three supratidal anhydrites were analyzed for F (Table 26). Massive anhydrite and anhydrite crystals contained 14.8 ppm and 10.0 ppm F respectively while the replacement anhydrite, containing 20% dolomite, contained 90 ppm F. If the anhydrite in the supratidal sediments is displacement in origin (added without removing any carbonate), a dilution effect would result. However, if the dolomite is replaced by anhydrite, no dilution would result. Textural evidence suggests a replacement origin for most of the anhydrite in the Zama member (Geological staff, Gulf Oil Canada, Research Lab., Calgary, personal communication). The lack of correlation between the anhydrite content and F content in the supratidal dolomites from the Zama member further indicates that the formation of anhydrite does not affect the F distribution.

Dolomitization of the lagoonal or quiet subtidal carbonates must be the result of brines undersaturated with respect to CaF_2 . The F depleted brines refluxing through the supratidal and intertidal zones are the most likely solutions.

The distribution of F within the barrier reef complex was also investigated. Dolomites from the reef complex are divided into the reef

TABLE 26

F in Supratidal Sulfates

Well	Location	Age	Formation	Sample	Mineralogy	F (ppm)
B.A. Zama North	6-33-117-JMS	M. Devonian	Maskeg Fm. Zama member	S-A-4795	Ay (20% D)	94.0
				S-A-5005	Ay	14.8
				S-A-5095	Ay	10.0

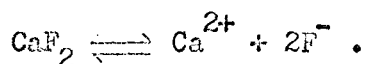
Descriptions of Samples -

- S-A-4795 Anhydrite replacing dolomite. Large porphyroblastic masses $\frac{1}{2}$ - 2 inches in diameter.
- S-A-5005 Secondary anhydrite. Massive, occurring in 2 inch veins.
- S-A-5095 Secondary anhydrite. Occurs in large crystals up to 3 cm long.

framework and reef flat (back reef debris). The reef flat debris has an average of 642 ppm F compared to an average of 427 ppm F in the reef framework dolomites. The distribution of F in the reef may be the result of two mechanisms. 1) Brines refluxing through the reef may be responsible for the distribution of F. Newell et al. (1953) suggested that the dolomitization of the Permian Reef Complex occurred by brines refluxing through the reef. 2) Corals, which contribute significant quantities of carbonate material to the reef, concentrate F. The major reef builders and binding agents in reef formation are algae. An analysis of the calcareous portion of the Recent algae, Halimeda sp. from the Bahamas, yielded a value of 1500 ppm F. Concentrations of F in the reef material could be the result of F concentration by shelled organisms and algae.

A stratigraphic correlation between the four wells was made on the basis of the F distributions in the cores. The interpretations shown in Fig. 20 agree in all major aspects with the original correlations based on petrologic data (Fig. 16).

The distribution of F in the Zama member dolomites is proposed to be the result of precipitation of CaF_2 during the refluxing of concentrated sea water through marine carbonate sediments. Fluorite is one of the least soluble fluorine compounds. Its solubility in water is represented by the expression:



The ionic solubility product of CaF_2 in a saturated solution is:

$$K_{sp} = \gamma_{\text{Ca}^{2+}} [\text{Ca}^{2+}] \gamma_{\text{F}^-}^2 [\text{F}^-]^2 \quad (\text{Butler, 1964}).$$

The solubility products of CaF_2 in sea water, concentrated brines, hydrothermal waters, and ground waters were calculated (25°C) (Table 27). The calculations have taken into account the ionic strength of the solutions and the common ion effect for Ca^{2+} . In the case of concentrated brines, Mg^{2+} complexing has been considered. The following have not been taken into account:

- 1) Reactions of cations and anions with water to produce hydroxide complexes and protonated species. As anion hydrolysis is more severe in acid solutions, it can be neglected here because the pH of the solutions is between 7 and 9. However, cation hydrolysis is more extensive in basic solutions. Both factors tend to increase the solubility of CaF_2 (Butler, 1964).
- 2) The activity of CaF_2 has been assumed to be 1. If the CaF_2 is in solid solution in CaCO_3 , the activity of CaF_2 would be equal to its mole fraction (X_{CaF_2}) times its activity coefficient (γ_{CaF_2}), or

$$A_{\text{CaF}_2} = X_{\text{CaF}_2} \times \gamma_{\text{CaF}_2} \quad (\text{Garrels and Christ, 1965}).$$
 For simplicity, it has been assumed that there is no solid solution of CaF_2 in CaCO_3 .

Single ion activity coefficients have been calculated using the Davies equation of the form:

$$-\log \gamma_{\pm} = A z^2 \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.21 \right]$$

where $A = 0.5085$

z = the charge of the ion

I = the ionic strength of the solution.

The ionic strength of sea water (0.72) and the activity coefficient

of Ca^{2+} in sea water (0.28) were taken from Garrels and Christ (1965). The ionic strength of the other solutions were determined from the linear relationship of conductance vs ionic strength and from the equation

$$I = \frac{1}{2} \sum c_i z_i^2$$

where c_i = the concentration of the ion in m/l

z_i = the charge on the ion.

The results of the calculations are shown in Table 27. Sea water and ground waters are undersaturated with respect to CaF_2 . The undersaturation of sea water with respect to CaF_2 is in agreement with Kramer's calculations (1965) and explains the low F content of limestones.

The calculations also verify the precipitation of CaF_2 from sea water concentrated two-fold. This is in accord with the sequence of reactions presented by Borchert and Muir (1964) for the concentration of sea water as shown below.

Concentration Factor	Precipitates	Dissolves
2 - 3 fold	CaF_2	
3 - 5 fold	MgF_2	CaF_2
over 6 fold	CaF_2	MgF_2

A. V. Kazakov (1950) investigated methods of precipitation of excess F in the system $\text{CaO-P}_2\text{O}_5\text{-F-H}_2\text{O}$. His experiments indicated that after the F content in the lattice of phosphate had reached the content of fluorapatite, F continues to precipitate as CaF_2 .

Rhyzhenko (1965) has shown that CaF_2 will precipitate and replace

TABLE 27

Solubility Products of CaF_2 in Various Aqueous Media

Medium	Ca (m/l)*	F (m/l)*	$\gamma_{\text{Ca}^{2+}}$	γ_{F^-}	I	K_{sp}	
Sea Water	1.0×10^{-2}	0.71×10^{-4}	0.28	0.79	0.72	2.16×10^{-11}	(1)
						6.10×10^{-12}	(2)
Sea Water (2x) **	2.0×10^{-2}	0.14×10^{-3}	0.22	0.68	1.44	6.80×10^{-11}	
Brines	17.6×10^{-3}	0.14×10^{-3}	0.45	0.82	0.34	7.45×10^{-10}	
Hydrothermal Waters	3.3×10^{-3}	0.29×10^{-3}	0.88	0.97	0.098	8.12×10^{-10}	
Ground Waters from limestone and dolomite terrains	1.7×10^{-3}	0.02×10^{-3}	1.00	1.00	0.008	3.10×10^{-11}	

(1) - no correction for MgF^+ .

(2) - $\text{MgF}^+ = 50\%$.

* - data from White et al. (1963).

** - assume 50% of the F^- is complexed as MgF^+ (Sillen, 1961).

CaCO_3 in weakly acid to alkaline solutions, the critical factor being the ratio of $[\text{F}^-]^2 / [\text{CO}_3^{2-}]$. Increase in the pH of the refluxing brines would result in a higher content of F^- and a lower content of CO_3^{2-} , favoring the precipitation of CaF_2 . Friedman (1968) reports pH values in excess of 8.0 in the waters associated with Recent dolomites in the Gulf of Aqaba.

The geological evidence presented here and the experimental results of other workers indicate that the precipitation of CaF_2 from refluxing brines is the mechanism responsible for the distribution of F in dolomites.

Suggestions for Further Research

If we are to fully explain the halogen distributions found in the geologic record in terms of natural processes which have taken place, and are still taking place, we must have a thorough knowledge of the chemistry of the halogens and the effects to be expected from various natural processes. In order to predict the effects of natural processes on halogen abundances and mobilities, we must first understand the physics and chemistry of these processes.

The present study on the distributions of the halogens in sedimentary carbonates and the processes bringing about these distributions has clearly demonstrated several "knowledge gaps" which need to be clarified. Some of the more obvious areas of weakness are:

- 1) The chemistry of the "refluxing brines" is vague and needs to be quantified in terms of chemical compositions and their changes within the framework of the model. Mineral-water reactions controlling the

distributions of specific minerals and elements can only be guessed at until we understand the detailed changes in brine composition in the system under consideration. A detailed and thorough investigation of the halogen composition of the brines in areas of Recent dolomite formation needs to be carried out.

- 2) Dolomites formed by post-lithification processes should be analyzed for F to complete our understanding of the distribution of F in dolomites. This would be an invaluable aid in working out the genesis of other ancient dolomites.
- 3) A more detailed investigation of the relationship of the F distribution to penecontemporaneous dolomite formation would strengthen the conclusions reached in the present study. It would also be instructive to determine the F distributions in undolomitized analogs of the Zama dolomites.
- 4) The use of trace elements as environmental indicators in limestones has been suggested by Chester (1965) and Cameron (1968). However, the use of chemical environmental indicators in dolomitized carbonates has not been suggested or previously attempted. The present study of F and an investigation of other selected trace elements by the author has shown that diagenetic processes can leave characteristic element distributions which indirectly reflect the original environment of deposition. These characteristic element distributions are the result of secondary inorganic processes controlled by the geomorphology of the system, physical properties of the sediments, permeability, porosity, and the presence of thin impermeable shale layers. These are primary features of the depositional basin.

If the original characteristic trace element distributions are completely lost during diagenesis, the secondary distributions may be just as useful in reflecting the depositional environment. Detailed investigations of other trace elements in dolomitized carbonates are needed to determine their use as indirect environmental indicators.

It must be emphasized that a knowledge of the physical processes involved is essential. Unfortunately, these are very seldom known.

CONCLUSIONS

The Cl/Br ratio of the water soluble and acid soluble phases of marine carbonates show a progressive increase from pre-Cambrian time (2×10^9 years) to Recent. The relationship of the Cl/Br ratio of the carbonates to the Cl/Br ratio of ocean water has remained constant for the past 2×10^9 years. This relationship holds true for limestones and dolomites, and is of the form:

$$R_{ot} = R_{rt} / K$$

where R_{ot} = the Cl/Br ratio of the ocean at time t

R_{rt} = the Cl/Br ratio of the carbonate at time t

$$K = 0.27.$$

From the above expression it is possible to estimate the Cl/Br ratio of ancient oceans. A change in the Cl/Br ratio of the oceans from 58/1 in the pre-Cambrian to 270/1 in the Recent oceans is calculated to have occurred, which is close to the predicted change from 60/1 (pre-Cambrian) to the present value of 292/1.

The fractionation of Cl and Br throughout geologic time can be explained by Br removal within the sedimentary cycle if crustal recycling is considered. The yearly Br budget in the ocean indicates that Br is not, and could not have been, in dynamic equilibrium with the ocean over the past 2×10^9 years.

Marine shelled organisms fractionate Cl and Br, and corals and algae concentrate F. Fresh water shelled organisms concentrate F, Cl, and Br and fractionate Cl and Br relative to fresh water. The effects

of shelled organisms on long term fractionations of Cl and Br are small because of the small mass of skeletal material. The role of marine organisms in fractionating Cl and Br throughout geologic time is small, but may be important in biogenic carbonate deposits.

Diagenesis of carbonate rocks results in the following changes in F, Cl, and Br contents:

Alteration from aragonite to calcite:

- 1) The Cl_W and Br_W contents decrease.
- 2) Aragonites contain approximately 1200 ppm Cl and 30 - 40 ppm Br in lattice sites compared to 80 - 100 ppm Cl and 8 - 15 ppm Br in calcite and dolomite lattices.
- 3) During alteration of aragonite skeletal material to calcite, Cl is preferentially removed relative to Br due to the presence of Cl in the shell in a more soluble phase. The original Cl and Br contents are retained until the shell material alters. There are no significant changes in the F content with alteration of the shells.
- 4) The F content of 1500 ppm in aragonite sediments decreases to 90 ppm in calcites.

Alteration from limestone to dolomite:

- 1) There is essentially no difference in the Cl content in limestones and dolomites. The same is true for Br.
- 2) The average F content of limestones is 90 ppm with a small variance; whereas, the average F content of dolomites is 370 ppm with a high variance. The variability of the F distribution in dolomites is explained by the two inorganic mechanisms of refluxing brines and precipitation of CaF_2 . The CaF_2 is preferentially precipitated in

certain environments depending on the chemistry of the refluxing brine. The F distributions have been shown to be characteristic of these environments. It is possible to determine the environment of deposition of the carbonate on the basis of the F content in the dolomite.

Alteration to marbles:

- 1) There is an apparent loss of F during diagenesis of carbonates to marbles.
- 2) The Cl and Br contents of the marbles are not significantly different from their respective abundances in limestones and dolomites. This point is significant in the chemical mass balance for the assumption of no loss of C and Br during metamorphism of sediments.

The F in the carbonates is believed to be in the form of CaF_2 as a separate phase and not as a solid solution substitution of CaF_2 in CaCO_3 . Calculations have shown that solid solution of CaF_2 in CaCO_3 would be very non-ideal. It has also been shown that clay minerals and CO_2 -F-apatite do not control the F distribution in the carbonates.

The Cl and Br are present in the carbonates largely in the form of intergranular salts and fluid inclusions. However, the Cl is more water soluble than the Br.

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APPENDIX I

SAMPLE DESCRIPTIONS

Note:

Ar = Aragonite

C = Calcite

D = Dolomite

Ay = Anhydrite

Shells of Recent Calcareous Marine Organisms

Sample	Species	Location	Mineralogy
CORALS			
*S-4	<u>Acropora cervicornis</u>	British Honduras	Ar
S-3	<u>Acropora palmata</u>	Florida	Ar
*M-1	<u>Montastrea annularis</u>	Bermuda-Florida	Ar
*M-2	<u>Porites</u> (sp. ?)	Bermuda-Florida	Ar ≈ C
*M-3	<u>Siderastrea sidera</u>	Bermuda-Florida	Ar
*M-5	<u>Millepora alcicornis</u>	Bermuda-Florida	C
MOLLUSCS			
Pelecypods			
**S-5	<u>Rangia cuneata</u>	Gulf Coast	Ar
**S-8	<u>Atrina serrata</u>	Gulf Coast	C(10% Ar)
**S-2	<u>Crassostrea virginica</u>	Atlantic Coast	C
50	<u>Crepidula fornicata</u>	Texas	Ar
51	<u>Crassostrea virginica</u>	Texas	C
52	<u>Arca incongrua</u>	Texas	Ar
Gastropods			
**S-1	<u>Conus millipunctus</u>	Atlantic Coast	Ar
S-6	<u>Strombus gigas</u>	Atlantic Coast	Ar
Cephalapods			
**S-7	<u>Nautilus pompilius</u>	Atlantic Coast	Ar
ALGAE			
	*** <u>Halimeda</u>	Bahamas	Ar

All species collected alive unless otherwise noted.

* - collected dead.

** - not known if living or dead when collected.

*** - this sample contained 13.9% insoluble residue.

Shells of Recent Calcareous Fresh Water Organisms

Sample	Species	Location	Mineralogy
MOLLUSCS-Pelecypods			
1NC-2a	<u>Nitocris carinata</u>	Chenango R., N.Y.	Ar
9NC-3	<u>Nitocris carinata</u>	Chenango R., N.Y.	Ar
10NC-2c	<u>Nitocris carinata</u>	Chenango R., N.Y.	Ar
11NC-1	<u>Nitocris carinata</u>	Chenango R., N.Y.	Ar
NC-2b	<u>Nitocris carinata</u>	Chenango R., N.Y.	Ar
2AC#1	<u>Andonta cataracta</u> (9.0-9.4)	Seneca Lake, N.Y.	Ar
3AC#3	<u>Andonta cataracta</u> (8.0-8.5)	Seneca Lake, N.Y.	Ar
7AC#7	<u>Andonta cataracta</u> (6.0-6.5)	Seneca Lake, N.Y.	Ar
8AC#4	<u>Andonta cataracta</u> (7.5-8.0)	Seneca Lake, N.Y.	Ar
AC#6	<u>Andonta cataracta</u>	Seneca Lake, N.Y.	Ar
5EC-4	<u>Elliptio complanatus</u> (6.5-7.0)	Seneca Lake, N.Y.	Ar
6EC-1	<u>Elliptio complanatus</u> (5.0-5.5)	Seneca Lake, N.Y.	Ar
12EC-6	<u>Elliptio complanatus</u> (7.5-8.0)	Seneca Lake, N.Y.	Ar
13EC-8	<u>Elliptio complanatus</u> (8.5-9.0)	Seneca Lake, N.Y.	Ar
EC-2	<u>Elliptio complanatus</u>	Seneca Lake, N.Y.	Ar
EC-3	<u>Elliptio complanatus</u>	Seneca Lake, N.Y.	Ar
EC-5	<u>Elliptio complanatus</u>	Seneca Lake, N.Y.	Ar
EC-7	<u>Elliptio complanatus</u>	Seneca Lake, N.Y.	Ar
GL-2	<u>Goniobasis liviscons</u> (med.)	Green Lake, N.Y.	Ar
#13GL-3	<u>Goniobasis liviscons</u> (small)	Green Lake, N.Y.	Ar
AT-5	<u>Lampsilis radiata</u>	Seneca Lake, N.Y.	Ar

Numbers in brackets refer to length (cm.) of shell
 All species collected alive.



Recent Carbonates

Sample	Location	Age	Mineralogy	Description	% Insoluble Residue
A217.1	Western tip of Andros Island, Bahamas	Recent*	C=D	High intertidal	0.0
B5.2	Inagua Island, Bahamas	Recent	C≈D Ar (tr.)	Dolomite crust	0.0
R-1	Bahamas	Recent	Ar	Oolite sand	0.2
R-2	Bahamas	Recent	C(30% Ar)	Foraminiferal sand, skeletal	0.7
R-3	Bahamas	Recent	C(5% Ar)	Carbonate mud. Shallow subtidal	6.8

*-0-60 years by C¹⁴ dating (Shinn et al., 1965).

Recent-Pleistocene Calcareous Marine Pelecypods

Sample	Species	Age	Formation	Location	Mineralogy
U-94	Spondylus sp.	Fleistocene	Belemont	Bermuda Gov't. Quarry	C
T-1	Spondylus sp.	Recent**		Harrington Sound, Bermuda	Ar
U-48	Cittarium pica	Fleistocene	Devonshire	Fort Devonshire, Bermuda	Ar >> C
*U-133	Cittarium pica	Recent***		Bailey's Bay, Bermuda	Ar
PR-2	Cittarium pica	Recent**		Puerto Rico	Ar >> C

*-poor sample - secondary calcite crust and leach pits.

**-collected alive.

***- > 200 years.

Cretaceous Pelecypod

Sample	Species	Age	Formation	Location	Mineralogy
*	Cretaceous Oyster	Cretaceous	Belly River	Banff, Alberta	C

*-this sample contained 1.7% insoluble residue.

Fleistocene Carbonates

Sample	Location	Formation	Age	Mineralogy	% Insoluble Residue
PP-68	?	?	Fleisto-Pliocene	D	1.0
P-1	Florida	Miami	Fleistocene	C	0.7
P-2	Florida	Miami	Fleistocene	C (minor Ar)	13.8
P-3	Florida	Miami	Fleistocene	D >> C	0.2

Miocene Carbonates

Sample*	Location	Age	Mineralogy	Description**	% Insoluble Residue
R-36-46	Midway Atoll	Post-miocene	55% Mg-C 45% Ar	Unlithified sediment	0.2
R-150	Midway Atoll	Post-miocene	50% C, 45% Ar 5% Mg-C	Unlithified sediment	3.3
R-219	Midway Atoll	Post-miocene	100% C	Partially leached and recrystallized	1.3
R-409	Midway Atoll	Post-miocene	100% C	Partially leached and recrystallized	1.1
R-425	Midway Atoll	Upper Miocene	100% D	Leached and recrystallized dolomite	3.5
R-474	Midway Atoll	Upper Miocene	100% D	Leached and recrystallized dolomite	3.9

*-numbers in sample code refer to core depths.

** - see Ladd et al. (1967) for a detailed description.

Cretaceous Carbonates

Sample	Location	Age	Formation	Mineralogy	% Insoluble Residue
SH-IV-4-B	Fredricksburg, Pa.	L. Cretaceous	Edwards	D	11.0
BR-II-3-A	Fredricksburg, Pa.	L. Cretaceous	Edwards	D	9.0
LB-II-4-A	Fredricksburg, Pa.	L. Cretaceous	Edwards	C	2.1
S-I-13-B	Fredricksburg, Pa.	L. Cretaceous	Edwards	C	1.5
BR-II-1-E	Fredricksburg, Pa.	L. Cretaceous	Edwards	C	3.6
CR-I-18-A	Fredricksburg, Pa.	L. Cretaceous	Edwards	C	1.7
MR-III-19-A	Fredricksburg, Pa.	L. Cretaceous	Edwards	C	2.8
SH-V-12-A	Fredricksburg, Pa.	L. Cretaceous	Edwards	C (minor D)	4.2
AR-I-2-A	Fredricksburg, Pa.	L. Cretaceous	Edwards	C	2.0
CR-I-24-A	Fredricksburg, Pa.	L. Cretaceous	Edwards	C	1.1
MR-III-16-A	Fredricksburg, Pa.	L. Cretaceous	Edwards	C	1.7
AR-I-5-B	Fredricksburg, Pa.	L. Cretaceous	Edwards	C	2.2

Note - all samples are from outcrop.

- see following page for description of depositional environment of these samples.

Environmental Interpretation of Cretaceous Carbonates

Sample	Description
SH-IV-4-B	Tidal flat dolomite.
BR-II-3-A	Possibly replacement dolomite in tidal flat or shoal area.
LB-II-4-A	Barrier trend. Good currents. Possible barrier flank.
S-I-13-B	High energy - barrier, possibly beach or bar shoal area.
BR-II-1-E	High energy, good currents, possible channel or break in shoal area. Nose of migrating bar.
CR-I-18-A	Quiet water, muddy lime bottom. Lagoonal environment.
MR-III-19-A *	Bedded dolomite? - replacement or diagenetic. Lagoonal area.
SH-V-12-A	Rudist "mound" - biohermal - deeper, quieter water relative to barrier. Lagoonal environment.
AR-I-2-A	Local shoal area in lagoonal environment. Possible tongue of barrier extending into lagoonal area.
CR-I-24-A	Moderate energy currents on seaward side of barrier.
MR-III-16-A	Shallow area around rudist mound. Possible thin tongue from barrier extending into lagoonal area.
AR-I-5-B	Rudist, oyster, biostrome. Lagoonal area, possibly intermediate area between "mounds".

* X-ray analysis indicated only calcite in the sample analyzed.

Triassic Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
Imperial Pan-Am Boundary	16-15-85-13W5	4606-10	Halfway	Triassic	Ay >> D	31.9
		4611-15			D	26.4
		4616-20			D	14.1
		4621-25			D(<10% Ay)	13.9
		4626-30			C(30% Ay)	7.2
		4631-35			C	4.0
Pan-Am IOE A-1 Willow	6-27-86-13W6	4031-32	Baldonnel		D	13.7
		4036-37			D	12.1
		4038-39			C(1% D)	3.0
		4040-41			C(1% D)	3.4
		4042-43			C	4.7
Imperial Pan-Am Bdylks	8-4-84-13W6	4444	Charlie Lake		C(5%D, 10%Ay)	5.3
		4450			C(20%D, 25%Ay)	7.1
Imperial Pan-Am Bdylks	10-20-82-12W6	4409			C	1.5
		* 4411			C(<10% D)	5.2
		4437			C=D=Ay	6.9

*-fossiliferous.

Mississippian Carbonates

Well	Location	Sample	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
Secony Granum	1-25-11-26-4	AC-7	7070-7090	Rundle	Mississippian	D ≈ C	1.5
		AC-23	7091-7100			D >> C	6.0
		AC-6	7101-7130			D >> C	3.1
		AC-18	7650-7675	Banff		D ≈ C	33.7
Pan-Am A-1 Whiskey Creek	13-17-21-4-5	AC-24	11197-11202	Turner Valley		D	5.1
		AC-17	11210-11215			D	8.0
		AC-13	11230-11235			D	2.1
		AC-14	11245-11250			D	4.0
		AC-26	11275-11280			D	1.3
		AC-20	11290-11316			D	1.7

Devonian Carbonates

Well	Location	Sample	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
Imperial Gibbons	2-16-56-22-4	AC-16	3225-3230	Wabamum	U. Devonian	D	18.1
Imperial Eastgate	1-22-57-22-4	AC-1	3693-3708	Ireton		C	0.4
		AC-10	3709-3724	Leduc		C	1.4
		AC-21	4526-4550	Cooking Lake		C	30.6
		AC-11	4551-4576			C	26.1
		AC-15	4727-4735	Beaverhill Lake		C	0.0
		AC-2	4736-4745			C	12.7
Banff Mobil Rainbow West	4-15-109-8-6	AC-12	5791-5805	Keg River	M. Devonian	D	32.6
		AC-4	5806-5820			D	10.0
		AC-3	5821-5838			D	10.0

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
B.A. Zama North	12-21-117-4W6	4725	Muskeg Fm. Zama member	M. Devonian	D	3.5
		4726			D	3.8
X-92		4727			D	1.7
		4728			D	4.6
		4729			D	2.5
		4730			D	1.0
		4731			D	2.5
		4732			D	2.1
		4733			D	1.4
		4734			D	1.3
		4735			D	4.5
		4736			D	2.2
		4737			D	2.6
		4738			D	5.8
		4739			D	2.6

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
X-92		4740	Muskeg Fm. Zama member	M. Devonian	D	2.2
		4741			D	4.9
		4765		D	2.2	
		4766		D	0.3	
		4768		D (7% Ay)	0.2	
		4769		D	0.6	
		4770		D	0.6	
		4771		D (3% Ay)	0.3	
		4772		D	0.4	
		4773		D	1.5	
		4774		D	0.1	
		4775		D	0.3	
		4776		D	0.5	
		4777		D	0.8	
		4778		D (3% Ay)	0.8	

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
X-92		4779	Muskeg Fm. Zema member	M. Devonian	D (8% Ay)	1.9
		4780			D (8% Ay)	0.5
		4781	D		0.4	
		4782	D		0.5	
		4783	D		0.3	
		4784	D (7% Ay)		1.0	
		4785	D (19% Ay)		2.3	
		4791	D (37% Ay)		1.6	
		4792	D (4% Ay)		0.9	
		4793	D		2.6	
		4794	D		1.6	
		4795	D		0.0	
		4796	D		0.2	

Note - Intervals 4725-4732 and 4791-4793 - Barrier reef framework.
 Intervals 4733-4741, 4768-4785, and 4794-4796 - Back reef debris (reef flat).
 Interval 4765-4766 - Patch reef material.

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
B.A. Zama North X-91	4-3-11-118-4W6	4782-4785	Upper Keg River	M. Devonian	D	6.5
		4786-4790			D	5.5
		4796-4805			D	2.1
		4806-4816			D	13.9
		4817-4826			D	2.6
		4827-4830			D	1.6
		4831-4835			D	12.6
		4836-4840			D	18.2
		4841-4845			D	17.5
		4846-4850			D	9.7
		4851-4860			D (10% Ay)	14.3
		4861-4865			Ay > D	17.9
		4866-4870			D = Ay	17.4
		4871-4880			D (10% Ay)	8.9
		4881-4885			D = Ay	9.6
4886-4890	D >> Ay	1.7				

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
X-91		4891-4895	Upper Keg River	M. Devonian	D >> Ay	2.8
		4896-4900			D = Ay	4.1
		4901-4905			D >> Ay	1.2
		4906-4910			D (10% Ay)	2.0
		4911-4917			D (10% Ay)	1.2
		4918-4924			D (10% Ay)	2.1
		4925-4929			D	2.1
		4930-4934			D	6.3
		4935-4939			D	1.1
B.A. Zama North	2-4-118-4N6	4801-4809	Upper Keg River	M. Devonian	D (10% Ay)	5.2
		4822-4826			D (tr. Ay)	10.3
X-94		4827-4831			D (tr. Ay)	2.0
		4832-4836			D (tr. Ay)	1.3
		4837-4841			D (tr. Ay)	1.2
		4842-4846			D (tr. Ay)	4.1

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
X-94		4847-4851	Upper Keg River	M. Devonian	D (tr. Ay)	1.7
		4852-4856			D (tr. Ay)	1.9
		4857-4861			D (tr. Ay)	3.2
		4867-4871			D (tr. Ay)	3.1
		4872-4876			D (10% Ay)	2.0
		4877-4881			D	2.2
		4882-4886			D	1.9
		4887-4891			D	1.4
B.A. Zama North	12-22-117-4W6	4671-4675	Upper Keg River	M. Devonian	D (10% Ay)	3.9
		4676-4680			D Ay	3.2
X-95		4681-4685			D (10% Ay)	3.7
		4686-4690			D (10% Ay)	1.5
		4691-4695			D	4.2
		4696-4700			D	0.6
		4701-4705			D	1.6

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
X-95		4706-4710	Upper Keg River	M. Devonian	D	0.5
		4711-4715			D	0.5
		4716-4720			D	0.3
		4721-4725			D	0.4
		4726-4730			D	0.5
		4731-4735			D (10% Ay)	1.2
		4736-4740			D	0.7
		4741-4745			D	0.6
		4746-4750			D	0.9
		4753-4759			D	0.9
		4760-4764			D	1.3
		4765-4769			D	0.6
		4770-4774			D	1.6
B.A. Zama North	9-5-114-8W6	4869-4873	Upper Keg River	M. Devonian	C	3.2
		4874-4878			C	4.5
X-97						

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
X-97		4884-4888	Upper Keg River	M. Devonian	D	4.7
		4889-4893			D	2.5
		4894-4898			D (tr. C)	2.6
		4899-4903			D (tr. C)	2.1
		4904-4908			D	2.3
		4909-4913			D	1.1
		4914-4918			D	3.1
		4919-4923			D	1.3
		4924-4928			D	1.6
		5513-5518			D = Ay	14.3
		5521-5525			D = Ay	11.2
		5526-5531			D = Ay	19.1
		5532-5536			D = Ay	20.7
		5537-5541			D = Ay	15.5
	5542-5546	D = Ay	17.4			

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
X-97		5547-5551	Upper Keg River	M. Devonian	Ay > D	25.6
		5552-5556			Ay > D	15.6
		5557-5561			Ay = D	27.1
		5562-5567			Ay > D	4.4
		5568-5572			Ay > D	2.6
B.A. Zama North	13-27-117-4W6	4318-4320	Muskeg	M. Devonian	C = D = Ay	20.3
		4321-4325			C = Ay	24.4
X-98		4326-4330			C	17.1
		4331-4335			C	30.8
		4336-4340			C	8.6
		4341-4345			C	19.0
		4346-4350			C	7.8
		4351-4355			C (10% D)	4.5
		4356-4360			C = D	0.1
		4361-4365			C	1.3

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
X-98		4366-4371	Muskeg	M. Devonian	C	0.9
		4372-4376			D >> C	1.5
		4377-4381			D > C	1.6
		4382-4386			D (<5% Ay)	3.0
		4387-4391			D (<5% Ay)	1.3
		4392-4396			D	0.8
		4397-4401			D (<5% Ay)	0.9
		4402-4406			D	0.8
		4407-4411			D	0.8
		4412-4416			D	4.3
		4417-4421			D	1.6
		4422-4426			D	3.1
		4427-4432			D	3.0
		4728-4737			Upper Keg River	M. Devonian
		4743-4747			D	3.7

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
X-98		4748-4752	Upper Keg River	M. Devonian	D	4.2
		4753-4757			D	1.3
		4758-4762			D	2.3
		4763-4767			D	1.5
		4768-4772			D	1.7
		4773-4777			D (<5% Ay)	2.8
		4778-4782			D	0.7
		4783-4787			D (<5% Ay)	2.3
		4788-4792			D (10% Ay)	2.4
		4793-4798			D	1.2
B.A. Zama North	16-19-116-445	4761-4766	Muskeg Fm. Zama member	M. Devonian	D = Ay	12.0
		4768-4771			Ay > D	19.9
X-99		4772-4776			Ay > D	25.1
		4777-4781			Ay > D	28.0
		4782-4786			D > Ay	3.3

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
X-99		4787-4791	Muskeg Fm. Zama member	M. Devonian	D = Ay	6.1
		4792-4796			D (<5% Ay)	3.8
		4797-4801			D	1.8
		4802-4806			D (<5% Ay)	5.1
		4807-4811			D	2.9
		4817-4821			D	3.2
		4822-4826			D (<5% Ay)	2.4
		4827-4831			D	0.7
		4832-4836			D	0.8
		4837-4841			D	2.1
		4842-4846			D	1.2
		4847-4851			D	2.4
		4852-4856			D	3.2
		4857-4861			D = Ay	25.8
	4862-4866	Ay >> D	20.6			

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
B.A. Zama North X-100	4-19-116-4W5	4840-4844	Muskeg Fm. Zama member	M. Devonian	Ay > D	23.1
		4845-4849			Ay >> D	19.1
		4850-4854			Ay >> D	24.7
		4855-4859			D = Ay	6.8
		4860-4864			D = Ay	20.1
		4865-4869			D (10% Ay)	1.9
		4870-4874			D (<5% Ay)	2.6
		4875-4879			D = Ay	3.8
		4880-4884			D > Ay	4.8
		4885-4889			D (<5% Ay)	3.1
		4890-4894			D (<5% Ay)	2.8
		4895-4899			D	5.5
		4900-4904			D	5.5
		4905-4909			D (10% Ay)	2.8
		4910-4914			D (<5% Ay)	1.7
4915-4919	D (<5% Ay)	1.3				

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
X-100		4920-4924	Muskeg Fm. Zama member	M. Devonian	D (<5% Ay)	4.8
		4925-4929			D	0.9
		4930-4934			D	1.1
		4935-4939			D	1.6
		4940-4944			D (10% Ay)	4.7
		4945-4949			Ay >> D	28.8
		4950-4951			Ay >> D	21.7
B.A. Zama North	5-30-116-446	4770-4774	Muskeg Fm. Zama member	M. Devonian	Ay >> D	29.7
		4975-4979			Ay = D	11.1
X-101		4980-4984			D >> Ay	2.4
		4985-4989			Ay >> D	16.9
		4990-4994			D (10% Ay)	2.4
		4995-4999			D	0.6
		5000-5004			D	5.7
		5005-5009			D (<5% Ay)	3.3

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
X-101		5010-5014	Muskeg Fm. Zama member	M. Devonian	D	1.6
		5015-5019			D	2.7
		5020-5024			C (>10% D)	1.0
		5025-5029			C = D	6.8
		5030-5034			D	2.2
		5035-5039			Ay = D	15.2
		5040-5044			Ay >> D	34.1
		5045-5049			Ay >> D	14.0
		5050-5051			Ay >> D	28.7
B.A. Zama North	2-25-117-5W5	4922	Muskeg Fm. Zama member	M. Devonian	D	5.2
		4923			D	5.6
		4924-4925			D	0.8
		4926-4930			D	9.2
		4931-4935			D (10% Ay)	0.9
		4936-4940			D	1.3
X-114						

Devonian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
X-114		4941-4945	Muskog Fm. Zama member	M. Devonian	D	1.4
		4946-4950			D = Ay	1.5
		4951-4955			Ay >> D	34.1
		4956-4960			D = Ay	22.7
		5095-5099	Keg River	M. Devonian	C	0.4
		5100-5104			C	0.6
		5105-5109			C	0.3
		5110-5114			C	0.3
		5115-5119			C	0.0
		5120-5124			C	0.1
		5126-5129			C	2.0
		5130-5134			C	1.4
		5135-5139			C (D+Ay=5%)	1.4
		5140-5144			C	0.0
		5145-5150			C (tr. D)	0.0

Silurian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
B.A. Taylorton	1-8-2-6W2	8734-8739	Interlake Group	U. Silurian	D (tr. Ay)	2.5
		8754-8759			D	4.2
		8766-8769			D	1.4
		8801-8804			D	6.9
		8811-8815			D	5.9
		8820-8825			D	7.2
		8826-8829			D	3.8
Imperial Hummingbird	6-13-2-19W2	9121-9123	Interlake Group	M. Silurian	D	2.2
		9129-9131			D	0.5
		9135-9137			D	1.0
		9139-9141			D	1.5
		9147-9149			D	1.5
		9152-9153			D	0.7
		9157-9159			D	2.9
		9163-9165			D	2.2

Silurian Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
Imperial Constance	8-26-3-4W2	8278-8279	Interlake Group	L. Silurian	D	0.9
		8293-8295			D	0.4
		8277-8278			D	1.3
		8267-8268			D	1.6
		8255-8257			D	10.6
		8286-8289			D	1.5
		8297-8299			D	1.2
Sample						
GB-5	Beaver Falls Grimsby, Ont.	Outcrop	Lockport Gasport member	L. Silurian	C (12% D)*	2.2
GB-6					D (20% C)*	2.9
GSY-6	Dundas, Ont.				D	6.1

*-crinoidal.

Ordovician Carbonates

Well	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
B.A. Can. Dev. Quinn	9-34-3-4W2	8563-8568	Upper Redriver	L.U.Ordovician	D	0.9
		8569-8573			D = C	1.4
		8579-8583			D (tr. Ay)	2.1
		8593-8597			Ay > C	9.2
		8607-8610			D	0.3
C.D.R. Scurry S. Lake Alma	1-14-1-117W2	10191-10195	Upper Redriver	L. U. Ordovician	C = D	3.2
		10211-10213			D	1.1
Sample						
L-72	Marion, Pa.	Outcrop	Row Park (St Paul Group)	M. Ordovician	C	2.1
L-77					C	0.8
L-78					C	1.9
L-79					C	1.8
L-272	Kaufman, Pa.	Outcrop	Newmarket (St Paul Group)	M. Ordovician	C	4.6
L-276					C	9.2
L-279					C	2.6
L-282					C	2.6

Ordovician Carbonates

Sample	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
L-202	Williamsburg, Pa.	Outcrop	Nittany Beckmantown Group	L. Ordovician	D	8.0
59-337					D	7.2
59-339					D	6.3
59-343					D	4.5

Cambrian Carbonates

Sample	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
59-1709	Henrietta, Blair Co. Pa.	Outcrop	Pleasant Hill	M. Cambrian	C	4.6
59-1728					C	3.8
59-1740					C	6.3

Pre-Cambrian Carbonates

Sample	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue				
p-CW#1	Waterton Lakes Alberta	Outcrop	Waterton	Pre-Cambrian (1000 m.y.)	D >> C	32.7				
p-CW#2					D = C	30.3				
p-CW#3					C >> D	15.5				
p-CW#4					C >> D	12.5				
p-CW#5					C (tr. D)	14.5				
p-CW#6					C (tr. D)	18.0				
p-CW#12					C >> D	20.6				
p-CW#13					C (tr. D)	10.5				
*p-CW#14					C	7.9				
p-C2A#8					Waterton Lakes Alberta	Outcrop	L. Altyn	Pre-Cambrian (1000 m.y.)	D	20.8
p-C2A#9									D	18.3
p-C2B#10									D	4.3
p-C2B#11									D	7.8

*-stromatolite.

Pre-Cambrian Carbonates

Sample	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
B-1	Cataract Falls Blind River, Ontario	Outcrop	Bruce Fm. Espanola Group (1700 m.y.)	Pre-Cambrian	C	51.1
B-2						58.4
B-3						50.8
E-3	Griffin Lake Espanola, Ont.	Outcrop	Espanola Fm. Espanola Group (1700 m.y.)	Pre-Cambrian	D	51.5
E-4						31.3

Pre-Cambrian Carbonates - D Series

Sample	Location	Core Interval	Formation	Age	Mineralogy	% Insoluble Residue
D-1	30 miles S.W. of Johannesburg, S. Africa	100	Transvaal System	Pre-Cambrian (1960 m.y.)	D	17.6
D-3		520				2.2
D-5		970				2.0
D-7		1480				2.1
D-9		1060				2.3
D-11		2500				2.1
D-13		3040				3.7

Pre-Cambrian Marbles

Sample	Location *	Age	Mineralogy	% Insoluble Residue	Description
T-68-0043	Thompson Mine	Pre-Cambrian	D	13.7	Crystalline marble
T68-0044	Pipe Mine		D (<5% C)	5.3	Vuggy marble
T68-0045	Klipper Lake		D (<5% C)	16.2	Very fine-grained marble
T68-0046	Thompson Mine area		D	19.2	Marble
T68-2802	Birchtree area		D	4.2	Marble
T68-2848	Birchtree Mine		D	4.7	Marble

Note - core samples, except samples T68-2802 and T68-2848 which are outcrop samples.

*-Thompson, Manitoba

APPENDIX II

ANALYTICAL RESULTS

Note:

All values in ppm unless otherwise indicated.

Cl/Br ratios expressed as weight ratios.

Recent Calcareous Marine Organisms

Sample	F _T	Cl _T	Br _T	Cl/Br _T	F _W	Cl _W	Br _W	Cl/Br _W	% P ₂ O ₅
M-1(a)*	725	8000	90.0	88.9	13.5	6250	68.8	90.8	0.00813
M-1(b)*	725	2600	75.0	34.7	17.0	3200	43.8	73.1	0.00513
M-1(c)*	675	1600	39.0	41.0	18.0	1300	21.0	61.9	0.00963
M-2	825	3900	85.0	45.9	17.5	3000	38.8	77.3	
M-3	725	5000	100	50.0	18.0	5000	55.0	90.9	0.00388
M-5	950	6500	178	36.6	12.0	6750	75.0	89.3	0.00225
S-1	5.0	380	13.0	29.3	3.0	175	6.8	25.7	
S-2	19.0	550	15.0	36.7	4.3	550	15.0	36.7	
S-3	1250	1250	26.5	47.2	29.5	475	14.0	33.9	0.00615
S-4	1000	300	8.5	35.3	46.3	100	3.3	30.3	
S-5	5.0	23	2.8	8.4	5.5	23	2.2	10.5	0.01163
S-6	5.0	625	16.5	37.9	4.1	350	8.8	39.8	
S-7	42.0	1800	60.0	30.0	6.9	1150	23.8	48.3	0.00513
S-8	12.5	485	13.0	37.3	3.1	250	12.5	20.0	0.00900
Halimeda	1511	135	0						
50	14.9	460	36.0	12.8	7.4	290	10.0	29.0	
51	21.5	820	38.0	21.6	6.5	820	19.5	42.1	
52	26.4	2680	75.0	35.7	9.4	1340	31.0	43.2	

* - all three samples from different segments of the skeleton of

Monastrea annularis.

Recent Calcareous Fresh Water Organisms

Sample	F _T	Cl _T	Br _T	Cl/Br _T	F _W	Cl _W	Br _W	Cl/Br _W
1NC-2a	7.6	52.0	22.4	2.3	5.6	49.0	4.0	12.3
9NC-3	9.8	76.0	27.0	2.8	7.8	85.0	1.0	85.0
10NC-2c	4.8	72.0	20.0	3.6	2.2	60.0	8.8	6.8
11NC-1	4.7	69.0	30.0	2.3	2.7	42.0	4.4	9.6
NC-2b	1.3	17.5	14.0	1.3	1.3	17.5	4.8	1.3
2AC#1	8.3	140	20.0	7.0	6.3	45.0	3.5	12.9
3AC#3	6.1	92.0	25.0	3.7	4.1	39.0	4.4	8.9
7AC#7	5.1	60.0	25.0	2.4	3.1	57.5	5.5	10.5
8AC#4	4.6	92.0	39.4	2.3	2.6	47.0	7.0	6.7
AC#6	3.0	18.0	14.5	1.2	1.6	20.0	5.4	1.4
5EC-4	5.1	76.0	21.0	3.6	3.1	75.0	6.0	12.5
6EC-1	5.6	107	25.0	4.3	3.6	70.0	7.5	9.3
12EC-6	4.2	76.0	22.4	3.4	2.2	57.5	4.0	14.4
13EC-8	4.6	114	55.3	2.1	2.6	90.0	12.0	7.5
EC-2	3.9	25.0	20.0	1.2	1.1	37.0	6.8	1.9
EC-3	2.0	25.0	17.5	1.4	1.7	28.0	7.8	1.6
EC-5	1.3	25.0	21.5	1.2	1.1	30.0	6.5	1.4
EC-7	6.9	16.5	15.0	1.1	1.6	20.0	6.3	1.3
GL-2	2.3	23.0	15.0	1.5	1.3	18.7	4.5	1.3
#13GL-3	2.7	38.0	16.0	2.4	3.0	31.7	7.5	1.9
AT-5	1.6	14.5	14.5	1.0	1.6	22.5	6.8	1.6

Recent Carbonates

Sample	F _T	Cl _T	Br _T	Cl/Br _T	F _W	Cl _W	Br _W	Cl/Br _W
R-1	1400	1325	43.0	30.8	27.5	1125	12.0	93.7
R-2	1157	6036	95.6	63.1	19.5	4625	46.2	100
R-3	616	16080	179.6	89.5	13.3	11750	115	102.2
B-5.2*	575	15500	200	77.5	9.0	13500	107.5	125.5
A-217.1	775	12000	160	75.0	13.0	11750	92.5	127.1

* - This sample contained 0.0775% P_2O_5 .

Recent - Pleistocene Calcareous Marine Pelecypods

T-1	34.0	25.0	24.5	10.2	9.2	250	2.0	125
U-94	43.0	50.0	44.0	1.2	6.0	57.5	1.4	41.1
PR-2	21.5	850	25.5	33.3	4.8	650	10.8	60.5
U-133	125	2500	39.0	64.1	11.0	2250	30.0	75.0
U-48	95.0	575	20.0	28.8	19.0	450	7.3	62.1

Pleistocene Carbonates

PP-68	656	80.8	6.6	12.3				
P-1	453	144	3.0	46.9	15.8	105	3.5	30.0
P-2	191	31.3	<1	>30	9.3	36.3	2.0	18.2
P-3	320	145	57.5	2.5	9.8	113	7.0	16.1

Miocene Carbonates

R-36-46	1050	2125	47.0	45.2	15.8	1925	27.5	70.0
R-150	750	4912	67.2	73.9	36.3	4500	47.5	96.8
R-219	185	3846	47.6	80.8	13.3	3325	33.5	98.7
R-409	91.1	5006	60.7	82.4	9.0	4250	43.2	93.4

(Miocene continued)

Sample	F _T	Cl _T	Br _T	Cl/Br _T	F _W	Cl _W	Br _W	Cl/Br _W
R-425	186	8547	93.3	91.6	7.3	7750	75.0	103
R-474	665	1456	17.2	84.7	12.0	1438	14.5	99.2

Cretaceous Carbonates

AR-I-2-A	26.5	42.3	4.9	8.7	2.2	14.0	1.1	12.7
S-I-13-B	26.4	112	12.9	8.7	3.2	14.5	0.9	15.8
CR-I-18-A	34.6	53.4	5.3	10.0	0.0	13.5	0.2	90.0
MR-III-19-A	35.0	50.9	5.1	9.9	2.2	14.5	0.8	18.1
MR-III-16-A	33.1	45.8	1.0	45.0	2.5	12.0	0.6	20.0
SH-V-12-A	58.5	96.6	6.0	16.1	2.9	84.0	2.3	36.5
AR-I-5-B	60.4	65.5	6.9	9.5	4.3	20.0	0.3	66.7
SH-IV-4-B	382	4883	214	22.6	3.9	3800	37.0	103
BR-II-3-A	403	188	20.7	9.1	7.2	92.0	0.3	307
LB-II-4-A	52.6	44.5	4.6	9.7	3.6	13.0	0.4	32.5
BR-II-1-B	41.5	54.5	7.0	7.8	3.2	25.0	1.4	17.9
CR-I-24-A	56.1	47.6	5.0	9.5	2.6	13.0	0.3	56.5

Cretaceous Pelecypod

Cret. Oyster	73.6	53.3	1.6	33.9	2.5	32.5	1.5	21.7
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Triassic Carbonates

4606-10	73.4	844	12.5	67.5	5.8	525	11.5	45.7
4611-15	1356	2983	35.3	84.5	13.8	1800	19.5	92.5
4616-20	1164	4947	50.1	98.7	18.0	3625	34.2	106
4621-25	725	1305	16.2	80.6	4.8	825	17.5	47.1

(Triassic continued)

Sample	F _T	Cl _T	Br _T	Cl/Br _T	F _W	Cl _W	Br _W	Cl/Br _W
4626-30	121	1372	18.8	73.0	1.7	937	11.5	81.5
4631-35	93.6	1404	17.2	81.6	1.7	1213	13.2	91.9
4031-32	869	1245	49.2	25.3	17.5	1025	36.0	28.5
4036-37	1250	625	7.9	78.6				
4038-39	170	129	3.6	35.8	9.0	140	4.7	29.4
4040-41	171	109	4.7	23.1	9.0	135	3.0	45.0
4042-43	330	126	3.8	33.1				
4444	111	507	10.6	47.8	2.4	425	7.0	60.1
4450	231	646	12.9	50.1	2.5	500	8.4	59.7
4409	114	140	2.8	50.0	3.9	95.0	4.3	22.1
4411	216	100	1.4	70.4	4.9	105	3.0	35.0
4437	354	183	3.4	54.0	4.3	103	2.5	43.0
Mississippian Carbonates								
AC-7	263	384	17.7	21.7	16.8	260	7.6	34.2
AC-23	371	318	15.4	20.7	17.5	220	7.8	28.2
AC-6	464	391	10.3	38.0	11.0	260	5.4	48.1
AC-18	378	166	6.3	26.2	13.5	120	8.0	15.0
AC-24	336	284	16.8	16.9	5.6	140	3.1	45.2
AC-17	180	104	9.1	11.5	8.1	115	11.0	10.5
AC-13	459	408	16.8	24.2	7.8	220	11.0	20.0
AC-14	510	494	13.5	36.5	6.4	340	9.0	37.8
AC-26	82.4	391	19.1	20.5	4.9	270	8.0	33.8
AC-20	439	357	11.0	32.4	8.8	240	8.8	27.3

U. Devonian Carbonates

Sample	F _T	Cl _T	Br _T	Cl/Br _T	F _W	Cl _W	Br _W	Cl/Br _W
AC-16	168	1464	29.2	50.0	8.8	1070	18.5	57.8
AC-1	15.0	475	14.5	32.7	1.7	440	9.0	48.9
AC-10	27.8	859	20.7	41.5	2.3	830	14.0	59.3
AC-21	101	2232	86.4	25.0	10.0	1550	25.0	62.0
AC-11	80.4	1675	33.5	50.0	8.4	1180	18.5	63.8
AC-15	56.8	2875	120.4	23.9	3.5	2700	36.0	75.0
AC-2	46.0	1093	21.3	51.4	6.0	830	18.5	44.9

H. Devonian Carbonates

AC-12	137	311	10.0	31.1	2.2	135	4.4	30.7
AC-4	500	683	18.3	37.3	3.9	385	13.0	29.6
AC-3	153	161	18.3	8.8	2.0	125	2.7	46.3
X114								
5095-99	115	1225	20.0	61.3	21.8	1250	19.3	64.8
5100-04	115	900	17.0	53.0				
5105-09	115	1550	26.5	56.7	15.3	1500	24.8	60.5
5110-14	87.0	1850	31.5	58.7	12.8	1875	23.5	79.8
5115-19	140	1750	31.5	55.5	17.5	1700	23.5	72.3
5120-24	150	1550	27.5	56.4	10.0	1540	22.5	68.5
5125-29	94.9	1632	36.7	44.5	4.0	1625	21.3	76.3
5130-34	81.0	2732	40.0	68.4	10.0	2250	25.0	90.0
5135-39	68.9	2226	36.4	61.1	3.5	1925	22.5	85.6
5140-44	87.0	2125	36.0	59.0	8.8	2075	24.8	83.7
5145-50	138	2200	37.5	58.8	25.0	2175	25.0	87.0

M. Devonian Carbonates

Sample	F _T	% Anhydrite	Sample	F _T	% Anhydrite
X-92 4725	145	0	X-92 4771	340	3
4726	213	0	4772	904	0
4727	209	0	4773	659	0
4728	231	0	4774	840	0
4729	441	0	4775	1100	0
4730	369	0	4776	734	0
4731	544	0	4777	907	0
4732	332	0	4778	736	4
4733	689	0	4779	306	8
4734	400	0	4780	1106	8
4735	429	0	4781	984	0
4736	404	0	4782	1256	0
4737	293	0	4783	980	0
4738	254	0	4784	242	7
4739	221	0	4785	184	19
4740	220	0	4791	711	37
4741	168	0	4792	373	4
4765	807	0	4793	1130	0
4766	1250	0	4794	1066	0
4768	1100	7	4795	790	0
4769	573	0	4796	670	0
4770	704	0			

(M. Devonian Carbonates continued)

Sample	F _T	Sample	F _T	Sample	F _T
X-91 4782-85	214	X-91 4930-34	53.7	X-95 4706-10	890
4786-90	286	4935-39	35.4	4711-15	970
4796-05	868	X-94 4801-09	237	4716-20	1200
4805-16	581	4822-26	2788	4721-25	1100
4817-26	873	4827-31	908	4726-30	780
4827-30	650	4832-36	790	4731-35	577
4831-35	425	4837-41	698	4736-40	600
4836-40	324	4842-46	490	4741-45	2100
4841-45	224	4847-51	702	4746-50	111
4846-50	443	4852-56	673	4753-59	75.7
4851-60	228	4857-61	599	4760-64	284
4861-65	171	4867-71	403	4765-69	190
4866-70	133	4872-76	673	4770-74	335
4871-80	203	4877-81	440	X-97 4869-73	30.0
4881-85	98.4	4882-86	418	4874-78	22.5
4886-90	137	4887-91	436	4884-88	35.1
4891-95	288	X-95 4671-75	603	4889-93	49.3
4896-00	136	4676-80	196	4894-98	45.2
4901-05	87.0	4681-85	343	4899-03	51.1
4906-10	46.9	4686-90	477	4904-08	45.0
4911-17	53.6	4691-95	100	4909-13	39.4
4918-24	49.0	4696-00	780	4914-18	38.2
4925-29	71.5	4701-05	1372	4919-23	39.5

(M. Devonian Carbonates continued)

Sample	F _T	Sample	F _T	Sample	F _T
X-97 4924-28	50.8	X-98 4372-76	234	X-98 4793-98	132
5513-18	77.0	4377-81	147	X-101 4970-74	145
5521-25	74.3	4382-86	237	4975-79	292
5526-31	72.9	4387-91	436	4980-84	302
5532-36	68.1	4392-96	343	4985-89	181
5537-41	96.6	4397-01	434	4990-94	220
5542-46	103	4402-06	635	4995-99	470
5547-51	128	4407-11	474	5000-04	127
5552-56	49.4	4412-16	355	5005-09	124
5557-61	35.7	4417-21	457	5010-14	539
5562-67	66.9	4422-26	158	5015-19	977
5568-72	91.4	4427-32	278	5020-24	434
X-98 4318-20	30.1	4728-37	286	5025-29	665
4321-25	27.8	4743-47	550	5030-34	337
4326-30	19.3	4748-52	100	5035-39	990
4331-35	20.2	4753-57	689	5040-44	129
4336-40	25.2	4758-62	859	5045-49	343
4341-45	21.0	4763-67	761	5050-51	126
4346-50	19.7	4768-72	976		
4351-55	64.9	4773-77	803		
4356-60	230	4778-82	890		
4361-65	75.0	4783-87	107		
4366-71	50.5	4788-92	420		

(M. Devonian Carbonates continued)

Sample	F _T	% P ₂ O ₅	Sample	F _T	Sample	F _T
X-99 4761-66	569	.00300	X-100 4855-59	1073	X-114 4926-30	694
4768-71	193	.01440	4860-64	250	4931-35	757
4772-76	194	.01105	4865-69	550	4936-40	329
4777-81	653	.00502	4870-74	852	4941-45	324
4782-86	589	.00520	4875-79	738	4946-50	1020
4787-91	383	.00665	4880-84	242	4951-55	393
4792-96	956	.01495	4885-89	124	4956-60	133
4797-01	520	.00922	4890-94	165		
4802-06	225	.00145	4895-99	102		
4807-11	160	.00648	4900-04	80.3		
4817-21	109	.00650	4905-09	165		
4822-26	174	.00471	4910-14	163		
4827-31	400	.00838	4915-19	527		
4832-36	423	.00615	4920-24	1050		
4837-41	218	.00766	4925-29	404		
4842-46	455	.00724	4930-34	324		
4847-51	121	.00784	4935-39	102		
4852-56	754	.00650	4940-44	600		
4857-61	836	.00420	4945-49	189		
4862-66	183	.00455	4950-51	128		
X-100 4840-44	48.1		X-114 4922	232		
4845-49	124		4923	196		
4850-54	179		4924-25	328		

M. Devonian Carbonates Grouped According to Depositional Environment

Supratidal			Intertidal			Turbulent Subtidal		
Sample		F _T	Sample		F _T	Sample		F _T
X-99	4768-71	193	X-99	4761-66	569	X-100	4920-24	1050
X-99	4772-76	194	X-99	4782-86	589	X-100	4930-34	324
X-99	4777-81	653	X-99	4822-26	174	X-100	4935-39	102
X-99	4787-91	383	X-99	4827-31	400	X-101	4990-94	220
X-99	4857-61	836	X-99	4832-36	423	X-101	4995-99	470
X-99	4862-66	183	X-99	4837-41	218	X-101	5010-14	539
X-100	4845-49	124	X-99	4842-46	455	X-101	5015-19	977
X-100	4850-54	179	X-99	4847-51	121	X-101	5020-24	434
X-100	4860-64	250	X-99	4852-56	754	X-101	5025-29	665
X-100	4945-49	189	X-99	4802-06	225	X-101	5030-34	337
X-100	4950-51	128	X-100	4940-44	600	X-114	4922	232
X-101	4970-74	145	X-100	4925-29	404	X-114	4923	196
X-101	4975-79	292				X-114	4924-25	328
X-101	4980-84	302	Turbulent Subtidal			X-114	4926-30	694
X-101	4985-89	181	X-99	4792-96	956	X-114	4931-35	757
X-101	5135-39	990	X-99	4797-01	520	X-114	4936-40	329
X-101	5140-44	129	X-100	4855-59	1073	X-114	4941-45	324
X-101	5145-49	343	X-100	4865-69	550	X-114	4946-50	1020
X-101	5150-51	126	X-100	4870-74	852	Quiet Subtidal to Lagoonal		
X-114	4951-55	393	X-100	4875-79	738	X-99	4807-11	160
X-114	4956-60	133	X-100	4881-84	242	X-99	4817-21	109
			X-100	4915-19	527			

Quiet Subtidal to
Lagoonal

Sample	F_T
X-100 4840-14	48.1
X-100 4885-89	124
X-100 4890-94	165
X-100 4895-99	102
X-100 4900-04	80.3
X-100 4905-09	165
X-100 4910-14	163
X-101 5000-04	127
X-101 5000-09	124

U. Silurian Carbonates

Sample	F _T	Cl _T	Br _T	Cl/Br _T	F _W	Cl _W	Br _W	Cl/Br _W
8734-39	164	2770	35.9	77.2				
8754-59	131	2923	41.8	69.9				
8766-69	125	4802	63.7	75.4				
8801-04	91.5	2636	53.8	62.8				
8811-15	239	2974	46.2	64.4				
8820-25	143	2479	35.0	70.8				
8826-29	119	2180	30.1	72.3				

M. Silurian Carbonates

9121-23	118	1891	35.3	53.6				
9129-31	165	875	29.0	30.2				
9135-37	172	1869	29.3	63.8				
9139-41	193	1930	33.5	57.6				
9147-49	109	2134	50.8	42.0				
9152-53	151	1459	59.4	24.6				
9157-59	56.7	350	67.0	5.2				
9163-65	179	1329	20.4	65.2				

L. Silurian Carbonates

8255-57	190	470	16.8	28.0				
8267-68	193	394	20.3	19.4				
8277-78	152	710	23.3	30.5				
8278-79	162	742	27.3	27.2				
8288-89	193	406	15.2	26.7				
8293-95	170	420	12.0	35.0				

(L. Silurian continued)

Sample	F _T	Cl _T	Br _T	Cl/Br _T	F _W	Cl _W	Br _W	Cl/Br _W
8297-99	162	405	17.2	23.5				
GB-5	25.5	663	22.4	29.5	2.3	635	19.0	33.4
GB-6	51.5	412	18.5	22.2	6.9	350	9.0	38.9
GSY-6	235	883	34.2	25.8	4.9	624	32.5	19.2

L.U. Ordovician Carbonates

8563-68	152	9343	101	92.5				
8569-73	335	1521	23.3	65.3				
8579-83	514	1226	18.9	64.9				
8593-97	220	551	8.0	65.2				
8607-10	230	2250	34.5	65.2				
10191-95	392	1060	20.7	51.2				
10211-13	385	2530	38.5	65.7				

M. Ordovician Carbonates

L-72	28.6	56.0	8.2	6.9	5.5	37.5	1.9	19.7
L-77	10.1	25.5	4.9	5.3	4.0	35.0	2.2	15.9
L-78	13.8	20.4	4.4	4.7	3.6	25.2	2.2	11.4
L-79	13.8	21.4	4.4	4.9	4.5	27.5	1.9	14.4
L-272	48.8	15.2	4.1	3.7	5.1	18.5	2.0	9.2
L-276	118	18.2	4.3	4.2	21.5	15.0	2.8	6.3
L-279	43.3	15.5	3.4	4.5	15.0	23.8	2.2	10.8
L-282	40.2	11.8	3.9	3.1	4.9	14.3	1.9	7.5

L. Ordovician Carbonates

Sample	F _T	Cl _T	Br _T	Cl/Br _T	F _W	Cl _W	Br _W	Cl/Br _W
L-202	28.3	125	10.1	12.4	6.3	90.0	3.8	24.0
59-337	42.1	75.6	5.4	14.0	3.0	52.5	2.2	23.6
59-339	30.0	150	9.4	16.0	10.5	55.0	2.5	22.0
59-343	23.1	78.8	6.3	12.5	5.5	67.5	1.9	35.5

Cambrian Carbonates

59-1709	52.4	175	14.8	11.8				
59-1728	62.3	318	28.2	11.1				
59-1740	56.0	299	28.8	10.4				

pre-Cambrian Carbonates

p-CW#1	69.0	145	3.9	37.1	3.2	19.0	1.5	12.7
p-CW#2	63.8	359	11.1	32.3	8.5	27.0	3.7	7.3
p-CW#3	39.5	205	5.9	34.9	25.0	21.5	1.9	11.3
p-CW#4	36.0	217	6.6	32.9	2.6	45.0	2.8	16.1
p-CW#5	28.1	76.1	3.5	21.7	1.6	40.0	2.0	20.0
p-CW#6	23.2	76.3	3.8	20.1	1.6	35.0	2.0	17.5
p-C2A#8	54.6	256	14.8	17.3	1.7	38.0	2.0	19.0
p-C2A#9	52.0	223	12.9	17.3	3.5	58.0	3.5	16.6
p-C2B#10	46.6	78.5	4.7	16.7	1.7	25.0	1.9	13.2
p-C2B#11	86.7	136	10.3	13.2	5.5	72.0	4.6	15.7
p-CW#12	59.1	44.0	8.5	5.1	5.0	40.0	1.7	23.5
p-CW#13	22.9	47.5	3.7	12.8	1.4	34.0	1.6	21.3
p-CW#14	21.7	48.9	4.5	10.8	1.0	26.0	1.3	20.0

(pre-Cambrian continued)

Sample	F _T	Cl _T	Br _T	Cl/Br _T	F _W	Cl _W	Br _W	Cl/Br _W
D-1	112	243	17.0	14.3				
D-3	118	99.7	9.2	10.8				
D-5	240	265	15.3	17.3				
D-7	94.5	133	10.2	13.0				
D-9	169	389	22.5	17.3				
D-11	61.3	99.7	6.4	15.6				
D-13	48.3	57.1	6.2	9.2				
B-1	68.8	37.0	7.1	5.2	2.4	13.0	1.4	7.1
B-2	66.0	36.0	8.2	4.4	2.2	12.5	1.5	8.7
B-3	53.8	28.4	6.7	4.2	1.8	14.5	2.7	4.3
E-3	24.7	0.0	1.0	0.0	4.6	18.0	4.6	3.9
E-4	10.9	0.0	11.9	0.0	3.3	26.0	2.3	11.3

pre-Cambrian Marbles

T68-0043	25.5	695	32.4	21.4				
T68-0044	36.4	565	24.3	23.3				
T68-0045	62.7	699	24.3	28.7				
T68-0046	17.3	50.8	4.1	12.4				
T68-2802	2.0	783	52.2	15.0				
T68-2848	27.3	2205	87.6	25.0				